# Synthesis and Properties of Open-Cage C<sub>60</sub> Derivatives Encapsulating Polar Molecules

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### **General Introduction**

Fullerenes can effectively serve as molecular containers for isolating guest species, such as small atom(s), molecule(s), and some metallic clusters.<sup>1</sup> For instance, the highly reactive species, atomic nitrogen N or Li, could be isolated inside the  $C_{60}$  cage in the form of N@ $C_{60}^2$  or Li@ $C_{60}^3$  through plasma discharge methods. Some rare metal ions such as La<sup>4</sup> and Sc<sup>5</sup> and their clusters<sup>6</sup> have also been enclosed inside the fullerene cages in a stable form through arcing charge methods. These endohedral fullerenes offer an ideal platform to study the species that are otherwise unstable in ambient environments, and these molecular complexes exhibit significantly altered physical properties from the empty cages.<sup>7</sup> However, the above physical methods are high-costing and the yield of endohedral fullerenes is lower than 0.1% after extraction from the soot followed by enrichments through the recycling HPLC (high performance liquid chromatography).<sup>8</sup>

Therefore, the chemical strategies,<sup>9</sup> including three key steps: incision of the carbon cages, insertion of the guest molecules, and suture of the openings, have been devised for the synthesis of endohedral fullerenes. In 2005, Komatsu and co-workers first achieved this 'molecule surgery' on a C<sub>60</sub> to afford an endohedral fullerene H<sub>2</sub>@C<sub>60</sub>.<sup>10</sup> The C<sub>60</sub> cage experienced several bond cleavages to provide an opening that allows the encapsulation of an H<sub>2</sub> molecule, followed by the repairment of all cleaved C-C/C=C bonds to afford H<sub>2</sub>@C<sub>60</sub>. Since then, various atom(s) and molecule(s) with relatively larger sizes than H<sub>2</sub>, such as H<sub>2</sub>O,<sup>11</sup> HF,<sup>12</sup> Ar,<sup>13</sup> Kr,<sup>14</sup> and CH<sub>4</sub><sup>15</sup>, have been completely confined inside C<sub>60</sub> from the ambient environment by similar approaches.

The unrepaired C<sub>60</sub> products with openings, denoted as cage-opened C<sub>60</sub> derivatives,<sup>16</sup> have been found to encapsulate large molecules with two or three heavy atoms when the orifices are further enlarged. For example, a CO<sub>2</sub> molecule, with a length exceeding the diameter of C<sub>60</sub>, can be isolated within the cavity of an open-cage C<sub>60</sub> derivative.<sup>17</sup> Thus, the use of cage-opened fullerene derivatives as hosts for encapsulations received much attentions.<sup>18</sup> Additionally, owing to the multiple functional groups at the orifices, modifications for cage-opened C<sub>60</sub> derivatives are feasible. The structural transformation to prevent the release of inside molecules has been developed.<sup>19</sup> Also, functionalizations such as  $\pi$ -extension could be achieved,<sup>20</sup> which enables further applications in perovskite optoelectronic devices. In this section, the author will

summarize the recent representative research works on open-cage  $C_{60}$  fullerenes from aspects of (i) transformation of orifices, (ii) encapsulations of molecules, (iii) and applications in solar cells.

### The transformation of orifices

In general, the ring atom count of the orifice was used to estimate the size of openings. In 1995, Wudl and co-workers synthesized ketolactam **2** (Figure 1a) with an orifice of 11-membered ring from 5,6-azafulleroid **1** bearing a 7-membered ring by the regioselective oxidation.<sup>21</sup> Such an enlarged opening does not allow any encapsulations. In 2001, Rubin and co-workers applied a similar oxidation of **3** with <sup>1</sup>O<sub>2</sub> (Figure 1b) to give an open-caged derivative **4** with 14-membered ring,<sup>22</sup> which enables the encapsulation of H<sub>2</sub> (5%) under 100 atm pressure and <sup>3</sup>He (1.5%) under 475 atm.<sup>22b</sup> The regioselective oxidative cleavage with singlet oxygen to widen the orifice then were widely used for different precursors, proving various open-caged C<sub>60</sub> derivatives with



Figure 1. Open-cage fullerenes with enlarged orifices by regioselective oxidations.

similar 12-membered rings (Figure 1c), such as diketone  $5^{23}$  (reported by Shizuaki Murata), compounds  $6^{24}$  (reported by Komatsu),  $7^{25}$  (reported by Komatsu), and their analogue  $8^{11a,26}$  (reported by Yasujiro Murata). In 2011, Y. Murata and co-workers also reported the regioselective oxidative cleavage of a C=C bond on 8 (Figure 1d) using *N*-methylmorpholine *N*-oxide (NMMO), affording a tetraketone derivative  $9^{11a}$  with an orifice of 16-membered ring, enabling the encapsulation of H<sub>2</sub>O (100%) under the condition of 120 °C and 9000 atm pressure. Compound 9 is easily *in situ* transferred to bis(hemiketal) 10 under the wet conditions, which was finally repaired to H<sub>2</sub>O@C<sub>60</sub>.<sup>11a,27</sup>

With the use of a hypervalent iodine oxidant  $PhI(OAc)_2$ , in 2002, Gan and coworkers reported the oxidation of vicinal diol on the carbon cage of **11**, which provided a hole consisting of a 10-membered ring on the cage of derivative **12** (Figure 2).<sup>28</sup> When this oxidant was applied to related open-cage derivatives with three adjacent hydroxy groups, **13** and **15**, the corresponding polyketone derivatives **14**<sup>29</sup> with an 11-membered ring orifice and **16**<sup>30</sup> with an 18-membered ring opening were obtained, respectively.



Figure 2. Open-cage fullerenes with enlarged orifices by hypervalent iodine oxidant.

It is known that a sulfur (S) atom can be inserted into activated C–C single bonds.<sup>31</sup> In 2003, Komatsu and co-workers achieved the insertion of a sulfur (S) atom incorporated into the rim of the orifice of **7** using S<sub>8</sub> in the presence of tetrakis(dimethylamino)ethylene (TDAE) (Figure 3a)<sup>25</sup>, affording **17** with a 13-membered ring orifice, which could encapsulate H<sub>2</sub> in 100% encapsulation ratio.<sup>32</sup> A similar approach for the insertion of selenium atom was also available for **7**.<sup>32b</sup> When the insertion of S was applied to **2** with two butadiene units at the orifice, a single sulfur-inserted **18** with a 12-membered ring and a double sulfur-inserted **19** with a 13-membered ring were formed (Figure 3b).<sup>33</sup> The electrophilic insertion of elemental S on **9** was found to afford three analogous enlarged open-cage derivatives **20**, **21**, and **22** (Figure 3c),<sup>34</sup> with large orifices of 17-, 17-, and 18-membered rings, respectively. A series of endohedral fullerenes Ar@C<sub>60</sub>, Kr@C<sub>60</sub>, and CH<sub>4</sub>@C<sub>60</sub> were devised from Ar@**21**,<sup>13</sup> Kr@**21**,<sup>14</sup> and CH<sub>4</sub>@**21**<sup>15</sup> through stepwise reactions. However, when the same reaction of S was applied on the orifice of an open-cage C<sub>70</sub> derivative **23** (Figure 3d), the original 16-membered ring was contracted to **24** with a 12-membered ring, owing to less electronegative than C<sub>60</sub> analogous **9**.<sup>35</sup>



Figure 3. Open-cage fullerenes with enlarged orifices by the insertion of sulfur atoms.

The reactions with aromatic amines were found to promote bond cleavage on the orifice of ketone derivatives, thus affording larger orifices.<sup>20,36</sup> In 2004, Iwamatsu and co-workers reported the synthesis of an open-cage  $C_{60}$  derivative **25**<sup>37</sup> (Figure 4a) from **5** using *o*-phenylenediamine in the presence of excess amount of pyridine. The original 12-membered ring orifice of **5** was enlarged to a 20-membered ring orifice of **25** by the cleavage of two C=C bonds, which enabled the encapsulation of H<sub>2</sub>O,<sup>37</sup> CO,<sup>38</sup> NH<sub>3</sub>,<sup>39</sup> and CH<sub>4</sub>.<sup>40</sup> Yeh and co-workers applied the similar reaction on **7** to give **26** (Figure 4b) with a 20-membered ring orifice, and the further treatment with ethanol afforded a product **27** with a 24-membered ring opening, which allows the encapsulation of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, and



Figure 4. Open-cage fullerenes with aromatic amines incorporated into skeletons.

HCN.<sup>41</sup> In 2023, Gan and co-workers synthesized related cage-opened derivatives **29** (Figure 4c) through a ring-enlargement reaction of **28** with 4,5-dichloro-1,2-diaminobenzene.<sup>42</sup> The host **29** was found to give molecular complexes MeOH@**29**, EtOH@**29**, and LiF@**29** by mixing **29** with these guest molecules under 60 °C in CHCl<sub>2</sub>CHCl<sub>2</sub> solution. They also reported the encapsulations of halide anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> using host **30** (Figure 4d), which was synthesized from 12 by the four steps, including a reaction with 1,2-diaminobenzene.<sup>43</sup> Most recently, Y. Murata and co-workers developed the consecutive addition of aromatic 1,2-diamine on **10** to give bilaterally cage-opened C<sub>60</sub> derivative **31** (Figure 4e), featuring two helicene motifs in its carbon skeleton.<sup>44</sup> In 2023, they also reported that the nucleophilic addition using aromatic amines could also be applied to analogous diketone derivatives of C<sub>70</sub>.<sup>45</sup>

Owing to the aromatic patterns incorporated into the cage skeletons, the resulting  $\pi$ -extended C<sub>60</sub> derivatives usually exhibit different electronic properties from the original



Figure 5. Functionalized open-cage fullerenes.

cage-opened C<sub>60</sub> derivative.<sup>20</sup> In 2012, Ding and co-workers reported the introduction of chromophore  $\pi$ -systems into a fullerene  $\pi$ -skeleton by the reactions of **7** with two *ortho*-diamino-containing oligothiophenes. The absorption edges of the skeleton-modified C<sub>60</sub> derivatives **32**<sup>20a</sup> and **33**<sup>20a</sup> (Figure 5a) were pushed into the NIR (near infrared) region of 920 and 1100 nm, respectively. In 2014, Gan and co-workers reported the related compound **34** (Figure 5b) which showed the absorption in the NIR region with the onset at 1352 nm.<sup>20b</sup> In 2023, Y. Murata and co-workers synthesized a *C*<sub>1</sub>-symmetric chiral open-cage C<sub>60</sub> fullerene **35** showing an intense absorption in far-red to NIR region and large dissymmetry factor of  $|g_{abs}|=0.12$  at 820 nm.<sup>46</sup> In the same year, they also reported the affinity of the Li<sup>+</sup> with the ligands of chiral cage-opened C<sub>60</sub> derivative **36**. The Li<sup>+</sup>-binding was found to enhance the chiroptical responses of the resulting complexes.<sup>47</sup>

Although the large orifices could facilitate the processes of encapsulation, spontaneous escape for trapped species is unavoidable, which usually causes a low encapsulation ratio.<sup>48</sup> Therefore, the strategies for preventing the release of the onceencapsulated molecules were developed. In 2007, Komatsu and co-workers reported the reactions of **17** with NaBH<sub>4</sub>, in which the orifice of a 13-membered ring for He@**17** was reduced into an 11-membered ring for He@**37** (Figure 6).<sup>49</sup> Thus, the release of He from



Figure 6. Open-cage fullerenes with stoppers.

He@37 was decreased. When the reduction using NaBH<sub>4</sub> was applied to 21 with the 17membered ring, one of the carbonyl groups at the orifice was reduced to an OH group with the orientation tilting inward, which could work as a 'stopper' at the orifice of 38 for inside isolated species.<sup>50</sup> By use of this strategy, Y. Murata and co-workers achieved the synthesis of N<sub>2</sub>@38,<sup>50</sup> O<sub>2</sub>@38,<sup>51</sup> NO@38,<sup>52</sup> H<sub>2</sub>CO@38,<sup>53</sup> and CO<sub>2</sub>@38<sup>50</sup> with the inside species prevented from escape by a hydroxy group. It should be noted that, in 2023, Gan and co-workers set an OH group at their open cage derivative with pointing towards the cavity, which was found to be coordinated to a metal cation  $[BeF]^+$ , forming a rare example of endohedral metallic fullerene BeF@39.<sup>42</sup>

### The encapsulation of molecules

In general, fullerene cages can induce magnetic shielding to encapsulated species, resulting in the observation of high-field <sup>1</sup>H NMR signals by encapsulations. This phenomenon is exemplified in molecules like H<sub>2</sub>O@25,<sup>37</sup> NH<sub>3</sub>@25,<sup>39</sup> and CH<sub>4</sub>@25 (Figure 4a),<sup>40</sup> where <sup>1</sup>H signals appeared at  $\delta$  –11.40 ppm, –12.30 ppm, and –12.32 ppm, respectively. Encapsulation also impacts the fullerene cages, altering chemical shifts of alkene and hydroxy protons at the orifices for cage-opened C<sub>60</sub> hosts, likely due to van der Waals and/or hydrogen-bonding (H-bonding) interactions between hosts and guests.<sup>40,50–53</sup> These interactions are further reflected in varying retention times in recycling preparative HPLC with Buckyprep columns, particularly after multiple cycles. Remarkably, the efficient separation of derivatives with encapsulation of larger and more polar molecules like  $H_2CO@38^{53}$  from the empty host 38 was realized, compared to  $N_2(@38^{50} \text{ and } O_2(@38^{51} \text{ (Figure 6) using the same HPLC conditions. A similar easy$ separation was observed for CH<sub>3</sub>OH@21<sup>53</sup> (Figure 3c) from empty 21. These results suggest that the size and polarity of encapsulated molecules play crucial roles in enhancing the interactions with cages and potentially inducing modifications in the molecular structures.

Some interesting phenomena have been revealed regarding the encapsulation of polar molecules in fullerene cages. In 2015, Gan and co-workers reported the facilitated removal of water from the cavity of **40** by hydrogen fluoride (HF) (Figure 7).<sup>54</sup> This process involves the formation of an HF••••H<sub>2</sub>O hydrogen bonding, which plays a key role in extracting the water molecule from the interior of the cage. In 2016, Yeh *et al.* observed that polar molecules H<sub>2</sub>O and HCN achieved higher filling factors in H<sub>2</sub>O@**27** and HCN@**27**, compared to C<sub>2</sub>H<sub>2</sub> in C<sub>2</sub>H<sub>2</sub>@**27** (Figure 4a).<sup>41</sup> This difference in encapsulation efficiency was attributed to the stronger dipole-dipole interaction between polar guests and the ester moiety at the orifice, in contrast to the weaker van der Waals interactions in the case of non-polar C<sub>2</sub>H<sub>2</sub>. In 2015, Matín and co-workers discovered that a carbanion at the cage was significantly stabilized by the encapsulated water molecule in H<sub>2</sub>O@**41** (Figure 7) through hydrogen-bonding,<sup>55</sup> highlighting the role of the polar molecule in influencing the chemical reactivity.

In 2018, Y. Murata and co-workers reported an inhibition of the encapsulated H<sub>2</sub>O molecule from H/D exchange within H<sub>2</sub>O@ $42-d_3$  (Figure 7). No H/D exchange was

observed over 48 hours despite strong hydrogen bonding between the OH group and the encapsulated H<sub>2</sub>O. This finding suggests that hydrogen-bonded water exhibits lower acidity as well as less basicity than bulk water.<sup>56</sup> In 2019, this group further advanced the understanding of intermolecular interactions by revealing a unique non-conventional hydrogen-bonding mechanism: the OH/ $\pi$  interaction.<sup>57</sup> This interaction involves the positively charged proton in H<sub>2</sub>O binding to the  $\pi$ -cloud of an olefin located at the orifice of the fullerene structure. In a remarkable extension of these results, this group isolated a fundamental H-bonding system H<sub>2</sub>O•••H<sub>2</sub>O within a C<sub>70</sub> cage (Figure 7),<sup>58</sup> revealing a perpetual formation and cleavage of hydrogen-oxygen for the water dimer in (H<sub>2</sub>O•H<sub>2</sub>O)@C<sub>70</sub>. Additionally, the group engineered another intriguing mono-hydrated HF, i.e., HF•H<sub>2</sub>O, in the same C<sub>70</sub> host. In this complex, (HF•H<sub>2</sub>O)@C<sub>70</sub> (Figure 7), despite the close molecular proximity of HF and H<sub>2</sub>O, there was a surprising absence of proton exchange between these molecules.<sup>59</sup>



Figure 7. Encapsulation of water molecule(s).

Recent studies by Y. Murata and co-workers have marked an advancement in the isolation of active species, specifically triplet oxygen ( ${}^{3}O_{2}$ ) and nitric oxide (NO), within the confines in the cavity of **38**. Notably, in the complex  ${}^{3}O_{2}@$ **38** (Figure 6),<sup>51</sup> the  ${}^{1}H$  NMR signals of hydroxy protons, in close proximity to the encapsulated  ${}^{3}O_{2}$ , were significantly diminished. This was accompanied by only weakly detectable  ${}^{13}C$  peaks for

the cage carbon atoms. These observations revealed the paramagnetic nature of  ${}^{3}O_{2}@38$ . Intriguingly, in complex NO@38 (Figure 6),  ${}^{52a}$  electron spin resonance (ESR) activity was prominently observed at low temperatures. The magnetism noticeably diminished as the temperature was elevated, highlighting the temperature-dependent magnetic properties of NO@38.

### **Applications in solar cells**

In the application of open-cage  $C_{60}$  fullerenes derivatives for bulk-heterojunction (BHJ) solar cells, Y. Murata and co-workers, in 2011, reported an open-cage  $C_{60}$  derivative **43** (Figure 8) having an 11-membered ring orifice, as accepter materials in BHJ solar cells.<sup>60</sup> This derivative presented a comparable power conversion efficiency (PCE) of 3.11% to that of 6,6-phenyl-C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM), which has a PCE of 3.12%, suggesting the potential of these novel C<sub>60</sub> derivatives in solar cells. Also in 2011, S.-C. Chuang and co-workers introduced an open-cage C<sub>60</sub> derivative **44** featuring a 13-membered ring orifice in BHJ solar cells,<sup>61</sup> which also served as an n-type material with comparable performance to that of PC<sub>61</sub>BM. Subsequently, they developed the



Figure 8. Open-cage fullerenes for application to solar cells.

related compound  $45^{62}$  as an additive in OPVs have reduced the phase aggregation rate within active layers, enhancing the lifetime of the device more than the control one. In 2022, they also synthesized derivative  $46^{63}$  as the additive in the active layer, which significantly improved both the electron mobility of the layer and the overall device stability.

Then, in parallel development for the usage as electron-transporting materials (ETM), L. Echegoyen and co-workers recently reported a series of open-cage  $C_{60}$  derivatives, **47**a-c,<sup>64</sup> as effective ETM in lead (Pb) halide perovskite solar cells with power conversion efficiency of 16.8% with enhanced open-circuit voltages of *ca*. 1.0 V. These studies highlighted the potential of open-cage  $C_{60}$  derivatives for optoelectronic applications.

### **Survey of This Thesis**

As described in the examples above, fullerenes possess unique hollow structures, enabling the insertion of atoms or molecules inside their cavity through 'molecular surgery,' resulting in novel molecular complexes. However, among those reports, the encapsulated molecules are predominantly nonpolar and small, leading to minimal changes in the structures and/or properties compared to their empty forms. Recognizing this, more polar and larger organic molecules are considered to be introduced inside the molecular cavity. In this thesis, the author has worked on the non-covalent modification of fullerene cages based on the encapsulation of polar organic molecules with large sizes inside their cavity. From the view of applications, while open-cage  $C_{60}$  derivatives have been reported to function as acceptor materials in organic photovoltaic solar cells and as electronic transporting materials (ETM) in lead-halide perovskite solar cells, their potential use in tin-halide perovskites has not yet been explored. This work has also extended to the application of open-cage  $C_{60}$  derivatives in lead-halide perovskite solar cells, specifically as ETM materials.

In Chapter 1, the author studied the encapsulation of a chemically active molecule,  $H_2O_2$ , inside the cavity of open-cage  $C_{60}$  derivatives. A hydroxy stopper at the orifice was constructed by the reduction of one of four carbonyl groups using  $BH_3$ . THF for the purpose of stabilizing the encapsulated  $H_2O_2$ . The X-ray analysis revealed two  $H_2O_2$ @open-fullerenes structural isomers, whose structures were differentiated by the position of the hydroxy group at the orifice, being located near or off the center position. For the former  $H_2O_2$ -containing complex, the short O(OH)••• $O(H_2O_2)$  distance of 2.939(5) Å was found, which was less than the donor-acceptor limits of hydrogen bonding,

indicating a strong interaction. DFT calculations showed that the centrally located hydroxy group enhanced the thermodynamic stability of  $H_2O_2$  threefold more than an off-centered one toward its escape.



Peroxosolvate: HO…H<sub>2</sub>O<sub>2</sub>

Figure 9. An H<sub>2</sub>O<sub>2</sub> molecule trapped inside an open-cage C<sub>60</sub> derivative.

In Chapter 2, the author conducted encapsulation of CH<sub>3</sub>CN (Figure 10), a molecule with a larger size and higher polarity than H<sub>2</sub>O<sub>2</sub>, into the host **22**. The successful insertion of CH<sub>3</sub>CN was achieved by treating the mixtures of host and an excess amount of CH<sub>3</sub>CN at a high temperature of 140 °C and under high pressure of 9000 atm. The resulting product CH<sub>3</sub>CN@**22** was found to allow easy separation from the mixture containing empty cages using silica gel column chromatography, thereby eliminating the need for



Figure 10. Easy separation of CH<sub>3</sub>CN@22 using silica gel column chromatography.

preparative HPLC, which was required in all previous cases. From the analysis of <sup>1</sup>H NMR spectroscopy, single-crystal X-ray analysis, and DFT calculations, the author

elucidated that the enhanced polarity of the resulting molecular complex was mainly owing to the overlapped dipole. Also, the author designed the competition experiments for the encapsulation of CD<sub>3</sub>CN and CH<sub>3</sub>CN, revealing the favored affinity for the deuterated one.

Owing to the large orifice of **22** featuring a large 18-membered ring orifice, the escape of the encapsulations with moderate sizes occurred unavoidably. Therefore, in chapter 3, the author addressed the issues by the construction of a double stopper comprising two hydroxy groups on the orifice of **22** (Figure 11), achieved through selective reduction of the two carbonyl groups using  $BH_3$ ·THF. Remarkably, this design proved to be effective in maintaining encapsulation such as N<sub>2</sub> or Ar inside the cages even under mass spectrometric analysis at 200 °C. DFT calculations showed that this double stopper significantly raised the energy barrier for the escape. The installation of two hydroxy groups at the orifice caused the dimerization in the solution as well as in the solid state.



Figure 11. Open-cage fullerene with a double stopper encapsulating Ar or N<sub>2</sub>.

However, the low yield of compound **22**, despite efforts on optimization, drives the demand for novel hosts with simple synthetic methods. Therefore, in chapter 4, the author focused on a one-step reaction for orifice expansion that achieved high yields. A series of naphthalene-fused fullerene derivatives, **48**, **49**, **50**, and **51** (Figure 12) were obtained from the reactions of a 12-membered ring of **8** with 1,2-, 2,3-, and 1,8-diaminonaphthalenes. For the former two, orifice enlargement proceeded by cleaving two C=C bonds, transforming the original 12-membered ring into a 20-membered ring (**48**, **49**, **50**) in *ca*. 90% yield. For the latter, one C=C bond was cleaved to give a 17-membered ring (**51**) with a fused pyrimidine moiety. In this reaction, a rearranged product with a 14-membered ring was also formed, and a unique structure of the C59 cage was confirmed

by crystallographic analysis.



Figure 12. The structures of naphthalene-fused fullerene derivatives.

In chapter 5, the author described the application of the open-cage fullerene with an 8-membered-ring orifice as an electron transport material in tin halide perovskite solar cells for reducing the energy gap against the perovskites (Figure 13). The LUMO level of the film spin-coated onto the ITO surface was estimated to be comparable to that of standard compounds, indicating good energy-matching toward the perovskite layer. As a consequence, Sn-based PSCs incorporating open-cage  $C_{60}$  as an ETM were found to present an impressive PCE of nearly 10% with an open-circuit voltage of 0.72 V, significantly higher than those of commercial PCBM. A key finding was the superior thermal stability of this  $C_{60}$  derivative, which retained 75% of their structure without decomposition after thermal vacuum deposition, facilitating a PCE of 7.6% in the corresponding PSCs.



**Figure 13.** *J-V* curves of the champion device of Sn-based PSCs incorporating the opencage C<sub>60</sub> derivative as an ETM.

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### Chapter 1

# An H<sub>2</sub>O<sub>2</sub> Molecule Stabilized inside Open-Cage C<sub>60</sub> Derivatives

### by a Hydroxy Stopper

Abstract: An H<sub>2</sub>O<sub>2</sub> molecule was isolated inside hydroxylated open-cage fullerene derivatives (open-C<sub>60</sub>) by mixing of H<sub>2</sub>O<sub>2</sub> solution with an open-C<sub>60</sub> precursor followed by reduction of one of the carbonyl groups on its orifice. Depending on the reduction sites, two structural isomers of H<sub>2</sub>O<sub>2</sub>@open-C<sub>60</sub> were obtained. The high encapsulation ratio of 81% was attained at low temperature. The structures of peroxosolvate complexes thus obtained were studied by <sup>1</sup>H NMR, X-ray analysis, and DFT calculations, showing a strong hydrogen bonding between the encapsulated H<sub>2</sub>O<sub>2</sub> and the hydroxy group located at the center of the orifice. This OH group was found to act as a kinetic stopper and the formation of hydrogen bonding caused the thermodynamic stabilization of H<sub>2</sub>O<sub>2</sub> molecule, both of which prevented its escape out of the cage. One of the peroxosolvates was isolated by recycle preparative HPLC, affording H<sub>2</sub>O<sub>2</sub>@open-C<sub>60</sub> with 100% encapsulation ratio likely due to the intramolecular hydrogen bonding interaction.

### Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which takes part in oxidation and radical coupling reactions, has been found in a variety of organic syntheses<sup>1</sup> as well as biological processes.<sup>2</sup> From a safety point of view, most of the commercially available aqueous solutions cannot be used stoichiometrically because of their low concentration (30%).<sup>3</sup> Therefore,  $H_2O_2$  complexes with well-defined composition ratios,<sup>4</sup> such as  $H_2O_2$ •urea,<sup>5</sup>  $M_2CO_3 \bullet 1.5H_2O_2$  (M: alkali metals),<sup>6</sup> and Ph<sub>3</sub>PO \bullet H<sub>2</sub>O<sub>2</sub>,<sup>7</sup> have been prepared during a few decades. Importantly, the isolation of  $H_2O_2$  in a pure form has received growing attention for the deeper understandings of the reactivity and dynamics at the molecular level,<sup>8</sup> as well as the redox signalling pathways in biotissues at the cellular level.<sup>9</sup> However, the study of a pure H<sub>2</sub>O<sub>2</sub> molecule is quite limited because of its high reactivity and instability caused by thermal decomposition.<sup>10</sup> So far, little is known about hydrogen-bonding (Hbonding) modes of small H<sub>2</sub>O<sub>2</sub> clusters with a short lifetime (milliseconds to minutes order) prepared by depositing them onto argon matrix<sup>11</sup> or water nanoparticles.<sup>8</sup> These studies were carried out by only a combination of mass spectrometry,<sup>12</sup> IR spectroscopy,<sup>13</sup> and DFT studies.<sup>14</sup> Thus, the molecular system that enables the kinetic and thermodynamic stabilization of a pure H<sub>2</sub>O<sub>2</sub> molecule is highly demanded.

Under these circumstances, the author focused on fullerene  $C_{60}$ , in which the inner cavity allows the accommodation of a small molecule.<sup>15</sup> Therefore, the fullerene cage is regarded as a physically protecting group without the use of any chemical protection reactions (Figure 1). So far, Y. Murata's research group, the author belongs to, has succeeded in isolating active molecules such as  $O_2^{16}$  and  $NO^{17}$  by applying this kinetic protection approach. Recently, Gan and co-workers demonstrated the feasibility of the encapsulation of H<sub>2</sub>O<sub>2</sub> inside an open-cage C<sub>60</sub> derivative albeit in a low occupation level of 14%.<sup>18</sup> This is probably due to the large opening with the 22-membered ring, which allows the encapsulated H<sub>2</sub>O<sub>2</sub> molecule to escape from the cage, as well as due to the enthalpic loss of  $H_2O_2$  by cleaving H-bondings from the bulk upon encapsulation. For gaining thermodynamic stabilization of H2O2 molecule, the author decided to introduce a hydroxy group on the fullerene orifice, which is expected to contribute to the formation of a peroxosolvate, i.e.,  $H_2O_2(a)$  open- $C_{60}$  complex in which  $H_2O_2$  molecule binds to the hydroxy group via an intramolecular H-bonding (Figure 1). An analogous molecular system involving OH•••H<sub>2</sub>O bondings, i.e., water@open-C<sub>60</sub> complex was recently constructed by the use of a triply-hydroxylated C<sub>60</sub> derivative.<sup>19</sup> This result prompted the author to create an H-bonded H<sub>2</sub>O<sub>2</sub> molecule in a stable form. Herein, the author reports two peroxosolvate systems, one of which achieved a high occupation level of 100% by

HPLC. The author also discusses the arrangement and difference of the  $OH^{\bullet\bullet\bullet}H_2O_2$  bondings between the two isomers on the basis of their solid-state structures, NMR spectroscopic analyses, and computational studies.



**Figure 1.** Kinetic and thermodynamic stabilization of the molecular complex by use of hydroxylated open-cage  $C_{60}$  fullerene derivatives.

### **Results and Discussion**

For the encapsulation of H<sub>2</sub>O<sub>2</sub>, the author selected 1 possessing a 17-membered ring opening.<sup>20</sup> Initially, the author examined the treatments using H<sub>2</sub>O<sub>2</sub>•urea and Na<sub>2</sub>CO<sub>3</sub>•1.5H<sub>2</sub>O<sub>2</sub> in toluene at 50 °C under 8,000 atm. However, 1 was partially decomposed and the desired product  $(H_2O_2(a)1)$  was not obtained at all. This is because of the poor solubility of these solid H<sub>2</sub>O<sub>2</sub> sources in organic solvents. Thus, the author tried to use a 30% aqueous solution of  $H_2O_2$ . To a CDCl<sub>3</sub> solution of 1, two drops of  $H_2O_2$ aq. was added at room temperature. In the <sup>1</sup>H NMR spectra, two singlet signals appeared at  $\delta$  -4.63 and -11.43 ppm which are assignable to H<sub>2</sub>O<sub>2</sub>@1 (1.5%) and water@1 (35%), respectively. This strongly suggested that the 17-membered ring orifice was suitable for the  $H_2O_2$ -encapsulation. The severely broadened <sup>1</sup>H NMR signal of the encapsulated water molecule was observed, while the encapsulated H<sub>2</sub>O<sub>2</sub> molecule was detected as a sharp <sup>1</sup>H NMR signal (Figure S3). This indicates that the encapsulation/escape equilibrium of the H<sub>2</sub>O<sub>2</sub> molecule is markedly slower than that of the water molecule probably due to the larger size of  $H_2O_2$  and/or greater stabilization of  $H_2O_2$  inside 1. The author also examined the high pressure effect on this encapsulation (toluene, under 8,000 atm, at room temperature for 20 h). Unfortunately, 1 was partly decomposed without significant improvement in the encapsulation ratio (5%) judged from the <sup>1</sup>H NMR analysis.

A partition coefficient of H<sub>2</sub>O<sub>2</sub> is larger by three times in benzene than that in

chloroform.<sup>21</sup> Due to the temperature limit of benzene (melting point: +5.5 °C), the author used toluene for the following studies. After subjecting the toluene solution of 1 to  $H_2O_2$ aq. for 1 h at +5 °C and -60 °C, the subsequent reduction was conducted by using 1.5 equiv of BH<sub>3</sub>•THF<sup>17,22</sup> at each temperature for 30 min (Scheme 1). After chromatographic purification, two hydroxylated derivatives, i.e., 2 and 3, were obtained in which the reduction occurred at C(a)=O and C(b)=O groups, respectively. The structures of 2 and 3 were determined by X-ray crystallography (vide infra). At both temperatures of +5 °C and -60 °C, 2 was preferred to be formed in 37% and 42% isolated yields, while 3 was obtained in 6 and 5% yields, respectively. In the borane reduction, the lowering of the temperature caused a noticeable improvement in the encapsulation ratio of H<sub>2</sub>O<sub>2</sub> for both 2 and 3. At -60 °C, the cavity of 3 was filled up with H<sub>2</sub>O<sub>2</sub> molecule at an occupation level of 81%, in which the rest of the components are regarded as empty one together with molecular complexes containing water and N2, confirmed by <sup>1</sup>H NMR and mass analyses. The control experiment demonstrated that an H2O2 molecule was trapped inside 2 in only 2% during the reaction, suggesting that an H<sub>2</sub>O<sub>2</sub> molecule was trapped inside 1 prior to the formation of the hydroxy group (Scheme 1).





The enrichment of  $H_2O_2@3$  into 100% was accomplished by recycling HPLC equipped with the Buckyprep columns after 9 cycles whereas  $H_2O_2@2$  was not obtained in a pure form even after 13 cycles (11% from 8%) (Figure S2). This implies that  $H_2O_2@3$  has different interaction toward the stationary phase on the column compared with the other species. Y. Murata's research group, which the author belongs to, has previously observed the similar separation of a hydroxylated open-cage C<sub>60</sub> derivative encapsulating a water molecule, in which the water molecule is tightly bound to the hydroxy group.<sup>19</sup>

Similarly, the observed separability in this study might be attributed to the presence of H-bonding between the  $H_2O_2$  molecule and the hydroxy group in **3**.

To verify the difference in H-bonding strengths between 2 and 3, <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>) were recorded. The encapsulated H<sub>2</sub>O<sub>2</sub> molecule gave a singlet signal at  $\delta$  –4.16 ppm for H<sub>2</sub>O<sub>2</sub>@2 and  $\delta$  –3.81 ppm for H<sub>2</sub>O<sub>2</sub>@3 (Figure 2), in which the latter was slightly shifted by  $\Delta\delta$  +0.35 ppm relative to the former owing to different shielding environment and/or intramolecular H-bonding(s). Upon seeing the signal corresponding to the hydroxy group, the difference in chemical shifts is negligible ( $\Delta\delta$  +0.03 ppm) between water@2 ( $\delta$  3.81 ppm) and H<sub>2</sub>O<sub>2</sub>@2 ( $\delta$  3.84 ppm) whereas H<sub>2</sub>O<sub>2</sub>@3 ( $\delta$  3.92 ppm) showed a noticeable downfield shift of  $\Delta\delta$  +0.43 ppm relative to water@3 ( $\delta$  3.49 ppm). This is indicative of the existence of a stronger intramolecular H-bonding interaction in H<sub>2</sub>O<sub>2</sub>@3 in which the hydroxy group on the opening of open-cage C<sub>60</sub> fullerene works as



Figure 2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra of  $H_2O_2@2$  ( $H_2O_2: 35\%$ ), water@3 (water: 86%), and  $H_2O_2@3$  ( $H_2O_2: 100\%$ ).

an H-bonding donor as well as an acceptor of the  $H_2O_2$  molecule. Importantly, the Hbonding interaction is not strong enough to prevent the rotational motion of an  $H_2O_2$ molecule inside **3** as was demonstrated by the <sup>1</sup>H NMR analysis confirming a singlet signal of the  $H_2O_2$  molecule even at 180 K (Figure S1). In CDCl<sub>3</sub> at room temperature, both  $H_2O_2@2$  and  $H_2O_2@3$  showed negligible change in their spectral features for three days, confirming no release of the  $H_2O_2$  molecule. Thereby, the  $H_2O_2$  molecule is considered to be kinetically isolated from the external environment. It should be noted that  $H_2O_2@3$  could be stored in a solid state over two years without decomposition, showing exceptional stability of the encapsulated  $H_2O_2$  molecule. In solution, however, **3** was partly oxidized upon exposure to air, giving an acid anhydride derivative<sup>16a,23</sup> as confirmed by <sup>1</sup>H NMR, MS, and X-ray crystallographic analyses (Figures S5 and S6).

The single crystals of  $H_2O_2@2$  and  $H_2O_2@3$  were grown in benzene solutions containing nickel(II) octaethylporphyrin (NiOEP). The occupancies of  $H_2O_2$  and water inside 2 were refined to be 0.116(5) and 0.728(9), respectively, both of which were found



Figure 3. Single crystal X-ray structures of (a)  $H_2O_2@2$  and (b)  $H_2O_2@3$  with thermal ellipsoids at 50% probability. The aryl groups, NiOEP, solvent molecules, and disordered moieties are omitted for clarity. The space-filling models are shown without aryl groups.

at the center of the cage with a long axis of H<sub>2</sub>O<sub>2</sub> being directed toward the opening (Figure 3a). The distances of the  $O(OH) \bullet \bullet O(H_2O_2)$  and  $O(OH) \bullet \bullet O(water)$  were determined to be 3.54(2) and 4.355(6) Å, respectively. Since the general H-bonding donor-acceptor limit is known to be 3.4 Å,<sup>24</sup> the  $H_2O_2$  molecule is considered to have no significant H-bonding interactions with the hydroxy group on the opening. In contrast, the short O(OH)•••O(H<sub>2</sub>O<sub>2</sub>) distance of 2.939(5) Å was found for H<sub>2</sub>O<sub>2</sub>(a)**3** (Figure 3b), indicating the presence of a strong intramolecular H-bonding. The difference in the distance of H-bonding for  $H_2O_2(a)$  and  $H_2O_2(a)$  can be attributed to the position of the OH group, which might contribute to the easy separation of  $H_2O_2(a)$  from others during the recycle HPLC process. The O-O bond length of the H<sub>2</sub>O<sub>2</sub> molecule was determined to be 1.412(5) Å which was shorter by 0.05 Å than that in a pure  $H_2O_2$  crystal (1.461(3)) Å) $^{25}$  probably due to a confinement effect from the cage of **3**. $^{26}$  The space-filling models clearly showed that the hydroxy stopper of 2 is found at the off-centered position on its orifice while that of **3** was located near the center. Thus, these hydroxy groups on **2** and 3 could act as loose and tight stoppers, respectively, in terms of prevention from escaping the H<sub>2</sub>O<sub>2</sub> molecule.

To get deep insights into the properties of the OH group, the author performed DFT calculations at the B3LYP-D3/6-31G(d,p) level of theory, in which the tert-butyl groups were replaced by hydrogen atoms (Figure 4). The most stable conformation of 3' was found to adopt the OH bond directing to the outside of the orifice, which is more stable by  $\Delta G_{298}$  –2.39 kcal/mol than that with the OH directing to the inside (Figure S7). Reflecting this stable conformation,  $H_2O_2(a3')$ , in which the hydroxy group works as an H-bond acceptor, is more stable by -5.86 kcal/mol than the other, affording the total stabilization energy of -16.33 kcal/mol by the encapsulation of the H<sub>2</sub>O<sub>2</sub> molecule. This degree of stabilization is larger than those of  $H_2O_2(a)$  and  $H_2O_2(a)$ , which shows stabilization energies of -14.49 and -13.30 kcal/mol, suggesting that the tight stopper in 3' contributes to larger thermodynamic stabilization for the encapsulated H<sub>2</sub>O<sub>2</sub> molecule by  $\Delta\Delta G_{298}$  –1.84 and –3.03 kcal/mol than those for H<sub>2</sub>O<sub>2</sub>@**2'** and H<sub>2</sub>O<sub>2</sub>@**1'**, respectively. The distance of  $O(OH) \bullet O(H_2O_2)$  in  $H_2O_2(a)$  (2.85 Å) was shorter than that in  $H_2O_2(a)$  2' (2.99 Å), suggesting that the stronger attractive interaction between the OH group and the  $H_2O_2$  molecule in  $H_2O_2@3'$  than that in  $H_2O_2@2'$ , as observed in the X-ray crystal structures, although the calculations seem to overestimate such attractive interaction. This interaction is considered to account for the change in the chemical shifts of the <sup>1</sup>H NMR signal of the OH groups.

Then, kinetic effects<sup>27</sup> of the hydroxy stopper were studied by calculation of the

transition states for the escape. The required energies for the escape are  $\Delta G^{\ddagger}$  +16.90, +27.82, and +38.70 kcal/mol for H<sub>2</sub>O<sub>2</sub>@1', H<sub>2</sub>O<sub>2</sub>@2', and H<sub>2</sub>O<sub>2</sub>@3', respectively. It was found that **3'-TS** showed the highest energy among them probably due to the larger deformation of the OH group at the transition state (Figure 4b), confirming that the position of the OH group has a significant influence on the escape. These results indicate that the introduction of the hydroxy group and its arrangement contribute to both thermodynamic and kinetic stabilization of the molecular complex.



Figure 4. (a) Release process of  $H_2O_2$  from  $H_2O_2@1'$ ,  $H_2O_2@2'$ , and  $H_2O_2@3'$ , calculated at the B3LYP-D3/6-31G(d,p) level of theory. The  $\Delta G$  values are shown in kcal/mol at 298 K. (b) Selected ground and transition states for  $H_2O_2@2'$  and  $H_2O_2@3'$ .

### Conclusion

In summary, the author succeeded in stabilizing a single  $H_2O_2$  molecule by use of the hydroxy group on the orifice of the open-cage  $C_{60}$  derivative to isolate a pure peroxosolvate,  $H_2O_2@3$ , as a distinct molecular structure. This complex was obtained by the treatment of the open-cage C<sub>60</sub> derivative with 30%  $H_2O_2$  aq., followed by the reduction of one of the carbonyl groups. Two structural isomers generated, in which the hydroxy group was located at different positions. The intramolecular H-bonding in this system was studied by <sup>1</sup>H NMR, recycle HPLC profile, X-ray crystallographic analysis, and DFT calculations. It was found that the OH group works as both the thermodynamic and kinetic stopper for the  $H_2O_2$  molecule due to the appropriate arrangement of the hydroxy group.

### **Experimental Section**

**General.** The <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out at room temperature (unless otherwise noted) with JEOL JNM ECA500, Bruker Avance III 600US Plus instruments, and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of CDCl<sub>3</sub> ( $\delta$  7.26 ppm in <sup>1</sup>H NMR,  $\delta$  77.00 ppm in <sup>13</sup>C NMR) and CD<sub>2</sub>Cl<sub>2</sub> ( $\delta$  5.32 ppm in <sup>1</sup>H NMR). ESI (electrospray ionization) and APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. IR spectrum was taken with a Shimadzu IR-Affinity 1S. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (two directly connected columns; 250 mm in length, 20 mm in inner diameter) for preparative purpose. The reactions at low temperature were conducted using a UC reactor (UCR-150N, Techno-Sigma Co., Ltd.). Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B or 100B (Fuji Silysia).

Fullerene  $C_{60}$  was purchased from SES Research Co. Toluene was purchased from Kanto Chemical Co., Inc. Hexane and ethyl acetate were purchased from Nacalai Tesque, Inc. 1.0 M BH<sub>3</sub>•THF was purchased from Sigma-Aldrich. Co. LLC. 30 wt% of H<sub>2</sub>O<sub>2</sub> aqueous solution, acetone, and carbon disulfide were purchased from FUJIFILM Wako Pure Chemical Corporation. Open-cage fullerene C<sub>60</sub> derivative **1** was synthesized according to the literature.<sup>20</sup>

All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification.

**Computational Methods.** All calculations were conducted with the Gaussian 09 program package. All structures at stationary and transition states were optimized at the B3LYP-D3/6-31G(d,p) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory.

#### Synthesis of H<sub>2</sub>O<sub>2</sub>@2 and H<sub>2</sub>O<sub>2</sub>@3.

### Reaction at 5 °C

Powdery **1** (water: *ca.* 30%, 20.1 mg, 17.6 µmol) was placed into a 10 mL two-neck glass tube and degassed through three vacuum-Ar cycles. Toluene (1.76 mL, 10.0 mM) was added and cooled down to 5 °C (thermostatic bath using acetone). A 30 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution (0.2 mL) was added and stirred for 1 h. Then, 1.0 M BH<sub>3</sub>•THF (26.5 µL, 26.5 µmol, 1.5 equiv) was added slowly. After stirred at 5 °C for 0.5 h, the crude mixture was directly charged onto a silica gel column (CS<sub>2</sub>/ethyl acetate (200:1) to (20:1)) giving H<sub>2</sub>O<sub>2</sub>@**2** (H<sub>2</sub>O<sub>2</sub>: 6%, water: 61%, 7.48 mg, 6.50 µmol, 37%), H<sub>2</sub>O<sub>2</sub>@**3** (H<sub>2</sub>O<sub>2</sub>: 41%, water: 53%, 1.24 mg, 1.07 µmol, 6%), and unreacted **1** (4.70 mg, 4.12 µmol, 23%) as brown powders.

### Reaction at -60 °C

Powdery **1** (water: *ca.* 30%, 20.2 mg, 17.7 µmol) was placed into a 10 mL two-neck glass tube and degassed through three vacuum-Ar cycles. Toluene (1.76 mL, 10.1 mM) was added and cooled down to -60 °C (thermostatic bath using acetone). A 30 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution (0.2 mL) was added and stirred for 1 h. Then, 1.0 M BH<sub>3</sub>•THF (26.5 µL, 26.5 µmol, 1.5 equiv) was added slowly. After stirred at -60 °C for 0.5 h, the crude mixture was directly charged onto a silica gel column (CS<sub>2</sub>/ethyl acetate (200:1) to (20:1)) giving H<sub>2</sub>O<sub>2</sub>@**2** (H<sub>2</sub>O<sub>2</sub>: 35%, water: 31%, 8.54 mg, 7.40 µmol, 42%), H<sub>2</sub>O<sub>2</sub>@**3** (H<sub>2</sub>O<sub>2</sub>: 81%, water: 11%, 1.13 mg, 0.97 µmol, 5%), and unreacted **1** (5.62 mg, 4.93 µmol, 28%) as brown powders. The complete isolation of H<sub>2</sub>O<sub>2</sub>@**3** was achieved by recycle HPLC.



H<sub>2</sub>O<sub>2</sub>@2 (H<sub>2</sub>O<sub>2</sub>: 35%, water: 28%, N<sub>2</sub>: 18%, and empty: 19%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 (t, 1H, J = 7.7 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.38–7.45 (m, 1H), 7.19–7.25 (m, 4H), 7.11 (d, 1H, J = 7.5 Hz), 6.60–6.67 (m, 1H), 3.84 (d, 0.35H, J = 4.6 Hz), 3.81 (d, 0.47H, J = 4.0 Hz), 3.77 (d, 0.18H, J = 4.0 Hz), 1.20 (s, 9H, two of singlet peaks), 1.10 (s, 9H, two of singlet peaks), -4.16 (for encapsulated H<sub>2</sub>O<sub>2</sub>, s, 0.70H), -11.06 (for encapsulated H<sub>2</sub>O, s, 0.56H), (The proton signals of X@2 (X = H<sub>2</sub>O<sub>2</sub>, water, N<sub>2</sub>, and empty) are separately observed.);  ${}^{13}$ C NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.99, 197.88, 197.77, 197.70, 185.95, 185.83, 185.79, 185.75, 182.97, 182.68, 182.56, 182.54, 168.69, 168.65, 168.46, 168.42, 164.00, 163.86, 163.82, 162.82, 162.77, 162.70, 162.64, 157.79, 157.50, 157.28, 157.14, 156.62, 156.53, 156.43, 156.32, 153.08, 152.99, 152.76, 152.69, 151.20, 150.92, 150.85, 150.79, 150.68, 150.64, 150.61, 150.53, 150.50, 150.44, 150.42, 150.40, 150.38, 150.29, 150.27, 150.22, 150.17, 150.14, 149.96, 149.91, 149.63, 149.59, 149.57, 149.49, 149.48, 149.44, 149.35, 149.28, 149.16, 149.12, 149.10, 149.06, 149.05, 149.03, 148.97, 148.89, 148.83, 148.74, 148.71, 148.52, 148.44, 148.34, 148.27, 147.08, 146.92, 146.79, 146.76, 146.48, 146.20, 146.12, 146.02, 145.55, 145.25, 145.19, 145.04, 144.98, 144.90, 144.86, 144.82, 144.77, 144.75, 144.67, 144.59, 144.43, 144.32, 144.27, 143.88, 143.83, 143.77, 143.65, 143.60, 143.55, 143.49, 143.45, 143.43, 143.42, 143.39, 143.35, 143.05, 142.95, 142.89, 142.83, 142.66, 142.35, 142.10, 141.99, 141.88, 141.78, 141.58, 141.53, 141.48, 141.47, 141.43, 141.33, 141.30, 141.22, 141.05, 140.76, 140.73, 140.71, 140.47, 138.73, 138.62, 138.52, 138.15, 138.09, 138.00, 137.98, 137.92, 137.88, 137.82, 137.75, 137.64, 137.59, 137.45, 137.42, 137.40, 137.34, 137.29, 137.21, 137.13, 137.07, 137.06, 137.01, 137.00, 136.93, 136.87, 136.80, 136.76, 136.67, 136.65, 136.53, 136.49, 136.45, 136.28, 136.22, 136.18, 136.16, 136.12, 136.09, 136.00, 135.80, 135.77, 135.08, 135.02, 134.79, 134.76, 134.55, 134.14, 134.10, 133.67, 133.37, 133.29, 133.25, 133.08, 132.96, 132.70, 132.66, 132.65, 132.00, 131.77, 131.76, 131.46, 131.10, 130.40, 130.33, 130.27, 130.24, 130.04, 129.97, 129.70, 129.59, 129.42, 129.32, 125.54, 125.09, 124.95, 124.89, 124.75, 124.74, 124.69, 124.64, 124.49, 120.47, 119.93, 119.88, 119.70, 119.66, 119.63, 119.52, 117.66, 117.48, 117.36, 117.33, 117.31, 117.10, 117.06, 82.47, 82.45, 82.38, 82.32, 59.04, 58.99, 58.95, 54.55, 54.44, 54.40, 37.75, 37.66, 37.63, 29.98, 29.90, 29.84, 29.70 (The <sup>13</sup>C signals of X@2 (X = H<sub>2</sub>O<sub>2</sub>, water, N<sub>2</sub>, and empty) are separately observed, some of which are overlapped both in aliphatic and aromatic regions. The sum of carbon signals must be 312 in theory. Observed 249.); HRMS (ESI): m/z [M+Na]<sup>+</sup> Calcd for C<sub>82</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>SNa (2Na): 1159.1662; found: 1159.1614; calcd for  $C_{82}H_{30}N_2O_5SNa$  (water@2Na): 1177.1768; found 1177.1729; calcd for  $C_{82}H_{28}N_4O_4SNa$  $(N_2@2N_a)$ : 1187.1723; found: 1187.1726; calcd for  $C_{82}H_{30}N_2O_6SN_a$   $(H_2O_2@2N_a)$ :

1193.1717; found 1193.1697.

H<sub>2</sub>O<sub>2</sub>@**3** (H<sub>2</sub>O<sub>2</sub>: 100%): IR (KBr) *v* 3591–3244(OH), 1732 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (dd, 1H, *J* = 8.1 Hz, *J* = 7.4 Hz), 7.40 (dd, 1H, *J* = 8.1 Hz, *J* = 7.4 Hz), 7.31 (d, 1H, *J* = 8.1 Hz), 7.21 (d, 1H, *J* = 7.4 Hz), 7.04 (d, 1H, *J* = 7.4 Hz), 6.87 (d, 1H, *J* = 10.3 Hz), 6.86 (d, 1H, *J* = 8.1 Hz), 6.68 (d, 1H, *J* = 6.3 Hz), 6.02 (d, 1H, *J* = 10.3 Hz), 3.92 (d, 1H, *J* = 6.3 Hz), 1.22 (s, 9H), 1.17 (s, 9H), -3.81 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 194.29, 186.31, 184.30, 168.23, 167.80, 164.31, 161.07, 155.95, 152.52, 152.38, 150.68, 150.66, 150.57, 150.12, 150.06, 149.69, 149.63, 149.61, 149.35, 149.07; 148.69, 148.01, 147.89, 147.55, 147.30, 146.83, 145.29, 145.27, 145.00, 144.98, 144.28, 143.64, 143.56, 143.37, 143.35, 143.20, 142.54, 142.10, 141.98, 141.34, 141.02, 140.98, 139.67, 139.64, 139.29, 138.87, 138.59, 138.46, 137.24, 136.95, 136.50, 136.41, 134.57, 134.18, 133.22, 133.19, 132.41, 131.70, 131.49, 131.10, 128.51, 128.34, 125.22, 120.92, 119.83, 116.97, 116.88, 71.94, 54.82, 50.37, 37.64, 37.58, 29.90, 29.88 (The sum of carbon signals must be 78 in theory. Observed 74. Four sp<sup>2</sup> carbon signals are overlapped in the aromatic region.); HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>82</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>SNa (H<sub>2</sub>O<sub>2</sub>@**3**Na): 1193.1717; found: 1193.1709.







\*HPLC (Buckyprep, 20φ×2, 25 °C, 6.0 mL/min, toluene)

Figure S2. HPLC profiles for 2 and 3 in which  $H_2O_2$  and water molecules were the major encapsulated species.

Synthesis of water@2 and water@3. Powdery 1 (water: *ca.* 30%, 20.5 mg, 17.9  $\mu$ mol) was placed into a 10 mL two-neck glass tube and degassed through three vacuum-Ar cycles. Toluene (1.76 mL, 10.2 mM) was added and cooled down to -60 °C (thermostatic bath using acetone). Distilled water (0.2 mL) was added and stirred for 1 h. Then, 1.0 M BH<sub>3</sub>•THF (26.5  $\mu$ L, 26.5  $\mu$ mol, 1.5 equiv) was added slowly. After stirred at -60 °C for 0.5 h, the crude mixture was directly charged onto a silica gel column (CS<sub>2</sub>/ethyl acetate (200:1) to (20: 1)) giving water@2 (water: 64%, 12.4 mg, 10.8  $\mu$ mol, 60%), water@3 (water: 91%, 0.95 mg, 0.82  $\mu$ mol, 5%), and unreacted 1 (1.81 mg, 1.59  $\mu$ mol, 9%) as brown powders. The structure of water@2 was determined from <sup>1</sup>H NMR and mass spectra which were matched well with the previously reported one.<sup>26</sup>



water @**3** (water: 86%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (dd, 1H, J = 8.0 Hz, J = 6.9 Hz), 7.39 (dd, 1H, J = 8.0 Hz, J = 6.9 Hz), 7.29 (d, 1H, J = 6.9 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.03 (d, 1H, J = 8.0 Hz), 6.88 (d, 1H, J = 10.3 Hz), 6.84 (d, 1H, J = 8.0 Hz), 6.65 (d, 1H, J = 6.9 Hz), 6.05 (d, 1H, J = 10.3 Hz), 3.49 (d, 1H, J = 6.9 Hz), 1.22 (s, 9H), 1.17 (s, 9H), -10.70 (s, 1.72H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  193.55, 186.11, 184.09, 168.22, 167.80, 164.21, 161.19, 155.99, 152.56, 152.15, 151.00, 150.68, 150.60, 150.12, 149.76, 149.70, 149.61, 149.54, 149.43; 149.06, 147.94, 147.24, 147.02, 146.83, 145.99, 145.60, 145.10, 145.01, 144.05, 143.86, 143.76, 143.23, 143.14, 143.10, 142.70, 142.30, 141.99, 141.74, 140.92, 140.20, 139.45, 139.26, 138.99, 138.00, 137.70, 137.55, 137.46, 136.94, 136.91, 136.77, 136.60, 136.47, 136.43, 134.42, 133.54, 132.94, 132.28, 131.92, 131.05, 130.82, 128.74, 126.90, 125.12, 120.91, 119.82, 116.99, 116.82, 71.90, 54.75, 50.55, 37.65, 37.58, 29.90, 29.88 (The sum of carbon signals must be 78 in theory. Observed 74. Four sp<sup>2</sup> carbon signals are overlapped in the aromatic region.).

water@3 (water: 70%): HRMS (APCI): m/z [M]<sup>-</sup> Calcd for C<sub>82</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>S (3): 1136.1775; found: 1136.1763 (Under the measured conditions, the signal corresponding to water@3 was not observed probably due to spontaneous escape of the water molecule).

**Encapsulation of H<sub>2</sub>O<sub>2</sub> inside 1.** To a CDCl<sub>3</sub> solution of **1** in an NMR tube (*ca*. 1mg, 0.5 mL), two drops of 30 wt%  $H_2O_2$  aq. were added at room temperature.



**Figure S3.** <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>) of **1**: (a) after and (b) before the addition of 30 wt%  $H_2O_2$  aqueous solution.

An Oxidized Derivative. During the storage of  $H_2O_2@3$  in CDCl<sub>3</sub> or toluene solution under air,  $H_2O_2@3$  was partly oxidized to form  $H_2O_2@4$ , which could be separated by recycle HPLC. Due to the limited amount of  $H_2O_2@4$ , the <sup>13</sup>C NMR spectrum could not be measured. The <sup>1</sup>H NMR signal pattern of  $H_2O_2@4$  was quite similar to that of  $H_2O_2@3$  and showed the presence of the CH(OH) moiety in  $H_2O_2@4$ . The mass spectrum showed a signal corresponding to  $H_2O_2@3+O^{-}$  at m/z 1185.1655. The single crystal X-ray analysis of  $H_2O_2@3$  (Figure S6) revealed that acid anhydride derivative  $H_2O_2@4$  exists as a minor component with an occupancy of 0.130(12). The group which the author belongs to previously showed that **1** was partly oxidized at the 1,2-dicarbonyl moiety to form an acid anhydride derivative upon expose to  $O_2$ .<sup>16a</sup> By accumulating these observation, the structure of  $H_2O_2@4$  was deduced to have a hydroxy group and an acid anhydride moiety, in which the structure fully satisfies the <sup>1</sup>H NMR and mass spectra.

 $H_2O_2@4$ : ( $H_2O_2$ : 75%, water: 21%, and empty: 4%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$
7.66 (t, 1H, J = 7.7 Hz), 7.47 (d, 1H, J = 8.0 Hz), 7.40 (t, 1H, J = 8.0 Hz), 7.22 (d, 1H, J = 6.9 Hz), 7.04 (d, 1H, J = 6.9 Hz), 6.80 (d, 1H, J = 7.4 Hz), 6.74 (d, 1H, J = 10.3 Hz), 6.72 (d, 1H, J = 6.3 Hz), 6.09 (d, 1H, J = 10.3 Hz), 3.76 (d, 0.75H, J = 6.3 Hz), 3.22 (d, 0.21H, J = 6.3 Hz), 1.21 (s, 9H), 1.18 (s, 9H), -3.68 (s, 1.50H), -10.51 (s, 0.42H); HRMS (APCI): m/z [M]<sup>-</sup> calcd for C<sub>82</sub>H<sub>30</sub>N<sub>2</sub>O<sub>7</sub>S (H<sub>2</sub>O<sub>2</sub>@**4**): 1185.1701; found 1185.1655.

Single Crystal X-Ray Structure of 1. Single crystals of 1 were obtained from a benzene solution by slow evaporation. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and graphite monochromator. A total of 35679 reflections were measured at the maximum  $2\theta$  angle of 50.06°, of which 13294 were independent reflections ( $R_{int} =$ 0.0201). The structure was solved by direct methods (SHELXT- $97^{28}$ ) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>28</sup>). One of *t*-butyl groups was disordered, which was solved using appropriate models. Thus, (C71-C72-C73) and (C114-C115-C117) were placed and their occupancies were refined to be 0.771(6) and 0.229(6), respectively, using a SIMU instruction. One of ethyl groups on cobalt(II) octaethylporphyrin (CoOEP) was disordered. Thus, (C97-C98) and (C97-C99) were placed and their occupancies were refined to be 0.765(7) and 0.235(7), respectively, using SIMU and ISOR instructions. The encapsulated N<sub>2</sub> molecule was disordered with an Ar atom at the same position. Thus, (N5-N6) and Ar1 were placed and their occupancies were refined to be 0.430(15) and 0.280(10), respectively, using DFIX and SIMU instructions. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $C_{112}H_{60}Ar_{0.28}Co_{0.50}N_{4.86}O_{4}S$ ; FW = 1610.38, crystal size  $0.42 \times 0.20 \times 0.03 \text{ mm}^{3}$ , monoclinic,  $P2_1/c$ , a = 17.123(6) Å, b = 14.563(5) Å, c = 31.127(11) Å,  $\beta = 103.752(5)^\circ$ , V = 7539(4) Å<sup>3</sup>, Z = 4,  $D_c = 1.419$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.0422$ ,  $wR_2$ = 0.1165  $(I > 2\sigma(I))$ , GOF = 0.965. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2113506).



Figure S4. Single crystal X-ray structure of 1.

Single Crystal X-Ray Structure of H<sub>2</sub>O<sub>2</sub>@2. Single crystals of H<sub>2</sub>O<sub>2</sub>@2 were obtained from a benzene solution by slow evaporation at 5 °C. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 13317 reflections were measured at the maximum  $2\theta$  angle of 49.96°, of which 11549 were independent reflections ( $R_{int} = 0.0202$ ). The structure was solved by direct methods (SHELXT-97<sup>28</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>28</sup>). The orifice substructure was disordered at two positions, which were solved using appropriate models. Thus, (C6-C7-O2-O3) and (C65-C66-O7-O8-O9) and O6 and O5 were placed and their occupancies were refined to be 0.837(4) and 0.163(4) and 0.281(10) and 0.719(10), respectively. One of t-butyl groups was disordered. Thus, (C73–C74–75) and (C123-C125-C126) were placed and their occupancies were refined to be 0.835(5) and 0.165(5), respectively. One of ethyl groups on nickel(II) octaethylporphyrin (NiOEP) was disordered. Thus, (C100-C104) and (C100-C101) were placed and their occupancies were refined to be 0.371(6) and 0.629(6), respectively. One of benzene molecules was disordered. Thus, (C111-C112-C113-C114-C115-C116) and (C117-C118-C119-C120-C121-C122) were placed and their occupancies were refined to be 0.414(17) and 0.586(17), respectively. The encapsulated water molecule was disordered with the H<sub>2</sub>O<sub>2</sub> molecule at the same position. Thus, O13 and (O10-O12) were placed and their occupancies were refined to be 0.728(9) and 0.116(5), respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for the encapsulated molecules were placed using AFIX instructions. The disordered benzene molecules, tbutyl groups, dicarbonyl moiety were refined using SIMU instructions. The encapsulated molecules were refined using DFIX instructions. The crystal data are as follows:  $C_{112}H_{63,13}N_4N_{10,50}O_{5,12}S$ ; FW = 1608.18, crystal size  $0.30 \times 0.24 \times 0.10$  mm<sup>3</sup>, monoclinic, 7600.8(7) Å<sup>3</sup>, Z = 4,  $D_c = 1.405$  g cm<sup>-3</sup>. The refinement converged to  $R_1 = 0.0368$ ,  $wR_2 =$ 0.1059  $(I > 2\sigma(I))$ , GOF = 1.088. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2113508).



Figure S5. Single crystal X-ray structure of H<sub>2</sub>O<sub>2</sub>@2.

Single Crystal X-Ray Structure of H<sub>2</sub>O<sub>2</sub>@3. Single crystals of H<sub>2</sub>O<sub>2</sub>@3 were obtained from a benzene solution by slow evaporation at 5 °C. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 16308 reflections were measured at the maximum  $2\theta$  angle of 50.14°, of which 12916 were independent reflections ( $R_{int} = 0.0307$ ). The structure was solved by direct methods (SHELXT-97<sup>28</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>28</sup>). The orifice substructure was disordered at two positions, which were solved using appropriate models. Thus, (C6-C153-O3-O11) and (C7-C152-O7-O9-O10) were placed and their occupancies were refined to be 0.870(12) and 0.130(12), respectively. Several benzene molecules were disordered. Thus, (C140-C141-C142-C143-C144-C145) and (C146-C147-C148-C149-C150-C151) and (C119-C120-C121-C122-C123-C124, C125-C126-C127-C128-C129-C130) and (C131-C132-C133-C134-C135-C136) were placed and their occupancies were refined to be 0.619(10) and 0.257(9) and 0.660(5) and 0.340(5), respectively. The occupancy of the encapsulated H<sub>2</sub>O<sub>2</sub> molecule was refined to be 0.944(9). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The disordered benzene molecules were refined using ISOR or SIMU instructions. The dicarbonyl moiety was refined using ISOR, DELU, and DFIX instructions. The C42 atom was refined using an ISOR instruction. The crystal data are as follows:  $C_{136.21}H_{92.10}N_6NiO_{6.02}S$ ; FW = 1999.89, crystal size  $0.37 \times 0.10 \times$ 0.07 mm<sup>3</sup>, monoclinic,  $P2_1/c$ , a = 29.029(7) Å, b = 13.461(3) Å, c = 24.308(6) Å,  $\beta = 12.461(3)$  Å, c = 24.308(6) Å,  $\beta = 12.461(3)$  Å, c = 24.308(6) Å,  $\beta = 12.461(3)$   $102.796(4)^{\circ}$ , V = 9262(4) Å<sup>3</sup>, Z = 4,  $D_c = 1.434$  g cm<sup>-3</sup>. The refinement converged to  $R_1$ = 0.0800,  $wR_2 = 0.1927$  ( $I > 2\sigma(I)$ ), GOF = 1.154. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2113507).



Figure S6. Single crystal X-ray structure of H<sub>2</sub>O<sub>2</sub>@3.

# DFT Calculations: Conformations of (a) H<sub>2</sub>O<sub>2</sub>@2' and (b) H<sub>2</sub>O<sub>2</sub>@3'.



**Figure S7.** Conformations of (a)  $H_2O_2@2'$  and (b)  $H_2O_2@3'$ , calculated at the B3LYP-D3/6-31G(d,p) level of theory.

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## Chapter 2

# CH<sub>3</sub>CN@open-C<sub>60</sub>: An Effective Inner-Space Modification and

# Isotope Effect inside the Nano-Sized Flask

**Abstract:** Despite several small molecules being encapsulated inside cage-opened  $C_{60}$  fullerene derivatives, such species have not considerably affected the structures and properties of the outer carbon cages. In this chapter, the author discussed an effective inner-space modification of an open-cage  $C_{60}$  derivative by insertion of a neutral CH<sub>3</sub>CN molecule into the cage. Thus, the obtained CH<sub>3</sub>CN@open-C<sub>60</sub> was found to show an enhanced polarity. An easy separation from a mixture containing the empty cage by column chromatography on silica gel was realized without the preparative recycle HPLC that was needed for the cases in chapter 1. The less negative reduction potentials with respect to those of empty cages reflect the decreased energy level of the LUMO, which was supported by the DFT calculations. It was revealed that both the presence of the encapsulated CH<sub>3</sub>CN and cage deformation caused by the CH<sub>3</sub>CN play an essential role in the change in the electronic properties, which were confirmed by NMR spectroscopy, single-crystal X-ray analysis, and theoretical calculations. Furthermore, the favored binding affinity of deuterated acetonitrile CD<sub>3</sub>CN with internal C<sub>60</sub> surface was discussed.

### Introduction

Modification of cage-like nanocarbons such as fullerene  $C_{60}$  and higher allotropes by encapsulating small species into their cavity has received attention owing to the unique hollow structures.<sup>1</sup> Physical properties, e.g., the size,<sup>2</sup> redox potentials,<sup>3</sup> and HOMO– LUMO levels,<sup>4</sup> were found to be altered when metals (Li,<sup>5</sup> La,<sup>6</sup> and Sc<sup>7</sup>) and their clusters<sup>8</sup> were encapsulated in the interior. Nevertheless, the preparation had been limited to physical techniques, including fast ion beam and co-vaporization, which are high-costing with low yields after extraction from the soot, followed by tedious purification by recycle HPLC.<sup>9</sup>

Therefore, a different pathway, "molecular surgery" was developed,<sup>10</sup> where selective cleavage and restoration of C-C/C=C bonds located on the surface of C<sub>60</sub> were already established methods of organic synthesis. Some polar molecules<sup>11</sup> or magnetic molecules<sup>12</sup> were encapsulated by this approach, and they were expected to influence the properties of the cages. However, the changes upon encapsulation are minimal for separation behavior on chromatography, redox potentials, and alignment in the solid state, probably due to weak intermolecular interactions between the cages and the inner molecules.<sup>13</sup> In 2016, Yeh et al. reported that attempts to separate their open-cage C<sub>60</sub> derivative containing HCHO from a mixture including H<sub>2</sub>O-encapsulating and empty ones by thin-layer chromatography (TLC) were unsuccessful.<sup>14</sup> In 2023, Gan et al. mentioned that the empty open-cages and the complexes encapsulating H<sub>2</sub>O and LiF have the same polarity.<sup>15</sup> Only halide anions inside have changed the polarity, but different halide-encapsulated complexes exhibit the same polarity and similar spectroscopic data.<sup>16</sup> As shown in Figure 1, Y. Murata's research group, which the author belongs to, isolated pure  $N_2(a)\mathbf{1}^{17}$  and  $O_2(a)\mathbf{1}^{12a}$  by employing recycle preparative HPLC with 15 and 16 recycles, respectively. The relatively easy separation was achieved when HCHO<sup>18</sup> and CH<sub>3</sub>OH<sup>18</sup> with large dipole moments and CO<sub>2</sub><sup>17</sup> with relatively large size were encapsulated. Since no other considerable changes in the structures or properties were observed previously by the above-described encapsulation, the author considered that encapsulation of a large molecule with a large dipole moment could provide more noticeable changes in the cage.

Acetonitrile, consisting of one nitrogen, two carbon, and three proton atoms, has a dipole moment of 3.9 Debye with the direction along the  $C-C \equiv N$  axis.<sup>19</sup> The low viscosity and low chemical reactivity make it a well-used eluent for purification. These characteristics of acetonitrile thus prompted the author to use it for inner-space modification. In this charpter 2, the author reported i) the encapsulation of CH<sub>3</sub>CN inside

open-cage  $C_{60}$  derivative **3** and ii) the electronic properties of the molecular complex, as well as iii) the equilibrium isotope effect for encapsulation of CH<sub>3</sub>CN over CD<sub>3</sub>CN.



**Figure 1.** Previous works for open-cage  $C_{60}$  derivatives **1** and **2** encapsulating molecules, which were separated by recycle HPLC equipped with the Buckyprep columns, and the present study of CH<sub>3</sub>CN@**3**, which was isolated by column chromatography on silica gel.

#### **Results and Discussion**

**Synthesis and purification.** Y. Murata's research group, which the author belongs to, has already reported that a CH<sub>3</sub>CN molecule can not be encapsulated into tetraketone **2** having a 17-membered ring orifice,<sup>18</sup> suggesting that larger openings are needed for encapsulation. Then, the author examined the use of thioester **3**,<sup>20</sup> which possesses a larger 18-membered ring orifice with two sulfur atoms on the opening as a host. As shown in Figure 2a, **3** was heated with an excess amount of CH<sub>3</sub>CN in *o*-dichlorobenzene (ODCB) at 150 °C under 9,400 atm for 24 h (Entry 1). After recovery of the resulting solution to ambient temperature and pressure, followed by treatment with a short pad of silica gel to remove ODCB, a mixture of CH<sub>3</sub>CN@**3** (40%), N<sub>2</sub>@**3** (10%), and empty **3** (50%) was obtained in 57% isolated yield. The high pressure was essential for the success of insertion (Entry 2). The lower temperature below 100 °C resulted in a lower encapsulation ratio of 9% (Entry 3), and no insertion occurred at room temperature even under high-pressure conditions (Entry 4).

The TLC analysis (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) showed the  $R_f$  values of 0.05 for CH<sub>3</sub>CN@**3** and 0.20 for empty **3**, respectively, showing a clear difference in polarity depending on the

presence/absence of the encapsulated CH<sub>3</sub>CN molecule. Thus, facile separation of complex CH<sub>3</sub>CN@**3** from **3** was achieved by the simple column chromatography as shown in Figure 2b, affording pure CH<sub>3</sub>CN@**3** in 24% isolated yield with 100% encapsulation ratio (Entry 1). On the analytical HPLC (Figure 2c), a longer retention time of 19.4 min was recorded for CH<sub>3</sub>CN@**3** while that of **3** was 11.0 min. The difference in retention time is known to reflect the strength of the intermolecular interactions between the encapsulated species and the outer carbon cage.<sup>18,21</sup> Therefore, the interactions between cage **3** and the encapsulated CH<sub>3</sub>CN molecule should be stronger than the reported cases for encapsulation of CH<sub>3</sub>OH,<sup>18</sup> HCHO,<sup>18</sup> and CO<sub>2</sub><sup>17</sup> inside **1** or **2** since those complexes with encapsulations have almost the same retention times as those for the empty cages by the same HPLC conditions.



Figure 2. (a) Encapsulation of CH<sub>3</sub>CN inside 3. The encapsulation ratio was determined by <sup>1</sup>H NMR. (b) Separation of CH<sub>3</sub>CN@3 from 3 by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. (c) The analytical HPLC chart using the Buckyprep column for CH<sub>3</sub>CN@3 and 3 with toluene as an eluent at 50 °C.

NMR studies. Regarding the structure of  $CH_3CN@3$ , there can be two orientations for the encapsulated  $CH_3CN$  molecule inside 3; the methyl group positioned at the

bottom/top of the carbon cage, i.e., CH<sub>3</sub>CN@3-down and CH<sub>3</sub>CN@3-up, respectively (Figure S8). As shown in Figure 3a, the <sup>1</sup>H NMR spectrum of CH<sub>3</sub>CN@3 at room temperature displayed only single species as judged from the sharp singlet signal at  $\delta$  – 11.91 ppm (singlet, three protons). The DFT calculations at B3LYP-D3/6-31G(d,p) level showed that CH<sub>3</sub>CN@**3**-down gains stabilization ( $\Delta G_{298}$  –2.43 kcal/mol) while CH<sub>3</sub>CN@**3**-up was suggested to be destabilized ( $\Delta G_{298}$  +2.45 kcal/mol). The gaugeindependent atomic orbital (GIAO) method at B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d,p) level predicted the chemical shifts of the CH<sub>3</sub>CN molecule being  $\delta$  –11.87 ppm for CH<sub>3</sub>CN( $\partial$ **3**-down and  $\delta$  –3.56 ppm for CH<sub>3</sub>CN( $\partial$ **3**-up. Therefore, the orientation observed in the <sup>1</sup>H NMR should be concluded as CH<sub>3</sub>CN@**3**-down. An equilibrium state through direct exchange between the two orientations is unlikely because of the high barrier of +60.3 kcal/mol (Figure S8). Since the insertion barrier toward CH<sub>3</sub>CN@3-down  $(\Delta G_{298} + 28.10 \text{ kcal/mol})$  is able to be overcome at high temperatures, CH<sub>3</sub>CN(*a*)**3**-down is considered to be directly generated, in sharp contrast to the reported case for insertion of CH<sub>3</sub>OH.<sup>18</sup> Isolated CH<sub>3</sub>CN@**3** was stable without any release of CH<sub>3</sub>CN at 5 °C for three months, checked by <sup>1</sup>H NMR.

Subsequently, <sup>1</sup>H relaxation was examined for CH<sub>3</sub>CN@**3** in CDCl<sub>3</sub> (Figure S1). The spin-lattice and spin-spin relaxation times ( $T_1$  and  $T_2$ ) were measured on an 800 MHz NMR instrument by applying the inversion-recovery and CPMG methods, respectively, to study the molecular motion. The results showed a tendency that  $T_1$  values increase with lowering the temperature from 340 to 260 K while  $T_2$  values decrease, resulting in a large  $T_1-T_2$  gap at low temperature. This temperature dependence indicates the dominant spin-rotation mechanism for the <sup>1</sup>H relaxation. Thus, at low temperatures, the rotational motion of the CH<sub>3</sub> group in CH<sub>3</sub>CN@**3** is considered to be restricted. These characteristics are reminiscent of a trapped H<sub>2</sub>O molecule inside an open-cage C<sub>60</sub> fullerene cage: restricted rotations are induced by electrostatic interactions with host fullerene cages such as C<sub>60</sub>RE<sup>22</sup> (E: heteroatom) and C<sub>59</sub>N.<sup>23</sup> Compared with the  $T_1$  value of neat CH<sub>3</sub>CN (*ca.* 15 s at 300 K under 25 MHz),<sup>24</sup> measured  $T_1$  value (*ca.* 1.5 s) of CH<sub>3</sub>CN@**3** is much smaller due to the faster relaxation, which should be owing to the strongly restricted rotational motion of the CH<sub>3</sub>CN molecule inside **3** and/or secondary effect through a heteronuclear dipole–dipole interactions with the <sup>13</sup>C fullerene wall.

From the <sup>13</sup>C NMR spectrum, signals of the cyano and methyl carbons of CH<sub>3</sub>CN appeared at  $\delta$  107.67 and -14.00 ppm, respectively (Figure 3b). With respect to free CH<sub>3</sub>CN in CDCl<sub>3</sub> ( $\delta$  116.20 ppm for CN and  $\delta$  0.96 ppm for CH<sub>3</sub>), the methyl signal is more down-field shifted ( $\Delta \delta$  = -13.04 ppm) than the cyano signal ( $\Delta \delta$  = -8.53 ppm),

supporting the orientation of CH<sub>3</sub>CN@**3**-down. Generally, a sharp and high-intensity signal is obtained for carbon directly connected to protons due to facile relaxation induced by dipole–dipole interactions, whereas a spin–rotation mechanism also contributes to the relaxation for the methyl group in CH<sub>3</sub>CN.<sup>25</sup> Interestingly, the ratio of the signal intensity  $I_{Me}/I_{CN}$  varies from 1.6 (CH<sub>3</sub>CN in CDCl<sub>3</sub>) to 0.6 (CH<sub>3</sub>CN@**3** in CDCl<sub>3</sub>). In addition, the signal height of the methyl carbon of CH<sub>3</sub>CN@**3** was abnormally low even compared with those of carbons without direct C–H bonds, such as the cyano and sp<sup>2</sup> carbons on the fullerene cage. This result suggests the long relaxation time of the methyl is contributed by the spin–rotation mechanism. On the other hand, the cavity of **3** could not offer the reorientation, leading to less contribution by the dipole–dipole mechanism, which considerably suppresses the signal-enhancement by nuclear Overhauser effect.<sup>26</sup>



**Figure 3.** (a) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra of **3** (55% for empty **3** and 45% for N<sub>2</sub> and other encapsulated species<sup>20</sup>) and CH<sub>3</sub>CN@**3** (100% encapsulation ratio). (b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of CH<sub>3</sub>CN@**3** (100% encapsulation ratio).

**Single crystal X-ray structure.** The single crystals of CH<sub>3</sub>CN@**3** were obtained with the same solvent molecules and the same arrangement of nickel octaethylporphyrin

(NiOEP), compared to the crystals reported for **3** containing H<sub>2</sub>O and N<sub>2</sub>.<sup>20</sup> As shown in Figure 4a, the X-ray structure clearly showed that the CH<sub>3</sub>CN molecule is encapsulated at the center of the cage with the methyl group directing to the bottom of the carbon cage. The distances between the methyl carbon and the center of the surrounding hexagons in the closest proximity were 3.1–3.3 Å, respectively (Figure 4b). These values are obviously shorter than the reported distances of 3.426 and 3.941 Å for the CH<sub>3</sub>CN encapsulated in cyclophanes<sup>27</sup> and metal-organic macrocycles,<sup>28</sup> indicating significant interactions of the encapsulated CH<sub>3</sub>CN in the open-cage C<sub>60</sub> **3**. Interestingly, the unit cell volume of CH<sub>3</sub>CN(**a**) (7664(3) Å<sup>3</sup>) decreases by  $\Delta V = -0.7\%$  when compared with that for H<sub>2</sub>O/N<sub>2</sub>(**a**)<sup>20</sup> (7720.4(18) Å<sup>3</sup>), possibly due to the interaction between the NiOEP and



Figure 4. (a) Single crystal X-ray structure of CH<sub>3</sub>CN@**3** with thermal ellipsoids at 50% probability. The aryl groups, NiOEP, solvent molecules, and disordered moieties are omitted for clarity. (b) Selected distances between the encapsulated CH<sub>3</sub>CN and the centroid of surrounding five hexagons. (c) Selected distances *a* and *b* on the orifice of CH<sub>3</sub>CN@**3**. (d) Overlapped view for empty **3**' (grey) and CH<sub>3</sub>CN@**3**' (green) optimized at the B3LYP-D3/6-31G(d,p) level, in which the *t*-butylpyridyl groups were replaced by hydrogen atoms.

the carbon cage influenced by the encapsulated CH<sub>3</sub>CN molecule or deformation of the cage parts. This contrasts with the cases where the volume for the CH<sub>3</sub>OH-encapsulating **2** and HCHO-encapsulating **2** increased by  $\Delta V = +0.8\%$  and +0.9% over the empty host

## 2, respectively.<sup>18</sup>

Compared with the crystal of **3** encapsulating H<sub>2</sub>O and N<sub>2</sub>, slight deformation of the cage was observed for CH<sub>3</sub>CN@**3** in the solid state (Figure 4c). The C–S distance *a* as the longer axis of the orifice and the C–C distance *b* as the shorter one are 7.009(4) and 4.969(4) Å, respectively, which showed a decrease by  $\Delta a$  –0.1 Å and an increase by  $\Delta b$  +0.1 Å. This deformation was also supported by DFT calculations for the model compounds CH<sub>3</sub>CN@**3**' and empty **3**' optimized at the B3LYP-D3/6-31G(d,p) level, in which the *t*-butylpyridyl groups were replaced by hydrogen atoms to avoid the structural influence by aryl groups. The calculations well reproduced the deformation in an emphasized manner with  $\Delta a'$  –0.2 and  $\Delta b'$  +0.5 Å (Figure 4d). The shape of the orifice changed into a circle, and one of the carbonyl groups tilted slightly outside along the short axis *b*'.

Electronic properties. To estimate the effects caused by the cage deformation, the GIAO calculations were conducted for empty **3**, CH<sub>3</sub>CN@**3**, and the deformed cage without CH<sub>3</sub>CN, giving the chemical shifts of one of the olefinic protons at  $\delta$  6.40, 6.95, and 6.97 ppm, respectively (the calculated signals of another one were at  $\delta$  7.21, 7.60, and 7.61 ppm, respectively, Figure S10). These results showed that the observed difference in chemical shifts ( $\Delta \delta = +0.23$  ppm) for CH<sub>3</sub>CN@**3** compared to **3** shown in Figure 3a could be mainly attributed to the cage deformation and that the existence of the CH<sub>3</sub>CN did not affect much on the chemical shifts. The deformed cage was shown to be only slightly destabilized by  $\Delta G_{298} + 1.33$  kcal/mol.

In order to clarify the electronic properties caused by the deformation of the cage as well as the presence of the CH<sub>3</sub>CN molecule, the author computed hypothetical molecule **3**<sub>D</sub>' obtained by removal of the CH<sub>3</sub>CN molecule from CH<sub>3</sub>CN@**3**' with keeping cage distortion, as well as those for empty **3**' and molecular complex CH<sub>3</sub>CN@**3**' (Figure 5). The dipole moments for CH<sub>3</sub>CN@**3**' and **3**' were calculated to be 9.2 and 7.6 Debye, respectively. The large differences (1.6 Debye) account for the facile separation of CH<sub>3</sub>CN@**3** from **3** on the silica gel column chromatography. The value for **3**<sub>D</sub>' (8.0 Debye) is close to that of **3**', suggesting that the difference is mainly attributed to the presence of CH<sub>3</sub>CN due to the vectorial overlap with the deformed cage.

The author also studied the Mulliken charges on the three parts of each molecule according to the direction of the total dipole moment (Figure 5). The values of the bottom part of empty **3'** (q –0.09) and **3**<sub>D</sub>' (q –0.10) were suggested to be similar, both of which are slightly higher than that of CH<sub>3</sub>CN@**3'** (q –0.20). Therefore, the difference in the

dipole moments between CH<sub>3</sub>CN@**3'** and **3'** is again explained by the presence of CH<sub>3</sub>CN. Note that the Mulliken charge on the CH<sub>3</sub>CN molecule is -0.01, which would be negligible compared to all changes. The LUMO level of CH<sub>3</sub>CN@**3'** is calculated to be lower by  $\Delta E$  -0.07 eV than that of **3'** (Figure 5), caused by the contribution of both the presence of CH<sub>3</sub>CN ( $\Delta E$  -0.04 eV) and deformation of the cage ( $\Delta E$  -0.03 eV).



Figure 5. The dipole moments, Mulliken charges, and orbital energies for empty 3', CH<sub>3</sub>CN@3', and hypothetical molecule  $3_D$ ' that was generated by the removal of the CH<sub>3</sub>CN from CH<sub>3</sub>CN@3' with keeping cage distortion. The *t*-butylpyridyl groups existing on 3 were replaced by hydrogen atoms. The Mulliken charge of CH<sub>3</sub>CN for CH<sub>3</sub>CN@3' was calculated to be negligible (-0.01) (B3LYP-D3/6-31G(d,p)).

Upon cyclic voltammetry in ODCB (Figure 6), CH<sub>3</sub>CN@**3** exhibited four reversible redox waves similar to those for **3**. Noticeably, the first reduction potential of CH<sub>3</sub>CN@**3** ( $-0.92 \text{ V vs. Fc/Fc}^+$ ) was anodically shifted by +0.04 V in comparison to that for **3** (-0.96 V), indicating the higher electron-accepting characteristics of CH<sub>3</sub>CN@**3** which is in accordance with the DFT calculations (Figure 5). Such anodic shifts were also observed for the second, third, and fourth redox waves, and the differential pulse voltammetry supported these results, which were not observed for other molecular complexes encapsulating H<sub>2</sub>,<sup>29</sup> H<sub>2</sub>O,<sup>11b</sup> and HF.<sup>11d</sup>



Figure 6. Cyclic voltammograms and differential pulse voltammograms of 3 (55% for empty 3 and 45% for N<sub>2</sub> and other encapsulating ones<sup>20</sup> determined by <sup>1</sup>H NMR) and CH<sub>3</sub>CN@3 (100% for CH<sub>3</sub>CN). Conditions: 1 mM sample with 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in ODCB at a scan rate of 20 mV s<sup>-1</sup>.

Equilibrium isotope effects (EIE). Then, EIE<sup>30</sup> was investigated for the encapsulation of isotopomer CD<sub>3</sub>CN inside **3** since the EIE for encapsulation of  $D_2/H_2$ and HD/H<sub>2</sub> were reported to be positive for an open-cage fullerene derivative.<sup>31</sup> As shown in Figure 7, the direct competition experiments using 5 mg of 3 with 100 µL of CD<sub>3</sub>CN and 100 µL of CH<sub>3</sub>CN were performed to give encapsulated materials with the ratio of 16.2% for CD<sub>3</sub>CN@3 and 13.2% for CH<sub>3</sub>CN@3 (Figure S5, 6). The binding affinity defined as a ratio of  $K_D/K_H^{32}$  was found to be 1.23. Another experiment with 150 µL of CD<sub>3</sub>CN, and 150  $\mu$ L of CH<sub>3</sub>CN was also conducted and gave the  $K_D/K_H$  value of 1.18 (Figure S7), supporting that the equilibrium state was attained under these conditions. These results reflected the favored affinity of deuterated CD<sub>3</sub>CN to the inner surface of **3**, which was supported by the DFT calculations where the  $K_D/K_H$  values were obtained as 1.33 and 1.16 at the B3LYP-D3/6-31G(d,p) and M06-2X/6-31G(d,p) levels of theory, respectively, due to more stabilization for CD<sub>3</sub>CN@3 (Figure S12, S13). The stronger  $CD/\pi$  interaction than  $CH/\pi$  interaction inside the  $\pi$ -conjugated cage might be suggested, as reported by Rebek et al., that a CD<sub>3</sub> group of paraxylene is more strongly attracted by their cylindrical capsules than a CH<sub>3</sub> group.<sup>33</sup>



Figure 7. Equilibrium isotope effects on encapsulation of CD<sub>3</sub>CN and CH<sub>3</sub>CN inside 3.

Intermolecular interaction. Finally, Head-Gordon's absolutely localized molecular orbital energy decomposition analyses (ALMO-EDA)34 was conducted for the X-ray coordinates for CH<sub>3</sub>CN@3, N<sub>2</sub>@3, and H<sub>2</sub>O@3 at B3LYP-D3(op)/6-31G(d,p) level (Figure 8a, S14). The major contribution to the stabilization energies is shown by the sum of  $E_{\text{elec}}$  and  $E_{\text{disp}}$ , which followed the order of CH<sub>3</sub>CN@ $3 > N_2@3 > H_2O@3$ , according to the size of the encapsulated molecules, and the values of  $E_{\text{Pauli-rep}}$  also followed the same order. On the other hand, the  $E_{\text{elec}}/E_{\text{disp}}$  ratio of CH<sub>3</sub>CN@**3** (0.95) is higher than those for H<sub>2</sub>O@**3** (0.61) and N<sub>2</sub>@**3** (0.51), implying that the higher dipole moments of encapsulated species afford the larger  $E_{elec}$  since the calculated dipole moments for the optimized structures at B3LYP-D3/6-31G(d,p) are 3.8 and 2.0 Debye for CH<sub>3</sub>CN and H<sub>2</sub>O, respectively. Then, qualitative analysis for intermolecular contacts on CH<sub>3</sub>CN@3 was performed by noncovalent interaction (NCI) plots,<sup>35</sup> using the fully optimized structures for CH<sub>3</sub>CN@3-down and CH<sub>3</sub>CN@3-up at B3LYP-D3/6-31G(d,p) level (Figure 8b, S15, S16). Whereas the methyl group in CH<sub>3</sub>CN@3-up located near the orifice showed repulsive interaction due to the steric bulk, most of the intermolecular region in CH<sub>3</sub>CN@**3**-down was represented as weak interactions, demonstrating that the shape of the carbon cage well fits CH<sub>3</sub>CN in that orientation.



**Figure 8.** (a) Contribution of various components to total interaction energy from ALMO-EDA<sup>34</sup> calculations on crystal structures of CH<sub>3</sub>CN@**3**, N<sub>2</sub>@**3**, and H<sub>2</sub>O@**3** at B3LYP-D3(op)/6-31G(d,p) level. The total intermolecular interaction energy was decomposed into electrostatics ( $E_{elec}$ ), dispersion ( $E_{disp}$ ), polarization ( $E_{pol}$ ), charge-transfer ( $E_{ct}$ ), and Pauli-repulsion ( $E_{Pauli-rep}$ ) components. The structures of CH<sub>3</sub>CN@**3**, N<sub>2</sub>@**3**, and H<sub>2</sub>O@**3** were extracted from the data of X-ray crystallographic analyses. (b) Noncovalent interaction (NCI) index representation<sup>35</sup> of CH<sub>3</sub>CN@**3**-down and CH<sub>3</sub>CN@**3**-up with reduced density gradient (RDG) isosurface. The structures were fully optimized at B3LYP-D3/6-31G(d,p), and NCIPLOT4<sup>35c</sup> was used to process the calculated electron densities. Blue, green, and red isosurfaces show regions with attractive, weak, and repulsive interactions, respectively. The aryl groups are omitted for clarity.

## Conclusion

In conclusion, the author demonstrated an effective inner-space modification for an open-cage C<sub>60</sub> derivative **3** by encapsulation of a polar molecule of CH<sub>3</sub>CN. The insertion of CH<sub>3</sub>CN was achieved at 150 °C under 9,400 atm. The resulting CH<sub>3</sub>CN@**3** was isolated in a pure form by a silica gel column chromatography and showed less negative redox potentials. The structure in the solid state showed enhanced intermolecular interaction and the deformation of the carbon cage. DFT calculations suggested that the cage deformation would be the main origin for the differences in <sup>1</sup>H chemical shifts, and

also that the LUMO is affected by both the cage deformation and the presence of the  $CH_3CN$ . The positive EIE was observed for the encapsulation of  $CD_3CN$ .

## **Experimental Section**

General. The <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out at room temperature (unless otherwise noted) with JEOL JNM ECA500 and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of CDCl<sub>3</sub> ( $\delta$  7.26 ppm in <sup>1</sup>H NMR,  $\delta$  77.00 ppm in <sup>13</sup>C NMR). ESI (electrospray ionization) mass spectra were measured on a Bruker micrOTOF-Q II. UVvis absorption spectra were measured with a JASCO V-780 spectrophotometer. IR spectrum was taken with a Shimadzu IR-Affinity 1S. The high-performance liquid chromatography (HPLC) was performed with the use of the Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose, and the same columns (two directly connected columns; 250 mm in length, 20 mm in inner diameter) for preparative purpose. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted on a BAS Electrochemical Analyzer ALS620C using a threeelectrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out using 1 mM solutions of substrate and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) as a supporting electrolyte, and the potentials were calibrated with ferrocene used as an internal standard which was added after each measurement. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B or 100B (Fuji Silysia).

Fullerene  $C_{60}$  was purchased from SES Research Co. Hexane, ethyl acetate, and dichloromethane were purchased from Nacalai Tesque, Inc. Acetonitrile- $d_3$  was purchased from Cambridge Isotope Laboratories, Inc. Acetonitrile (super dehydrated), acetone, and carbon disulfide were purchased from FUJIFILM Wako Pure Chemical Corporation. Open-cage fullerene  $C_{60}$  derivative **3** was synthesized according to the literature.<sup>20</sup> Unless otherwise noted, materials purchased from commercial suppliers were used without further purification.

**Computational Methods.** Most of the calculations were conducted with the Gaussian 09 program package.<sup>36</sup> All structures at stationary and transition states were optimized at the B3LYP-D3/6-31G(d,p) or M06-2X/6-31G(d,p) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of

theory. The calculated <sup>1</sup>H NMR chemical shifts were obtained at the GIAO B3LYP-D3/6-311G(d,p) level using the optimized structures at B3LYP-D3/6-31G(d,p). These calculated shifts were calibrated by that of tetramethylsilane obtained at the same level. The isotope effect on the stabilization energies were investigated in terms of the zero-point correction using the freqchk utility implemented in Gaussian 09 software. Noncovalent interaction (NCI) plot was calculated and visualized by NCIPLOT4.<sup>35</sup> Head-Gordon's absolutely localized molecular orbital energy decomposition analyses (ALMO-EDA)<sup>34</sup> was conducted at B3LYP-D3(op)/6-31G(d,p)<sup>37</sup> level of theory by Q-Chem 6.0.0.<sup>38</sup>

Synthesis of CH<sub>3</sub>CN@3. (Figure. 2, Entry 1) Powdery 3 (5.1 mg, 4.4  $\mu$ mol) was placed into a 1 mL Teflon container. A solution of the mixture of *o*-dichlorobenzene (0.9 mL) and CH<sub>3</sub>CN (0.1 mL, 400 equivalent) was added and the lid was closed. The container was kept at 150 °C under 9,400 atm for 24 hours. After getting back to ambient conditions, the resulting mixture was directly passed through a short silica gel column (CS<sub>2</sub>/hexane (1:1)) to give 3.0 mg (2.5  $\mu$ mol, calculated as a mixture of CH<sub>3</sub>CN@3 (40%), N<sub>2</sub>@3 (10%) and empty 3 (50%)) of encapsulated materials in 57% isolated yield as a brown powder. Further purification by the silica gel column (CH<sub>2</sub>Cl<sub>2</sub>) gave pure CH<sub>3</sub>CN@3 (1.3 mg, 1.1  $\mu$ mol) in 24% yield.



CH<sub>3</sub>CN@**3** (CH<sub>3</sub>CN: 100%): IR (KBr) *v* 1738 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (dd, 1H, *J* = 8.0 Hz, 7.4 Hz), 7.51 (dd, 1H, *J* = 8.0 Hz, 7.4 Hz), 7.24 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.18 (d, 1H, *J* = 8.0 Hz), 7.17 (d, *J* = 10.3 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 10.3 Hz, 1H), 1.18 (s, 9H), 1.10 (s, 9H), -11.91 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  192.02, 185.25, 182.86, 181.00, 168.71, 168.28, 163.80, 161.14, 156.02, 152.81, 152.77, 151.12, 150.99, 150.89, 150.46, 150.20, 149.81, 149.62, 149.54, 148.07, 148.05, 146.34, 145.79, 145.66, 145.51, 145.49, 145.29, 144.47, 144.39, 144.25, 143.70, 143.56, 143.48, 142.94, 142.28, 142.19, 141.90, 141.78, 141.23, 140.32, 139.00, 138.57, 138.02, 137.95, 137.56, 137.53, 137.34, 137.04, 136.79, 136.41, 136.31, 135.77, 135.42, 134.87, 133.87, 131.16, 130.89, 130.77, 130.40, 129.69, 129.52, 128.71, 127.97, 125.13, 121.96, 120.23, 119.51, 117.44, 117.12, 107.67, 59.21, 54.89, 37.71, 37.66, 29.89, -14.00 (The sum of carbon signals must be 80 in theory. Observed 76. Four sp<sup>2</sup> carbon signals are overlapped in the aromatic region.); HRMS (ESI): *m/z* [M+Na]<sup>+</sup> Calcd for C<sub>84</sub>H<sub>29</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>Na<sup>+</sup> (CH<sub>3</sub>CN@**3**+Na): 1230.1492; found: 1230.1489.

<sup>1</sup>H NMR Relaxation Times of CH<sub>3</sub>CN@3. The sample concentration was set to 1.0 mM of CH<sub>3</sub>CN@3 (CH<sub>3</sub>CN: 100%) in CDCl<sub>3</sub> and as-prepared sample solution was used since it was reported that dissolved oxygen does not affect much on relaxation time for the encapsulated chemical species surrounded by fullerene cages.<sup>39</sup> The measurements were conducted on an 800 MHz NMR instrument by applying the inversion-recovery method for  $T_1$  and CPMG (Carr Purcell Meiboom Gill) method for  $T_2$ . The 90° pulse width was determined at each temperature.



**Figure S1.** Relaxation times *T*<sub>1</sub> and *T*<sub>2</sub> of CH<sub>3</sub>CN@**3** (CH<sub>3</sub>CN:100%) (800 MHz, 1.0 mM in CDCl<sub>3</sub>, 260–340 K).

UV-vis Spectra of 3 and CH<sub>3</sub>CN@3.



**Figure S2.** UV-vis absorption spectra for 50  $\mu$ M solutions of **3** (55% for empty **3** and 45% for N<sub>2</sub> and other encapsulating species<sup>20</sup> determined by <sup>1</sup>H NMR) and CH<sub>3</sub>CN@**3** (CH<sub>3</sub>CN: 100%) in toluene.

Single Crystal X-Ray Structure of CH<sub>3</sub>CN@3. Single crystals of CH<sub>3</sub>CN@3 were obtained from a benzene solution in the presence of nickel(II) octaethylporphyrin by slow evaporation. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and graphite monochromator. A total of 36772 reflections were measured at the maximum  $2\theta$  angle of 50.08°, of which 13504 were independent reflections ( $R_{int} = 0.0256$ ). The structure was solved by direct methods (SHELXT-97<sup>40</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>40</sup>). One of *t*-butyl groups was disordered, which was solved using appropriate models. Thus, (C71–C72–C73) and (C74–C75–C76) were placed and their occupancies were refined to be 0.67(3) and 0.33(3), respectively, using a SIMU instruction. The encapsulation ratio of CH<sub>3</sub>CN was determined as 0.898(7) based on

atomic occupancy for C86–C87–N5. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using HFIX instructions. The crystal data are as follows:  $C_{113.8}H_{62.69}N_{4.9}Ni_{0.5}O_4S_2$ ; FW = 1655.97, crystal size 0.23 × 0.08 × 0.05 mm<sup>3</sup>, monoclinic,  $P2_1/c$ , a = 17.059(3) Å, b = 14.800(3) Å, c = 31.120(6) Å,  $\beta =$  $102.73(3)^\circ$ , V = 7664(3) Å<sup>3</sup>, Z = 4,  $D_c = 1.435$  g cm<sup>-3</sup>. The refinement converged to  $R_1 =$ 0.0533,  $wR_2 = 0.1450$  ( $I > 2\sigma(I)$ ), GOF = 1.057, without any treatment of SQUEEZE procedure. Thus, the independent part is expressed as (CH<sub>3</sub>CN)<sub>0.90</sub>@(**3**)<sub>1</sub>-(benzene)<sub>2</sub>-(NiOEP)<sub>0.5</sub>, which is almost the same as the reported one as (N<sub>2</sub>)<sub>0.48</sub>(H<sub>2</sub>O)<sub>0.52</sub>@(**3**)<sub>1</sub>-(benzene)<sub>2</sub>-(NiOEP)<sub>0.5</sub>.<sup>20</sup> The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2232001).



Figure S3. Single crystal X-ray structure of CH<sub>3</sub>CN@3.



Figure S4. Packing structure of  $CH_3CN@3$  from the view of a-b plane. The data for 3 was taken from ref.20.

### Encapsulation of CH<sub>3</sub>CN and CD<sub>3</sub>CN inside 3.

#### <u>100.0 µL of CH<sub>3</sub>CN and 100.0 µL of CD<sub>3</sub>CN</u>

Powdery **3** (5.2 mg, 4.4 µmol) was placed into a 1 mL Teflon container. A solution of the mixture of *o*-dichlorobenzene (0.8 mL), CH<sub>3</sub>CN (100.0 µL, by gas-tight syringe of 100.0 µL,  $\rho = 0.786$  g cm<sup>-3</sup>, M.W. = 41.05 g mol<sup>-1</sup>, 1.91 mmol), and CD<sub>3</sub>CN (100.0 µL, by gas-tight syringe of 100.0 µL,  $\rho = 0.844$  g cm<sup>-3</sup>, M.W. = 44.07 g mol<sup>-1</sup>, 1.91 mmol) was added and the lid was closed. The container was kept at 140 °C under 9,000 atm for 24 hours. After getting back to ambient conditions, the resulting mixture was directly passed through a short silica gel column (CS<sub>2</sub>/hexane (1:1)) to give 2.8 mg (2.4 µmol, 54%, determined by <sup>1</sup>H NMR as a mixture of 70.6% of **3**, 13.2% of CH<sub>3</sub>CN@**3**, and 16.2%

of CD<sub>3</sub>CN@**3**) of encapsulated materials as a brown powder, giving  $K_D/K_H = 1.23$ .

#### <u>150.0 μL of CH<sub>3</sub>CN and 150.0 μL of CD<sub>3</sub>CN</u>

Powdery **3** (5.2 mg, 4.4 µmol) was placed into a 1 mL Teflon container. A solution of the mixture of *o*-dichlorobenzene (0.7 mL), CH<sub>3</sub>CN (150.0 µL, by gas-tight syringe of 150.0 µL,  $\rho = 0.786$  g cm<sup>-3</sup>, M = 41.05 g mol<sup>-1</sup>, 2.87 mmol), and CD<sub>3</sub>CN (150.0 µL, by gas-tight syringe of 150.0 µL,  $\rho = 0.844$  g cm<sup>-3</sup>, M = 44.07 g mol<sup>-1</sup>, 2.87 mmol) was added and the lid was closed. The container was kept at 140 °C under 9,000 atm for 24 hours. After getting back to ambient conditions, the resulting mixture was directly passed through a short silica gel column (CS<sub>2</sub>/hexane (1:1)) to give 3.0 mg (2.5 µmol, 57%, determined by <sup>1</sup>H NMR as a mixture of 78.0% of **3**, 10.1% of CH<sub>3</sub>CN@**3**, and 11.9% of CD<sub>3</sub>CN@**3**) of encapsulated materials as a brown powder, giving  $K_D/K_H = 1.18$ .



Figure S5. Equilibrium isotope effects of the encapsulation of CD<sub>3</sub>CN and CH<sub>3</sub>CN.



**Figure S6.** Selected part of the <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for the olefin protons for the mixture of CD<sub>3</sub>CN@**3**, CH<sub>3</sub>CN@**3**, and **3** (empty one and N<sub>2</sub>@**3**) (100  $\mu$ L scale). The signal of one of the olefin protons for CD<sub>3</sub>CN@**3** and CH<sub>3</sub>CN@**3** showed at the same chemical shift of  $\delta$  6.6 ppm, which is different from that of  $\delta$  6.4 ppm for **3** (empty one and N<sub>2</sub>@**3**). Thus, the ratio of CD<sub>3</sub>CN@**3**, CH<sub>3</sub>CN@**3**, and **3** in the mixture from the competition experiments of encapsulation were determined at 16.2%, 13.2%, and 70.6% by the integration of the olefin protons, respectively.



Figure S7. Selected part of the <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for the olefin protons for the mixture of CD<sub>3</sub>CN@3, CH<sub>3</sub>CN@3, and 3 (empty one and N<sub>2</sub>@3) (150  $\mu$ L scale). The signal of one of the olefin protons for CD<sub>3</sub>CN@3 and CH<sub>3</sub>CN@3 showed at the same chemical shift of  $\delta$  6.6 ppm, which is different from that of  $\delta$  6.4 ppm for 3 (empty one and N<sub>2</sub>@3). Thus, the ratio of CD<sub>3</sub>CN@3, CH<sub>3</sub>CN@3, and 3 in the mixture from the competition experiments of encapsulation were determined at 11.9%, 10.1%, and 78.0% by the integration of the olefin protons, respectively.



Computational Studies: Energy Profiles for CH<sub>3</sub>CN@3.

**Figure S8.** Energy profile for CH<sub>3</sub>CN@**3**-up and CH<sub>3</sub>CN@**3**-down, calculated at the B3LYP-D3/6-31G(d,p) level of theory. The  $\Delta G$  values were shown with kcal/mol at 298 K.

# Computational Studies: GIAO Calculations of CH<sub>3</sub>CN@3.



(a) Experimental (500 MHz, CDCl<sub>3</sub>)

Figure S9. The experimental <sup>1</sup>H NMR spectrum and calculated ones by the GIAO-B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d,p) level: (a) experimental one for CH<sub>3</sub>CN@**3**, (b) calculated one for CH<sub>3</sub>CN@**3**-up, and (c) calculated one for CH<sub>3</sub>CN@**3**-down.



Figure S10. The selected regions of calculated <sup>1</sup>H NMR spectra by the GIAO B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d,p) level: (a) hypothetical empty  $3_D$  (b) CH<sub>3</sub>CN@3-down and (c) empty 3.

**Computational Studies: Mulliken Charges.** For the three parts of each molecule, the sum of the Mulliken charges are summarized. The Mulliken charges on hydrogens are included in the connecting atoms.



Figure S11. The Mulliken charges on the selected parts for empty 3',  $CH_3CN@3'$ , and hypothetical molecule  $3_D$ ' that was generated by removal of the  $CH_3CN$  from  $CH_3CN@3'$  with keeping cage distortion. The structures of empty 3' and  $CH_3CN@3'$  were optimized at the B3LYP-D3/6-31G(d,p) level, in which the *t*-butylpyridyl groups existing on 3 were replaced by hydrogen atoms. Single point calculation was performed for the geometry of hypothetical molecule  $3_D$ ' at the same level. The Mulliken charges were shown for the three parts of each caged molecule; the orifice part (coloured in grey), the middle part composed of the 20 carbons (coloured in red), and the bottom part composed of the 28 carbons (coloured in blue). The Mulliken charge of the  $CH_3CN$  for  $CH_3CN@3'$  was calculated to be negligible (-0.01).

**Computational Studies: Stabilization Energy of CD<sub>3</sub>CN@3.** The isotope effect on the stabilization energies for the encapsulation of CH<sub>3</sub>CN and CD<sub>3</sub>CN were investigated in terms of the zero-point correction using the freqchk utility implemented in Gaussian 09 software, in which temperature and pressure were set at 298.15 K and 1 atm, respectively.



**Figure S12.** The stabilization energy of CD<sub>3</sub>CN@**3** and the value of  $K_D/K_H$ , calculated at the B3LYP-D3/6-31G(d,p) level of theory. The  $\Delta G$  values were shown with kcal/mol at 298.15 K.



**Figure S13.** The stabilization energy of CD<sub>3</sub>CN@**3** and the value of  $K_D/K_H$ , calculated at the M06-2X/6-31G(d,p) level of theory. The  $\Delta G$  values were shown with kcal/mol at 298.15 K.
**Computational Studies:** ALMO-EDA Calculation of CH<sub>3</sub>CN@3. Second generation absolutely localized molecular orbitals (ALMO)<sup>4</sup> energy decomposition analysis (EDA) was used to decompose the noncovalent interaction energy ( $E_{int}$ ) into electrostatics ( $E_{elec}$ ), dispersion ( $E_{disp}$ ), Pauli repulsion ( $E_{pauli-rep}$ ), polarization ( $E_{pol}$ ), and charge-transfer ( $E_{ct}$ ) contributions (eq. 1). The structures of CH<sub>3</sub>CN@3, N<sub>2</sub>@3,<sup>20</sup> and H<sub>2</sub>O@3<sup>20</sup> were taken from the X-ray crystallographic analyses and single-point calculations were conducted at the B3LYP-D3(op)/6-31G(d,p) level by Q-Chem 6.0.0.<sup>37</sup>



 $E_{int} = E_{elec} + E_{disp} + E_{pauli-rep} + E_{pol} + E_{ct}$  (eq. 1)

**Figure S14.** Contribution of various components to total interaction energy from ALMO-EDA calculation of CH<sub>3</sub>CN@**3**, N<sub>2</sub>@**3**, and H<sub>2</sub>O@**3** at B3LYP-D3(op)/6-31G(d,p) level. The structures of CH<sub>3</sub>CN@**3**, N<sub>2</sub>@**3**<sup>20</sup>, and H<sub>2</sub>O@**3**<sup>20</sup> were extracted from the data of Xray crystallographic analyses.

## DFT calculations: NCI Analysis of CH<sub>3</sub>CN@3.



**Figure S15.** (a) Noncovalent interaction (NCI) index<sup>3</sup> representation of CH<sub>3</sub>CN@**3**-down with reduced density gradient (RDG) isosurface in two different views and (b) RDG plot against sign( $\lambda_2$ ) $\rho$ , where  $\nabla^2 \rho = \lambda_1 + \lambda_2 + \lambda_3$  ( $\lambda_1 < \lambda_2 < \lambda_3$ ),  $\rho$  is the electron density, and s is the reduced density gradient. The structure of CH<sub>3</sub>CN@**3**-down was fully optimized at B3LYP-D3/6-31G(d,p) and NCIPLOT4 was used to process the calculated electron densities. A RDG cut-off is sign( $\lambda_2$ ) $\rho = 0.06$  a.u., and color code based on sign( $\lambda_2$ ) $\rho$  is -0.06 a.u. (blue) < 0.0 a.u. (green) < 0.06 a.u. (red). Blue, green and red isosurfaces show regions with attractive, weak and repulsive interactions, respectively.



**Figure S16.** (a) Noncovalent interaction (NCI) index<sup>3</sup> representation of CH<sub>3</sub>CN@**3**-up with reduced density gradient (RDG) isosurface in two different views and (b) RDG plot against sign( $\lambda_2$ ) $\rho$ , where  $\nabla^2 \rho = \lambda_1 + \lambda_2 + \lambda_3$  ( $\lambda_1 < \lambda_2 < \lambda_3$ ),  $\rho$  is the electron density, and s is the reduced density gradient. The structure of CH<sub>3</sub>CN@**3**-up was fully optimized at B3LYP-D3/6-31G(d,p) and NCIPLOT4 was used to process the calculated electron densities. A RDG cut-off is sign( $\lambda_2$ ) $\rho = 0.06$  a.u., and color code based on sign( $\lambda_2$ ) $\rho$  is – 0.06 a.u. (blue) < 0.0 a.u. (green) < 0.06 a.u. (red). Blue, green and red isosurfaces show regions with attractive, weak and repulsive interactions, respectively.

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# Chapter 3

## Synthesis of an Open-Cage C<sub>60</sub> Derivative with a Double Stopper

**Abstract:** The construction of a suitable stopper on a  $C_{60}$  orifice is important to prevent the release of once-encapsulated chemical species. However, a single stopper on a large orifice is usually not sufficient to retain a small molecule within the  $C_{60}$  cavity. In this chapter, the author discusses a double stopper, constituted of two hydroxy groups, on a huge orifice with a ring-atom count of 18 by a reduction using BH<sub>3</sub>·THF. The resulting double stopper was demonstrated to effectively isolate an argon atom inside the cavity so that the argon was retained even under mass spectrometric conditions at 200 °C. The structure of the open-cage  $C_{60}$  derivative with the double stopper was confirmed by Xray crystallography analysis, showing a dimeric configuration via intermolecular hydrogen-bondings. The dimerization behavior in the solution was also studied.

#### Introduction

Open-cage  $C_{60}$  derivatives could effectively serve as hosts for the isolation of small guests, providing an ideal platform for an in-depth understanding of their properties at a molecular level.<sup>1</sup> Recently, molecules with a relatively large size, such as CH<sub>3</sub>OH,<sup>2</sup> CO<sub>2</sub>,<sup>3</sup> and C<sub>2</sub>H<sub>5</sub>OH,<sup>4</sup> have been successfully encapsulated by designing orifice structures. The larger orifice facilitates a passage of molecules while spontaneous release could also occur easily, resulting in a low encapsulation ratio or sometimes no observation of spectral evidence of encapsulation.<sup>5</sup>

To address this issue, methods to introduce a stopper on the orifice, i.e., a hydroxy or ether group that is tilted inward, have been developed.<sup>6</sup> For instance, the group, which the author belongs to, reported a reaction of one carbonyl group with Grignard reagent (RMgCl), in which the resulting stopper prevents He and H<sub>2</sub> from escape.<sup>7</sup> The reduction by NaBH<sub>4</sub> was also applicable to selectively reduce one of four carbonyl groups on the C<sub>60</sub> orifice.<sup>3,6</sup> The research group of Su, Lu, and Gan also reported the reduction of open-cage C<sub>60</sub> derivatives by use of MBH<sub>4</sub>, in which counter cation (M<sup>+</sup>) determines the reaction degree so that one, two, and three carbonyl groups were reduced by  $M = K^+$ , Na<sup>+</sup>, and Li<sup>+</sup>, respectively.<sup>8</sup> In 2018, the group, which the author belongs to, demonstrated a high-yielding triple reduction *via* the Luche conditions employing NaBH<sub>4</sub> with CeCl<sub>3</sub>.<sup>9</sup> The same group also found that even weak/mild reductants, such as BH<sub>3</sub>·THF<sup>10</sup> and Frustrated Lewis pairs using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and HSiPh<sub>3</sub>,<sup>11</sup> worked for reducing a carbonyl group on the C<sub>60</sub> orifice to generate a hydroxy stopper.

Open-cage  $C_{60}$  derivative **1** possesses an 18-membered ring opening that has the potential to allow various molecules to pass through (Figure 1).<sup>12</sup> However, due to a low production ratio, **1** has received less attention. Recently, this group developed a stepwise synthesis of **1** by a reaction with S<sub>8</sub> in the presence of a single-electron reductant.<sup>13</sup> In chapter 2, the author demonstrated that **1** can encapsulate a large polar molecule, i.e., CH<sub>3</sub>CN, which results in an enhanced polarity of the molecular complex relative to the empty cage.<sup>14</sup> Though the reactivity of **1** is currently less studied, phosphorous-functionalization was found to proceed as in the case of the related open-cage C<sub>60</sub> derivatives (Figure 1).<sup>13,15</sup> In this chapter, the author showed the construction of double stoppers on **1** through a selective double reduction, revealing a kinetic stabilization of encapsulated Ar and/or N<sub>2</sub>.

#### **Results and Discussion**

The reduction of 1 was treated with BH3. THF in toluene under an argon atmosphere

at  $-30^{\circ}$ C for 12 h, followed by treatment with NH<sub>4</sub>Cl aq. (Figure 2). When 1.5 equiv. of BH<sub>3</sub>·THF<sup>10</sup> was used, dihydroxylated derivative **2** was obtained in 13% isolated yield with uncreated **1** in 82% recovery. The reaction with 31 equiv. of BH<sub>3</sub>·THF then increased the yield of **2** to 41%. In this reaction, a mono-hydroxylated derivative was formed only in a trace amount. The increased reaction temperature (0 °C) caused a complete consumption of **1** with no detectable amount of **2**.



Figure 1. Construction of a double stopper on 1 to form 2.



Figure 2. Synthesis of 2.

The two hydroxy protons of **2** appeared in a range of  $\delta$  5.4–5.0 and 2.7–2.4 ppm in <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> (1:1)) spectrum (Figure 3a), whose signal intensities decreased upon addition of D<sub>2</sub>O. As shown in the inset (Figure 3a), three sets of doublets were observed due to the encapsulation of small molecules during the reaction and/or the work-up process.<sup>2,3,5,10</sup> The presence of an encapsulated H<sub>2</sub>O molecule was confirmed by a signal at  $\delta$  –9.69 ppm (Figure 3a), while empty **2**, N<sub>2</sub>@**2**, and Ar@**2** were detected by mass analysis (*vide infra*). From the integrated peak area, the ratio of H<sub>2</sub>O@**2**, N<sub>2</sub>@**2** (+ empty **2**),<sup>2,3</sup> and Ar@**2** was determined to be 10, 14, and 76%, respectively.

By comparing the <sup>13</sup>C NMR spectrum (126 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> (1:1)) with the simulated one at GIAO-B3LYP-D3/6-311G(d,p) for **2**, two sp<sup>3</sup> signals at  $\delta$  78.57 and 72.13 ppm were assignable to C2 and C3, respectively. The two carbonyl signals at  $\delta$ 

196.46 and 181.07 were suggested to correspond to C4 and C1, respectively. Thus, **2** possesses a vicinal diol at C2 and C3. The structure was clearly confirmed crystallographically (*vide infra*).

In the mass spectrum (Figure 3c), the molecular ion peak of 2 was detected at m/z 1170.1629. In addition, another two sets of peaks appeared at m/z 1198.1715 and 1210.1316 with smaller and larger intensities, corresponding to N<sub>2</sub>@2<sup>--</sup> and Ar@2<sup>--</sup>, respectively, which are in accordance with the <sup>1</sup>H NMR results. It is noted that the encapsulated Ar and N<sub>2</sub> were found to retain even under the mass spectrometric conditions<sup>16</sup> at 200 °C, suggesting that the vicinal diol can work as the double stopper for the encapsulated molecules. On the contrary, the double stopper is inefficient for the H<sub>2</sub>O molecule since the insertion/escape dynamics<sup>9</sup> was confirmed by <sup>1</sup>H NMR through the H<sub>2</sub>O/D<sub>2</sub>O exchange at room temperature.



Figure 3. (a) <sup>1</sup>H NMR spectra (500 MHz,  $CS_2/CDCl_3$  (1:1)), (b) <sup>13</sup>C NMR spectra of experimental (126 MHz,  $CS_2/CDCl_3$  (1:1)) and simulated (GIAO-B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d,p)) ones, and (c) mass spectrum (atmospheric pressure chemical ionization, negative ion mode) for 2 (H<sub>2</sub>O@2, 10%; Ar@2, 76%; N<sub>2</sub>@2 (+ empty 2), 14%).

To gain better understandings on the effect of the double stopper, the author performed DFT calculations at the B3LYP-D3/6-31G(d,p) level of theory where the aryl groups in 2 and 1 were replaced with hydrogen atoms. From the top view of the space-

filling models (Figure 4a), the available orifice area in **2**' is apparently smaller than that in **1**' owing to the formation of the double stopper. The energy barrier for the Ar-escape from Ar@**2**' was determined to be  $\Delta G^{\ddagger}$  +38.8 kcal/mol at 298 K, which is considerably higher than that of Ar@**1**' (+21.2 kcal/mol) by  $\Delta \Delta G^{\ddagger}$  +17.6 kcal/mol (Figures 4b, c), indicating the favored kinetic stabilization for Ar@**2**'. The release of N<sub>2</sub> required an activation barrier of  $\Delta G^{\ddagger}$  +36.2 kcal/mol, which is smaller by  $\Delta \Delta G^{\ddagger}$  -2.6 kcal/mol relative to the Ar escape (Figure 4c).<sup>16,17</sup> This activation barrier is higher than that of N<sub>2</sub>@**1**' (+20.2 kcal/mol) by  $\Delta \Delta G^{\ddagger}$  +16.0 kcal/mol as in the case of Ar. The stabilization energies upon encapsulation of Ar/N<sub>2</sub> in **1**' (-3.8/-6.3 kcal/mol) are comparable to those in **2**' (-4.1/-5.9 kcal/mol). Thus, the introduction of the double stopper does not provide significant thermodynamic stabilization toward them, while the kinetic effect contributes most solely to prevent them from escape. These activation barriers are considered to be high enough to keep Ar/N<sub>2</sub> inside **2** under the mass spectrometric conditions (Figure 3c).



Figure 4. (a) Space-filling models of 1' and 2'. (b) Structures of TS-Ar@1' and TS-Ar@2'. (c) The energy diagram for release of  $Ar/N_2$  from  $Ar/N_2@1$ ' and  $Ar/N_2@2$ '. All calculations were performed at B3LYP-D3/6-31G(d,p).

The single crystals of **2** were grown in  $CS_2$ /acetone at room temperature, and the position of the vicinal diol moiety was unambiguously determined by X-ray crystallography analysis (Figure 5). It showed that the O(2)–C(2) bond tilts to outside of the orifice with hydrogen bonding (3.333(4) Å) between O(2) and S(1) and the O(3)–C(3) tilts inside the orifice having hydrogen-bonding (3.395(6) Å) between O(3) and O(4).

Within the crystal, two molecules of **2** formed a meso dimer with its enantiomer in a faceto-face fashion through two intermolecular hydrogen-bondings<sup>18</sup> with a distance of 2.824(5) Å. This arrangement is reminiscent of a related open-cage C<sub>60</sub> derivative with triple OH groups.<sup>9</sup> The encapsulated species were refined as Ar and N<sub>2</sub> with occupancies of 0.67(3) and 0.33(3), respectively, supported by the mass spectrometric observation. The distance between the Ar and the closest hydroxy oxygen was measured to be 4.113(5) Å, which is apparently larger than the sum of van der Waals radii (3.40 Å).<sup>19</sup> On the contrary, 16 short contacts were detected between the Ar and the caged carbon with an average distance of 3.49 Å (Figure S2), which is similar to the previously reported Ar@open-C<sub>60</sub> (3.50 Å)<sup>17c</sup>. These results further support the calculation results that the hydroxy groups have negligible interactions with the Ar atom on the ground state structure.



**Figure 5.** (a) Solid-state structure of **2**, showing thermal ellipsoids at 50% probability. (b) Packing structure. The solvent molecules and aryl groups are omitted for clarity.



Figure 6. (a) <sup>1</sup>H NMR spectra (500 MHz,  $CS_2/CDCl_3$  (1:1)) of 2 at 0.1 and 10 mM. (b) Changes in chemical shifts.

The author then examined a dimerization behaviour of **2** in a solution of CS<sub>2</sub>/CDCl<sub>3</sub> (1:1) at 300 K. As shown in Figure 6a, one of two alcoholic protons at  $\delta$  *ca*. 2.5 ppm showed a lower-filed shift by increasing the sample concentration while no change was observed for another alcoholic proton signal at  $\delta$  *ca*. 5.1 ppm. Thus, the former signal is considered to participate in the intermolecular hydrogen-bonding in (**2**)<sub>2</sub>. The change in chemical shift values was employed for estimating the association constant. Upon assuming that, at a concentration of 0.10 mM, **2** exists as a monomer and the association constant was estimated to be  $K_a = 5 \times 10^{-2} \text{ M}^{-1}$  (Figure 6b) which is smaller by two-order than the triple-hydroxylated derivative (9.63 M<sup>-1</sup>)<sup>9</sup> and by four-order than another double-hydroxylated derivative (22.2 M<sup>-1</sup>).<sup>18b</sup> This indicates that the strength of the hydrogenbondings in those open-cage C<sub>60</sub> dimers is governed not only by the numbers of the hydroxy groups but also by the orientations of the hydroxy groups. Note that **2** exists as a monomer form even at 10.0 mM since the ratio of (**2**)<sub>2</sub> was estimated to be 0.001%.

## Conclusion

In summary, the author introduced double stoppers, i.e., two hydroxy groups on open-cage  $C_{60}$  derivative **2** having a large 18-membered ring orifice by a selective reduction of **1** with the use of BH<sub>3</sub>·THF. The obtained **2** contains Ar and N<sub>2</sub> in its cavity where the two hydroxy groups work as a kinetic stopper, while it does not work for H<sub>2</sub>O as supported by mass spectrometric and NMR analysis as well as DFT calculations. In the solid state, **2** adopts a dimeric configuration via intermolecular hydrogen-bondings.

### **Experimental Section**

**General.** The <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out at room temperature (unless otherwise noted) with JEOL JNM ECA500. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of CDCl<sub>3</sub> ( $\delta$  7.26 ppm in <sup>1</sup>H NMR,  $\delta$  77.00 ppm in <sup>13</sup>C NMR) and acetone-*d*<sub>6</sub> ( $\delta$  2.05 ppm in <sup>1</sup>H NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (two directly connected columns; 250 mm in length, 20 mm in inner diameter) for preparative purpose. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia).

Fullerene  $C_{60}$  was purchased from SES Research Co. Hexane, ethyl acetate, and toluene were purchased from Nacalai Tesque, Inc. BH<sub>3</sub>·THF (1.0 M) was purchased from Sigma-Aldrich. Acetone and carbon disulfide were purchased from FUJIFILM Wako Pure Chemical Corporation. Open-cage fullerene  $C_{60}$  derivative 1 was synthesized according to the literature.<sup>12</sup> All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification.

**Computational Methods.** All calculations were conducted with the Gaussian 09 program package. All structures at stationary and transition states were optimized at the B3LYP-D3/6-31G(d,p) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory. The GIAO calculations were conducted at the GIAO-B3LYP-D3/6-311G(d,p) using the optimized structure.

Synthesis of 2. Powdery 1 (19.9 mg, 17.0  $\mu$ mol) was placed into a 10 mL two-neck glass tube and degassed through three vacuum-Ar cycles. Toluene (2.0 mL) was added and the reaction vessel cooled to -30 °C (thermostatic bath using acetone). Then, 1.0 M BH<sub>3</sub>·THF (530  $\mu$ L, 530  $\mu$ mol, 31 equiv) was added slowly. After stirred at -30 °C for 12 h, the mixture was quenched with sat. NH<sub>4</sub>Cl aq. (5.0 mL). The organic layer was separated and then dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and charged onto a silica gel column (CS<sub>2</sub>/ethyl acetate (30:1) to (10:1)) to give a mixture containing 1 (7.31 mg) followed by 2 (8.30 mg, 6.92  $\mu$ mol, 41%) as brown powders, which was found to be a mixture of H<sub>2</sub>O@2 (10%), Ar@2 (76%), and N<sub>2</sub>@2 (+ empty 2) (14%) as described in the main text. Further purification of the mixture containing 1 by preparative HPLC afforded 1 (5.11 mg, 4.38  $\mu$ mol, 26%) as recovery.



**2**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> (1:1))  $\delta$  7.54 (t, 1H, *J* = 8.0 Hz), 7.49 (t, 1H, *J* = 8.0 Hz), 7.25 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.15 (d, 1H, *J* = 8.0 Hz), 7.11 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 10.5 Hz, 1H), 6.74 (d, *J* = 10.5 Hz, 1H), 6.06 (dd, *J* = 10.5 Hz, *J* = 5.0 Hz, 1H), 5.70 (t, *J* = 5.0 Hz, 0.10H), 5.64 (t, *J* = 5.0 Hz, 0.76H), 5.61 (t, *J* = 5.0 Hz), 5.61 (t, J = 5

<u>J = 5.0 Hz, 0.14H</u>), <u>5.34 (d, J = 10.5 Hz, 0.1H</u>), 5.14 (d, J = 10.5 Hz, 0.76H), <u>5.05 (d, J = 10.5 Hz, 0.14H</u>), <u>2.62 (d, J = 5.0 Hz, 0.1H</u>), 2.49 (d, J = 5.0 Hz, 0.76H), 2.40 (<u>d, J = 5.0 Hz, 0.14H</u>), 1.20 (s, 9H), 1.13 (s, 9H), <u>-9.69 (s, 0.20H, encapsualted H<sub>2</sub>O)</u> (Part of signals corresponding to <u>H<sub>2</sub>O@2</u> and <u>N<sub>2</sub>@2 (+ empty 2)</u> was separately observed in addition to Ar@2.); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> (1:1))  $\delta$  196.46, 181.07, 168.41, 168.01, 165.14, 162.84, 156.16, 152.24, 151.82, 150.49, 150.45, 150.40, 150.18, 149.96, 149.77, 149.68, 149.30, 148.07, 147.82, 147.24, 145.32, 145.28, 144.87, 144.85, 144.68, 144.45, 144.04, 143.76, 143.69, 143.28, 143.03, 142.99, 142.86, 141.56, 140.91, 140.75, 139.98, 139.74, 138.39, 137.96, 137.88, 137.36, 136.97, 136.75, 136.55, 136.44, 136.37, 136.23, 135.53, 135.37, 134.86, 134.47, 134.11, 133.45, 133.42, 130.67, 130.25, 129.97, 129.73, 129.32, 127.26, 127.18, 126.99, 125.52, 122.89, 119.81, 119.77, 117.11, 116.51, 78.57, 72.13, 59.87, 52.93, 37.40, 37.28, 29.78, 29.77 (The sum of carbon signals must be 78 in theory. Observed 77. One sp<sup>2</sup> carbon signal is overlapped in the aromatic region.); HRMS (APCI): *m/z* [M]<sup>+</sup> Calcd for C<sub>82</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>Ar (Ar@**2**): 1210.1276; found: 1210.1316.

Single Crystal Structure of (Ar)0.67(3)(N2)0.33(3)@2•(CS2)2.22. Single crystal of 2 was obtained from an acetone/CS<sub>2</sub> solution by slow evaporation. Intensity data were collected at 100 K on a Rigaku Oxford Diffraction 2023 instrument (XtaLAB Synergy R, HyPix) with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and mirror monochromator. A total of 31434 reflections were measured at the maximum  $2\theta$  angle of 50.74°, of which 10366 were independent reflections ( $R_{int} = 0.0779$ ). The structure was solved by direct methods (SHELXT-2018/2) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-2018/3) <sup>20</sup>. This crystal contains several CS<sub>2</sub> molecules. One of the CS<sub>2</sub> molecules was disordered, which was solved using appropriate models. Thus, (S12-C86-S9), (S11-C84-S6), and (S10-C87-S4) were placed and their occupancies were refined to be 0.319(8), 0.225(10), and 0.274(11), respectively, using SIMU, DFIX, ISOR instructions. The occupancies of other two CS<sub>2</sub> molecules, i.e., (S8–C85–S7) and (S5–C83–S3), were refined to be 0.654(6) and 0.752(5), respectively. The encapsulated species were refined to be Ar and N<sub>2</sub>, using SIMU and DFIX instructions, whose occupancies were converged to 0.67(3) and 0.33(3), respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $C_{84.22}H_{30}Ar_{0.67}N_{2.66}O_4S_{6.45}$ ; FW = 1376.53, crystal size 0.11 × 0.09 × 0.06 mm<sup>3</sup>, monoclinic,  $P2_1/c$ , a = 18.7331(10) Å, b = 13.4599(4) Å, c = 24.2944(10) Å,  $\beta =$  $106.023(5)^{\circ}$ , V = 5887.7(5) Å<sup>3</sup>, Z = 4,  $D_{c} = 1.553$  g cm<sup>-3</sup>. The refinement converged to  $R_{1}$ = 0.0790,  $wR_2 = 0.1735$  ( $I > 2\sigma(I)$ ), GOF = 1.109. The data was deposited at the

Cambridge Crystallographic Data Centre (CCDC 2301934).



Figure S1. Single crystal X-ray structure of (Ar)<sub>0.67(3)</sub>(N<sub>2</sub>)<sub>0.33(3)</sub>@2•(CS<sub>2</sub>)<sub>2.22</sub>.



**Figure S2.** The 16 short contacts between Ar and the carbon cage with an average distance of 3.49 Å.

H/D Exchange of H<sub>2</sub>O@2.



Figure S3. <sup>1</sup>H NMR spectra (500 MHz, CS<sub>2</sub>/acetone- $d_6$  (5:1)) of 2 (H<sub>2</sub>O@2, 5%; Ar@2, 85%; N<sub>2</sub>@2 (+ empty 2), 10%) in the presence of D<sub>2</sub>O.

**Determination of association constant.** The solutions of **2** in CS<sub>2</sub>/CDCl<sub>3</sub> (1:1) with concentrations of 0.10 mM, 0.25 mM, 0.50 mM, 1.0 mM, 2.0 mM, 4.0 mM, 6.0 mM, 8.0 mM, and 10.0 mM were prepared. The <sup>1</sup>H NMR spectra were recorded at 300 K. The chemical shifts of one of the alcoholic protons were used to determine the association constant ( $K_a$ ).<sup>21</sup>

**Dimerization Constant of 2.** 



Figure S4. <sup>1</sup>H NMR spectra (500 MHz,  $CS_2/CDCl_3$  (1:1)) of **2** at different concentrations. The sample consists of a mixture of **2** (H<sub>2</sub>O@**2**, 10%; Ar@**2**, 76%; N<sub>2</sub>@**2** (+ empty **2**), 14%).



**Figure S5.** Nonlinear least squares fitting<sup>21</sup> based on chemicals shift of one of alcoholic protons.

## **DFT Calculations.**



Figure S6. The calculated <sup>13</sup>C NMR spectra for (a) 1 and (b) 2 by the GIAO-B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d,p) level.



**Figure S7.** The release process of  $Ar/N_2$  from  $Ar/N_2@1$  and  $Ar/N_2@2$ , in which the *t*-butylpyridyl groups were replaced by hydrogen (B3LYP-D3/6-31G(d,p)). The  $\Delta G$  values were shown with kcal/mol at 298K.



**Figure S8.** Optimized structures of (2)<sub>2</sub> calculated at the B3LYP-D3/6-31G(d,p) level of theory. The  $\Delta G$  values were shown with kcal/mol at 298K.

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# **Chapter 4**

## **Reactions of Diaminonaphthalenes with an Open-Cage C<sub>60</sub> Derivative**

Abstract: The reactions of open-cage  $C_{60}$  derivatives with aromatic diamines are known to cause an orifice-enlargement in association with incorporating the aromatic  $\pi$ -system into  $C_{60}$  skeletons. In this chapter, the author focuses on 1,2-, 2,3-, and 1,8-diaminonaphthalenes for the synthesis of a series of naphthalene-fused  $C_{60}$  fullerene derivatives. As for the former two, orifice enlargement proceeded by cleaving two C=C bonds to afford an opening with a ring-atom count of 20, in which the naphthalene moiety was fused through a pyrazine ring. As for the reaction with 1,8-diaminonaphthalene, only one C=C bond was cleaved to give a 17-membered ring opening where the diaminonaphthalene moiety was fused through a pyrimidine ring.

## Introduction

The reactions of open-cage  $C_{60}$  fullerene derivatives<sup>1</sup> with aromatic diamines are useful for the synthesis of  $\pi$ -extended novel compounds with intense NIR (near infrared) absorption originating from both spherical and planar  $\pi$ -systems.<sup>2</sup> During the reaction, in some cases, one or two C=C bonds were cleaved and the opening size of the resulting  $\pi$ extended  $C_{60}$  derivatives is enlarged in comparison with their original ones. This enables supramolecular complexation with some guest molecules.<sup>3</sup>

In 2004, S. Murata and co-workers reported the reactions of a diketone derivative of  $C_{60}$  fullerene with aromatic diamines, affording a large orifice with a ring-atom count of 20.<sup>4</sup> Subsequently, they employed the products as hosts that could encapsulate  $H_2O$ ,  $^4CO$ ,  $^5$ NH<sub>3</sub>,<sup>6</sup> and CH<sub>4</sub>.<sup>7</sup> In 2014, Gan and co-workers synthesized the related C<sub>60</sub> derivatives with an extended  $\pi$ -system<sup>2b</sup> by dehydration reaction with aromatic 1,2-diamines,<sup>8</sup> which exhibited intense absorption in NIR region. Most recently, they synthesized another opencage system by reaction with aromatic diamine, enabling encapsulation of MeOH, EtOH, LiF, and  $[BeF]^{+,9}$  The similar large orifice was prepared on C<sub>60</sub> with the use of aromatic 1,2-diamine by Yeh and co-workers. In their cases, HCHO,<sup>10</sup> HCN,<sup>10</sup> and C<sub>2</sub>H<sub>2</sub><sup>11</sup> were encapsulated. In 2022, Y. Murata's research group, which the author belongs to, reported that a  $\pi$ -extended C<sub>60</sub> derivative underwent a timed orifice expansion triggered by the release of *in situ* encapsulated NH<sub>3</sub>.<sup>12</sup> They also found that a consecutive addition of aromatic 1,2-diamine gives a huge orifice which allows for H<sub>2</sub>O, N<sub>2</sub>, Ar, and MeOH to be encapsulated.<sup>13</sup> This method was also used successfully for the synthesis of a bilaterally  $\pi$ -extended C<sub>60</sub> derivative<sup>14</sup> as well as a  $\pi$ -extended C<sub>70</sub> derivative.<sup>15</sup> Note that, the nucleophilicity of diamines was found to change annulation and orifice cutting modes drastically (Figure 1) such as A (fused pyrazine, 20-atom ring) and B (fused imidazole, 17-atom ring).<sup>16</sup> In this chapter, the author reported a novel type of annulation mode C (fused pyrimidine, 17-atom ring) by use of 1,8-diaminonaphthalene, while the reactions with 1,2- and 2,3-diaminonaphthalenes gave type-A products. The author also presented a unique rearranged product as well as the electronic properties of the three  $\pi$ -extended C<sub>60</sub> derivatives.

### **Results and Discussion**

According to the reported procedure, **2** was synthesized by the reaction of **1** with 2,3-diaminonaphthalene in ODCB (*o*-dichlorobenzene) (Figure 2a).<sup>16</sup> With use of 1,2-diaminonaphthalene under similar conditions, two isomers, **3a** and **3b**, were obtained as a mixture in total 87% isolated yield. The ratio of **3a/3b** was determined to be 74/26 by



**Figure 1.** Three different  $\pi$ -extended modes of open-cage C<sub>60</sub> derivatives. The numbers denote orifice sizes.

<sup>1</sup>H NMR, indicating the favored formation of 3a. The separation of the two isomers by silica gel column chromatography failed due to their similar polarity. The <sup>1</sup>H NMR spectra (500 MHz,  $CS_2$ /acetone- $d_6$  (5:1)) of **2** and a mixture of **3a** and **3b** were shown in Figure 2b. The two quinoxaline protons in 2 (color code: red) were detected as two singlets at  $\delta$ 8.89 and 8.80 ppm. The corresponding protons in **3a** and **3b** were observed at  $\delta$  ca. 8.3 ppm as a doublet which was shifted to a higher-field region by  $\Delta\delta$  ca. -0.6 ppm compared to those in **2**. The coupling constants of these  ${}^{1}$ H signals in **3a** and **3b** were measured to be  ${}^{3}J=9.2$  Hz, which clearly indicates K-region protons with a high double bond character. Considering a closer distance of the quinoxaline proton to the electron-withdrawing carbonyl group, the signal observed at a lower field than another was traced to 3b, whose integrated area was 2.8-fold smaller than 3a. The bay region protons in 3a and 3b (color code: purple) were detected at  $\delta$  9.43 and 9.41 ppm, respectively, reflecting the effect of the adjacent nitrogen atom. Upon seeing the high-field region, <sup>1</sup>H signals corresponding to encapsulated H<sub>2</sub>O molecules were found at  $\delta$  -11.28, -11.27, and -11.29 ppm for  $H_2O(a)2$ ,  $H_2O(a)3a$ , and  $H_2O(a)3b$ , respectively, indicating negligible influence of the fused pattern of the naphthalene ring.

The plausible mechanism is shown in Figure 2c. By the reaction of 1 with diaminonaphthalene, INT1 is considered to be formed through a direct addition of the diamine to an electron-deficient olefinic bond on the orifice.<sup>3</sup> The intramolecular  $S_N2$  addition then gives INT2. Note that both two routes, a and b, potentially give both INT3a and INT3b. Thus, the product distribution of 3a/3b should be determined by either or both the thermodynamic stability of INT3a/3b and the kinetic demand in the final step where an intramolecular direct amination in INT3b seems to be sterically disfavoured. Theoretical calculations suggested that INT3b is less stable than INT3a by  $\Delta G$  +2.73

kcal/mol (B3LYP/6-31G(d)) while there is a negligible difference in energies between **3a** and **3b**. Thus, the formation of **INT3b** seems to be less favored.



Figure 2. (a) Reactions of 1 with 1,2- and 2,3-diaminonaphthalenes. (b) <sup>1</sup>H NMR spectra (500 MHz, CS<sub>2</sub>/acetone- $d_6$  (5:1)) of 2 and a mixture of 3a and 3b. (c) Plausible mechanism with relative Gibbs energies of isomers b toward isomers a (B3LYP/6-31G(d), 298 K, units in kcal/mol).

Next, the author carried out the reaction of **1** with 1,8-diaminonaphthalene (Figure 3a). As the result, the author obtained two products, **4** and **5**, in 22% and 4% isolated yields, respectively. The molecular ion peak of **4** was detected at m/z 1226.2663 which corresponds to  $[\mathbf{1} + \text{diamine} - 2\text{H}]^{-}$ . The <sup>13</sup>C NMR spectrum (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **4** showed only one carbonyl carbon at around  $\delta$  180–200 ppm region. The <sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) displayed only one set of methylene signals ( $\delta$  5.07 and 4.89 ppm, <sup>2</sup>*J* = 20.1 Hz). These characteristics are similar to type **B**, which has a fused imidazole (Figure 1). The structure of **4** was finally determined by X-ray crystallographic analysis, revealing a fused perimidine structure (type **C**). This cyclization mode was different from those of **2** and **3a/3b**. The molecular ion peak of **5** was detected at m/z 1230.2988 as  $[\mathbf{1} + \text{diamine} + 2\text{H}]^{-}$ . The <sup>1</sup>H NMR spectrum (500 MHz, CS<sub>2</sub>/acetone-*d*<sub>6</sub> (5:1)) (Figure 3b) showed the absence of the olefinic protons, suggesting that the reaction occurred at this position. In the spectrum, two sets of methylene protons were observed  $\delta$  4.93 and 3.88 ppm (<sup>2</sup>*J* = 19.0 Hz) as well as  $\delta$  4.24 and 2.58 ppm (<sup>2</sup>*J* = 14.4 Hz) while the

latter was further coupled with a vicinal proton with a coupling constant of  ${}^{3}J = 2.3$  Hz, suggesting arrangement of HCCH with a dihedral angle of *ca*. 60°.<sup>17</sup> The weakly coupled <sup>1</sup>H pair of HCCH was also found at  $\delta$  6.57 and 5.46 ppm with  ${}^{3}J = 0.6$  Hz, suggesting a dihedral angle of *ca*. 90°. The X-ray crystallographic analysis revealed that all these protons were attached to the orifice. The plausible mechanism for the formation of **5** was shown in Figure 3a. In the initial step, the addition of 1,8-diaminonaphthalene to **1** yields a spiro-intermediate **INT-i**. The subsequent C–C bond cleavage provides Fischer-type carbene **INT-ii**, which undergoes the C–C bond formation by the reaction with the olefin moiety to give **INT-iii**. Finally, a reduction of the C=C bond on the opening proceeds to give **5**. The structure of **INT-iii** showed a close structure to the previously reported compound, which was formed by the reaction with water instead of diamine through a similar mechanism supported by DFT calculations.<sup>18</sup>



**Figure 3.** (a) Reaction of **1** with 1,8-diaminonaphthalene. (b) <sup>1</sup>H NMR spectrum (500 MHz,  $CS_2$ /acetone- $d_6$  (5:1)) of **5**.

The single crystals of **4** and **5** were grown in  $CH_2Cl_2$  and toluene solutions, respectively, at room temperature, and the structures were unambiguously determined by X-ray crystallographic analysis.<sup>19</sup> As shown in Figure 4a, the naphthalene ring in **4** was fused as perimidine. Although the orifice size is enlarged to a 17-membered ring from the initial 12-membered ring, there are no encapsulated species inside the cage. Within the crystal, **4** is stacked with another molecule in distances of 3.72 Å and 3.22 Å. Upon seeing the structure of **5** (Figure 4b), one of the caged carbon atom (C1) was found to be moved out of the cage, affording a unique  $C_{59}$  skeleton<sup>20</sup> where the C1 atom was embedded into a perimidine ring which is connected to the fullerene skeleton through a single C–C bond. This rearrangement occurred in association with new bond formation between C2 and C3. Consequently, the orifice size changed from a 12-atom ring (for 1) to a 14-atom ring (for **5**).



**Figure 4.** Solid-state and packing structures of (a) **4** and (b) **5**, showing thermal ellipsoids at 50% probability. The solvent molecules and aryl groups are omitted for clarity.

Finally, the author studied the electronic properties of **2**, a mixture of **3a** and **3b**, and **4**, in which fused patterns of the naphthalene ring differ from each other. As shown in Figure 5a, **4** with a fused perimidine showed an intense absorption band tailing to 850 nm. The absorption edge of **2** showed a small bathochromic shift relative to a mixture of **3a** and **3b**, while stronger absorption coefficients were found at the UV region for the former, implying a better conjugation for the linear  $\pi$ -extension (**2**) than *ortho*-elongation (**3a** and **3b**). In cyclic voltammograms (Figure 5b), all naphthalene-incorporated derivatives were found to exhibit reversible four-step reduction waves. Compounds **2** and **4** showed the same first reduction potential at -1.14 V, while it appeared at -1.20 V for a mixture of **3a** and **3b** with a cathodic shift by  $\Delta E^1$  –0.06 V, being in good agreement with the calculated LUMO levels for 2 (-3.11 eV), 3a (-3.02 eV), 3b (-3.02 eV), and 4 (-3.11 eV) (B3LYP/6-31G(d)) (Figure 5c). The difference between the third and fourth reduction potential was -0.28 V for 2 which is smaller than structurally related 3a and 3b (-0.39 V). This is probably due to better delocalization of polyanionic charges over the entire  $\pi$ -skeleton in 2 than those in 3a and 3b. Focusing on molecular orbitals of 2, 3a, and 3b (Figure 5c), the distribution of the HOMOs is comparable to each other with almost the same energy levels, while the LUMO coefficients of 2 were more spread to the benzene ring next to the pyrazine ring than those of 3a and 3b. In contrast, the HOMO of 4 is mainly distributed on the perimidine moiety with a significantly increased HOMO level. This might cause a narrower HOMO–LUMO gap to achieve NIR absorption.



**Figure 5.** (a) Absorption spectra of **2**, a mixture of **3a** and **3b**, and **4** (50  $\mu$ M in benzene). (b) Cyclic voltammograms of **2**, a mixture of **3a** and **3b**, and **4** (1 mM in ODCB, 0.1 M *n*-Bu<sub>4</sub>N·BF<sub>4</sub>, and 100 mV/s). (c) Molecular orbitals of **2**, **3a**, **3b**, and **4** (B3LYP/6-31G(d)).

#### Conclusion

In summary, the author synthesized open-cage  $C_{60}$  derivatives **2**, **3a**, **3b**, and **4** with different fused modes of the naphthalene ring through the reaction of **1** with 2,3-, 1,2-, and 1,8-diaminonaphthalenes. The former two diamines afforded pyrazine-fused naphthalene rings in **2**, **3a**, and **3b**. Their orifices were enlarged from a 12-atom ring to a

20-atom ring through cleavage of two C=C bonds, which allows the encapsulation of a water molecule inside the cage. For the reaction with 1,8-diaminonaphthalene, the naphthalene ring was fused by a pyrimidine ring in 4 and the orifice was enlarged to a 17-membered ring through cleavage of only one C=C bond. In this reaction, the rearranged product 5 with a 14-membered ring was obtained. X-ray crystallographic analysis revealed that the naphthalene moiety extracted a caged carbon atom to form a perimidine ring that is attached to the  $C_{60}$  cage by a single C-C bond in 5. The different fused modes of the naphthalene ring affect electronic properties, in which 4 showed an intense NIR absorption band tailing to 850 nm.

## **Experimental Section**

**General.** The <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out at room temperature (unless otherwise noted) with JEOL JNM ECA500. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of CD<sub>2</sub>Cl<sub>2</sub> ( $\delta$  5.32 ppm in <sup>1</sup>H NMR,  $\delta$  53.84 ppm in <sup>13</sup>C NMR) and acetone-*d*<sub>6</sub> ( $\delta$  2.05 ppm in <sup>1</sup>H NMR,  $\delta$  29.84 ppm in <sup>13</sup>C NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia).

Fullerene C<sub>60</sub> was purchased from SES Research Co. Hexane, ethyl acetate, and toluene were purchased from Nacalai Tesque, Inc. Acetone, carbon disulfide, pyridine, and 1,2-diaminonaphthalene were purchased from FUJIFILM Wako Pure Chemical Corporation. 2,3-Diaminonaphthalene and 1,8-diaminonaphthalene were purchased from Tokyo Chemical Industry Co. Ltd. ODCB (*o*-dichlorobenzene) were purchased from Sigma-Aldrich Co. LLC. All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. **2** was synthesized according to literature procedures.<sup>16</sup>

**Computational Methods.** All calculations were conducted with the Gaussian 09 program package. All structures at stationary were optimized at the B3LYP/6-31G(d) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory.

Synthesis of 3a and 3b. Powdery 1 (50.0 mg, 46.7 µmol) and 1,2diaminonaphthalene (37.0 mg, 234 µmol, 5.0 equiv) were placed into a Schlenk tube and degassed through three vacuum–Ar cycles. ODCB (2.50 mL) and pyridine (189 µL,  $\rho$  = 0.982 g/mL, 2.35 mmol, 50 equiv) were added and the resulting solution was heated at 100 °C for 2 h (aluminum block heater). The reaction mixture was purified by column chromatography using silica gel (CS<sub>2</sub>/acetone (100:1)) to give a mixture of 3a and 3b (50.1 mg, 40.1 µmol, 87%) as a reddish-brown powder. The ratio of 3a/3b was determined to be 74/26 by <sup>1</sup>H NMR.



A mixture of **3a** and **3b** (74/26): <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/acetone- $d_6$  (5:1))  $\delta$  9.43 (d, 0.26H, J = 8.0 Hz), 9.41 (d, 0.74H, J = 8.0 Hz), 8.30 (d, 0.26H, J = 9.2 Hz), 8.25 (d, 0.26H, J =<u>0.74H, J = 9.2 Hz</u>), <u>8.20 (d, 0.74 H, J = 9.2 Hz</u>), <u>8.18 (d, 0.26 H, J = 9.2 Hz</u>), 8.07–8.12 (m, 1H), 7.83-7.90 (m, 2H), 7.68 (t, 1H, J = 8.0 Hz), 7.57 (t, 1H, J = 8.0 Hz), 7.52 (d, <u>0.74H, J = 10.3 Hz</u>), <u>7.51 (d, 0.26H, J = 10.3 Hz</u>), 7.47 (d, 1H, J = 8.0 Hz), 7.25 (d, 1H, J = 8.0 Hz), 7.17 (d, 1H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), <u>6.40 (d, 0.17H, J = 10.3</u> <u>Hz), 6.39 (d, 0.09H, J = 10.3 Hz), 6.38 (d, 0.49H, J = 10.3 Hz), 6.37 (d, 0.25H, J = 10.3</u> Hz), 4.75 (d, 0.26H, J = 19.5 Hz), 4.74 (d, 0.74H, J = 19.5 Hz), 4.55 (d, 0.26H, J = 19.5 <u>Hz</u>), <u>4.53</u> (d, 0.74H, *J* = 19.5 Hz), <u>3.40</u> (d, 0.17H, *J* = 19.5 Hz), <u>3.39</u> (d, 0.49H, *J* = 19.5 Hz), <u>3.38 (d, 0.09H, J = 19.5 Hz)</u>, 3.36 (d, 0.25H, J = 19.5 Hz), 3.11 (d, 0.49H, J = 19.5 Hz), 3.08 (d, 0.17H, J = 19.5 Hz), 3.07 (d, 0.25H, J = 19.5 Hz), 3.04 (d, 0.09H, J = 19.5 <u>Hz</u>), 1.24 (s, 9 H), 1.15 (s, 9 H), -11.27 (br s, 0.50H, 34% for H<sub>2</sub>O(*a*)**3a**), -11.29 (br s, <u>0.18H, 34% for H<sub>2</sub>O(a3b)</u> (Part of signals corresponding to <u>3a</u> and <u>3b</u> was separately observed. These signals are further split into at most two sets of signals due to unavoidable encapsulation of H<sub>2</sub>O. From the integrated area, the ratio of empty and H<sub>2</sub>O(a)**3** was determined to be 66:34.); <sup>13</sup>C NMR (126 MHz, CS<sub>2</sub>/acetone- $d_6$  (5:1))  $\delta$  195.20, 195.15, 188.05, 168.44, 168.05, 163.91, 163.88, 163.82, 163.80, 163.48, 163.41, 156.51, 155.15, 154.32, 154.19, 153.02, 152.98, 152.94, 152.89, 152.78, 152.74, 151.65, 151.58, 151.49, 151.37, 151.34, 150.88, 150.84, 150.47, 150.45, 150.22, 150.15, 150.00, 149.63, 149.57,

149.51, 149.48, 149.41, 149.37, 149.34, 149.24, 149.20, 149.13, 149.07, 148.70, 148.67, 148.64, 148.53, 148.50, 148.42, 148.38, 148.23, 148.20, 148.15, 147.89, 147.63, 147.26, 147.26, 146.94, 146.83, 146.71, 146.68, 146.47, 146.44, 146.37, 146.08, 145.14, 144.90, 144.86, 144.72, 144.62, 144.59, 144.08, 144.01, 143.93, 143.78, 143.75, 143.61, 143.50, 143.47, 143.37, 143.11, 143.08, 142.85, 142.82, 142.29, 142.15, 142.13, 142.08, 141.54, 141.51, 140.02, 139.79, 139.76, 138.98, 138.95, 137.73, 137.68, 137.22, 137.16, 137.01, 136.06, 135.78, 135.58, 135.43, 135.31, 135.18, 135.14, 134.17, 134.13, 133.45, 133.05, 133.01, 132.54, 132.38, 132.08, 131.95, 131.89, 131.86, 131.80, 131.55, 131.44, 131.40, 130.83, 130.56, 130.41, 130.25, 129.18, 129.13, 129.10, 128.96, 128.85, 128.78, 128.67, 127.74, 127.29, 126.01, 125.87, 125.31, 125.28, 123.94, 120.74, 120.55, 117.69, 59.23, 53.32, 42.67, 42.51, 42.37, 42.25, 37.86, 37.78, 30.46, 30.31 (The sum of carbon signals must be 176 in theory. Observed 155. One carbonyl, 14 sp<sup>2</sup>, and 6 sp<sup>3</sup>carbon signals are overlapped.); HRMS (APCI): m/z [M]<sup>-</sup> Calcd for C<sub>92</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub> (**3a/3b**): 1228.2844; found: 1228.2814.

Synthesis of 4 and 5. Powdery 1 (50.0 mg, 46.7  $\mu$ mol) and 1,8-diaminonaphthalene (147.6 mg, 934  $\mu$ mol, 20.0 equiv) were placed into a Schlenk tube and degassed through three vacuum–Ar cycles. ODCB (2.50 mL) was added and the resulting solution was heated at 180 °C for 3 h. The reaction mixture was purified by column chromatography using silica gel (toluene/hexane (1:1) to toluene) to give 4 (12.6 mg, 10.3  $\mu$ mol, 22%) as a green-brown powder and 5 (2.3 mg, 1.8  $\mu$ mol, 4%) as a reddish-brown powder.



4: <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.99 (d, 1H, J = 7.5 Hz), 7.77 (d, 1H, J = 7.5 Hz), 7.73 (d, 1H, J = 7.5 Hz), 7.70 (t, 1H, J = 7.5 Hz), 7.68 (t, 1H, J = 7.5 Hz), 7.62 (t, 1H, J = 8.0 Hz), 7.45 (t, 1H, J = 8.0 Hz), 7.51 (d, 1H, J = 7.5 Hz), 7.40 (d, 1H, J = 8.0 Hz), 7.23 (d, 1H, J = 8.0 Hz), 7.22 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.09 (d, 1H, J = 10.3 Hz), 6.73 (d, 1H, J = 10.3 Hz), 5.07 (d, 1H, J = 20.1 Hz), 4.89 (d, 1H, J = 20.1 Hz), 1.19 (s, 9H), 1.14 (s, 9H); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  198.75, 168.55, 168.50, 164.56, 164.14, 163.90, 155.50, 151.62, 150.26, 149.92, 149.64, 149.60, 149.55, 149.43, 149.36,

149.21, 149.16, 148.92, 148.43, 148.36, 148.33, 148.07, 147.77, 147.68, 147.46, 147.25, 146.77, 145.93, 145.68, 145.50, 145.21, 145.12, 145.05, 144.58, 143.82, 143.64, 143.42, 142.36, 142.30, 142.18, 141.62, 141.59, 140.57, 139.57, 139.34, 138.91, 137.99, 137.90, 137.82, 137.56, 137.41, 137.35, 137.09, 136.59, 136.18, 135.99, 135.65, 134.89, 134.66, 133.78, 132.38, 131.45, 131.25, 130.45, 129.21, 128.38, 128.07, 128.05, 126.78, 126.35, 125.12, 124.03, 123.95, 121.37, 121.21, 120.72, 120.59, 117.88, 117.29, 114.51, 59.67, 55.38, 46.52, 37.89, 37.86, 30.08, 29.97 (The sum of carbon signals must be 88 in theory. Observed 87. One sp<sup>2</sup> carbon signal is overlapped in the aromatic region.); HRMS (APCI): m/z [M]<sup>-</sup> Calcd for C<sub>92</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> (4): 1226.2687; found: 1226.2663.

**5**: <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/acetone- $d_6$  (5:1))  $\delta$  10.11 (s, 1H), 7.64 (t, 1H, J = 8.0Hz), 7.62 (t, 1H, J = 8.0 Hz), 7.40 (d, 1H, J = 8.0 Hz), 7.28 (d, 1H, J = 8.0 Hz), 7.25 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.15 (t, 1H, J = 8.0 Hz), 7.10 (t, 1H, J = 8.0Hz), 7.05 (d, 1H, J = 8.0 Hz), 7.02 (d, 1H, J = 8.0 Hz), 6.73 (d, 1H, J = 7.8 Hz), 6.57 (d, 1H, J = 0.6 Hz), 6.38 (d, 1H, J = 7.8 Hz), 5.46 (d, 1H, J = 0.6 Hz), 4.93 (d, 1H, J = 19.0Hz), 4.24 (dd, 1H, J = 14.4, 2.3 Hz), 3.88 (d, 1H, J = 19.0 Hz), 3.58 (dd, 1H, J = 7.0, 2.3 Hz), 2.58 (dd, 1H, J = 14.4, 7.0 Hz), 1.25 (s, 9H), 1.23 (s, 9H); <sup>13</sup>C NMR (126 MHz,  $CS_2$ /acetone- $d_6$  (5:1))  $\delta$  205.89, 194.62, 173.42, 169.48, 168.81, 163.27, 162.97, 156.60, 154.11, 152.82, 152.20, 151.14, 150.48, 150.12, 149.98, 149.73, 149.55, 149.44, 149.35, 149.32, 148.93, 148.56, 148.50, 148.21, 148.17, 148.14, 147.37, 146.97, 146.48, 146.46, 146.07, 145.79, 145.50, 145.43, 145.04, 145.01, 144.67, 144.29, 144.10, 143.53, 143.43, 142.86, 142.70, 140.77, 140.53, 140.37, 140.29, 139.47, 138.47, 138.38, 137.86, 137.59, 137.54, 136.06, 135.97, 135.92, 135.80, 135.64, 135.46, 134.58, 129.59, 129.24, 129.10, 128.34, 128.02, 124.44, 122.85, 121.03, 119.56, 119.46, 119.38, 118.35, 117.93, 116.17, 103.35, 59.31, 54.85, 53.88, 52.60, 41.26, 40.82, 37.89, 37.86, 30.51, 30.39, 27.05. (The sum of carbon signals must be 88 in theory. Observed 86. Two sp<sup>2</sup> carbon signal is overlapped in the aromatic region.); HRMS (APCI): m/z [M]<sup>-</sup> Calcd for C<sub>92</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub> (5): 1230.3000; found: 1230.2988.

Single Crystal X-Ray Structures of 4•(CH<sub>2</sub>Cl<sub>2</sub>)<sub>3.43</sub>. Single crystals of 4 were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution by slow evaporation. Intensity data were collected at 100 K on a Bruker APEX-III CCD X-ray Diffractometer with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and graphite monochromator. A total of 53517 reflections were measured at the maximum 2 $\theta$  angle of 50.09°, of which 11481 were independent reflections ( $R_{int}$  = 0.1153). The structure was solved by direct methods (SHELXT-2018/2) and refined by

the full-matrix least-squares on  $F^2$  (SHELXL-2018/3).<sup>21</sup> This crystal contains several disordered CH<sub>2</sub>Cl<sub>2</sub> molecules, which were solved using appropriate models. Thus, (C93–Cl3–Cl4) and (C96–Cl3–Cl4), (C101–Cl11–Cl17), (C102–Cl13–Cl18), and (C104–Cl21–Cl22), and (C95–Cl4–Cl5), (C100–Cl5–Cl6), and (C103–Cl19–Cl20) at a special position were placed and their occupancies were refined to be 0.702(5) and 0.298(5), 0.548(5), 0.257(5), and 0.195(5) and 0.247(4), 0.128(5), and 0.127(6), respectively, using SIMU and DFIX instructions. The occupancy of one of CH<sub>2</sub>Cl<sub>2</sub> molecules, i.e., (C94–Cl1–Cl2), was refined to be 0.924(4). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>95,43</sub>H<sub>40.85</sub>Cl<sub>6.85</sub>N<sub>4</sub>O<sub>2</sub>; FW = 1518.29, crystal size 0.26 × 0.10 × 0.07 mm<sup>3</sup>, triclinic, *P*-1, *a* = 12.300(4) Å, *b* = 13.575(5) Å, *c* = 20.773(8) Å, *a* = 89.490(11)°,  $\beta$  = 74.320(13)°,  $\gamma$  = 106.023(5)°, *V* = 3327(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.515 g cm<sup>-3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0768, *wR*<sub>2</sub> = 0.2165 (*I* > 2 $\sigma$ (*I*)), GOF = 1.062. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2313270).



Figure S1. Single crystal X-ray structure of 4•(CH<sub>2</sub>Cl<sub>2</sub>)<sub>3.43</sub>.

Single Crystal X-Ray Structures of 5-toluene. Single crystals of 5 were obtained from a toluene solution by slow evaporation. Intensity data were collected at 100 K on a Rigaku Oxford Diffraction 2023 instrument (XtaLAB Synergy R, HyPix) with Mo K*a* radiation ( $\lambda = 0.71073$  Å) and mirror monochromator. A total of 30820 reflections were measured at the maximum  $2\theta$  angle of 50.98°, of which 11218 were independent reflections ( $R_{int} = 0.0511$ ). The structure was solved by direct methods (SHELXT-2018/2) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-2018/3).<sup>21</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions except for H3 (amine proton). The crystal data are as follows: C<sub>99</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>; FW = 1323.40, crystal size  $0.18 \times 0.14 \times 0.11$  mm<sup>3</sup>, triclinic, *P-1*, *a* = 10.0587(4)Å, *b* = 14.5547(6)Å, *c* = 21.1395(5)Å, *a* = 90.795(2)°, *β* = 100.894(3)°, *γ* = 97.253(3)°, *V* = 3012.50(19) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.459 g cm<sup>-3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0560, *wR*<sub>2</sub> = 0.1483 (*I* > 2 $\sigma$ (*I*)), GOF = 1.015. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2313271).



Figure S2. Single crystal X-ray structure of 5•toluene.
#### **DFT Calculations.**



**Figure S3.** Plausible mechanism with relative Gibbs energies of isomers **b** toward isomers **a** (B3LYP/6-31G(d), 298 K, units in kcal/mol).

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# Chapter 5

# An Open-Cage Bis[60]fulleroid as an Efficient Electron Transport

# Material for Tin Halide Perovskite Solar Cells

**Abstract:** An open-cage bis[60]fulleroid (OC) was applied as an efficient electron transport material (ETM) in tin (Sn) halide perovskite solar cells (PSCs). Due to the reduced offset between the energy levels of Sn-based perovskites and ETMs, the power conversion efficiency (PCE) of Sn-based PSCs with OC reached 9.6% with an opencircuit voltage ( $V_{OC}$ ) of 0.72 V. In addition, OC exhibited superior thermal stability and provided 75% of the material without decomposition after vacuum deposition. The PSC using vacuum-deposited OC as ETM could afford a PCE of 7.6%, which is a big leap forward compared with previous results using vacuum-deposited fullerene derivatives as ETMs.

#### Introduction

Metal halide perovskite solar cells have been widely regarded as one of the most promising candidates to replace silicon solar cells, owing to their PCE of over 26% achieved with the low-cost solution-processed neat lead (Pb) perovskites.<sup>1</sup> However, the Pb involved in the most efficient PSCs is notorious for its toxicity, which may hinder the widespread application of this technology.<sup>2,3</sup> In this regard, Sn-based perovskites have attracted increasing interest due to their similar photophysical properties as Pb-based perovskites and environmentally benign properties.<sup>4–8</sup> Despite their great potential, the highest reported PCE of Sn-based PSCs is currently lower than 15%,<sup>9</sup> far below their theoretical limit of over 30%.<sup>10</sup>

One of the biggest challenges for Sn-based PSCs is the considerable  $V_{oc}$  loss, primarily induced by the energy level mismatch between the conduction band minimum of Sn-based perovskites and the lowest unoccupied molecular orbital (LUMO) levels of traditional fullerene ETM, i.e., C<sub>60</sub>.<sup>11</sup> Thus, it is highly desirable to develop ETMs with shallower LUMO levels. The introduction of functional groups onto the C<sub>60</sub> cages is an effective way to adjust the LUMO level.<sup>12,13</sup> Phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and indene-C<sub>60</sub> bisadducts (ICBA) (Figure 1) are typical mono and bis-functionalized fullerene derivatives that have been used to reduce  $V_{OC}$  loss in Sn-based PSCs.<sup>11</sup> However, bis- and multiple-additions often yield isomers possessing similar polarity, which requires extensive recycling using high-performance liquid chromatography (HPLC) for separation and leads to low yields.<sup>14</sup> Moreover, since each isomer exhibits both different energy levels and varied quality on the films, it is difficult to distinguish the respective effects when using the mixture as an ETM.<sup>15,16</sup>

Open-cage C<sub>60</sub> fullerene derivatives<sup>17–19</sup> enabled flexible adjustment of their energy levels by the selective modifications, which resulted in a controlled functionalization degree as opposed to conventional C<sub>60</sub> derivatization generating a complex mixture of isomers. These characteristics make them promising ETMs in PSCs. Nevertheless, there are limited reports on applying them in PSCs, except for a few reports on organic photovoltaics<sup>20–22</sup> and Pb-halide solar cells.<sup>23</sup> In this chapter, the author focused on an open-cage bis[60]fulleroid (OC) (Figure 1) which possesses two [5,6]-open structures (the bond between hexagon and pentagon is cleaved) with retaining the intact 60 $\pi$  system of parent C<sub>60</sub>. This is totally different from PCBM which features a [6,6]-closed structure (the addend is attached on a bond between hexagons) with a 58 $\pi$  system. Although the use of [5,6]-open PCBM has been hampered due to a rapid chemical transformation into a [6,6]-closed analogue,<sup>24–27</sup> bis-[5,6]-open OC is thermally stable even at 260 °C without showing any isomerism owing to the disfavoured generation of an intermediate having two [5,6]-closed structures at the *cis*-1 disposition in close proximity.<sup>28,29</sup> Furthermore, bis-functionalization of C<sub>60</sub> (bis-[6,6]PCBM and ICBA) usually leads to a greater  $V_{OC}$ , owing to the higher-lying LUMO level.<sup>30</sup> Therefore, the bis-[5,6]-open structure in the OC is highly attractive for application into PSCs as ETM. In this chapter, the author and his collaborators discussed that the resultant Sn-based PSCs using OC as ETMs presented a PCE of 9.6% with a  $V_{OC}$  of 0.72 V, comparable with those based on ICBA and significantly higher than those of PCBM. The vacuum-deposited OC to be an ETM layer was also developed, which afforded a PCE of 7.6% in PSCs.



Figure 1. Structures of PCBM, ICBA, and OC.

#### **Results and Discussion**

OC was synthesized according to the reported procedures<sup>31</sup> and the purity was confirmed by <sup>1</sup>H NMR and MS analysis, in which no observation of unreacted C<sub>60</sub> and the solvent molecule in the sample. To compare the electronic properties of OC with commercial ETMs, i.e., PCBM and ICBA, the author performed UV-vis. measurements (Figure 2a). From the spectra, OC was found to show the similar absorption behavior to PCBM owning to the (pseudo)  $C_s$  symmetry, while ICBA exhibited stronger absorption, especially at the UV and visible region, reflecting its modified  $\pi$ -conjugations. Then, the author conducted cyclic voltammetry in *o*-dichlorobenzene (ODCB) using Fc/Fc<sup>+</sup> as an internal standard (Figure 2b). The first reduction potential of OC (-1.23 V) showed a cathodic shift relative to PCBM of -1.16 V and an anodic shift relative to ICBA of -1.33 V, consistent with the tendency of the LUMO levels calculated at the B3LYP-D3/6-31G(d,p) level: -2.93 eV (OC), -2.99 eV (PCBM), and -2.92 eV (ICBA, isomer *trans*-1). Although OC has a 60 $\pi$  system, the LUMO level is much higher than that of C<sub>60</sub> (-3.22 eV). This is caused by two sp<sup>3</sup> units operating as the effective electron-donating groups. Accordingly, the LUMO level of OC became comparable to that of ICBA but higher than that of PCBM. This MO level modification is different from those for conventional C<sub>60</sub> fullerene derivatives whose MO levels are mainly governed by the functionalization degree (such as mono, bis, and tris).

To further explore the energy level, which is more reflective of the actual ETM layer in PSCs, the films of ETMs onto the surface of ITO were fabricated, which were used for the CV measurements in acetonitrile (Figure 2c). The LUMO levels for the spin-coated PCBM, OC, and ICBA films were estimated to be -4.14, -3.98, and -3.95 eV based on the  $E_{\text{onset}}$  (-0.96, -1.12, and -1.15 V), respectively, with the trend aligning closely with the results from the measurements in solutions. These results indicated a compatible energy-matching of OC toward the 2D/3D PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> perovskite (Figure 2d). This component of perovskite could afford high  $V_{\text{oc}}$  for Sn-based PSCs.<sup>11,32</sup>

Scanning electronic microscopy (SEM) measurements were performed to investigate the morphology of OC, PCBM, and ICBA on PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> (PEA: phenylethylammonium, FA: formamidinium) perovskite layers (Figure S1). These derivatives are fabricated by a mixed solvent<sup>32</sup> of chlorobenzene (CB)/CS<sub>2</sub>/1,2,4trichlorobenzene (TCB) (10/5/1, v/v). They showed similar solubility in this solvent system. The average thickness was *ca*. 40 nm prepared with a precursor solution of 15 mg mL<sup>-1</sup> with spin coating at 2000 rpm. (Figure S2). All the fullerene derivatives showed similar morphologies without discernible pinholes. In the atomic force microscopy (AFM) results (Figure S3), the average root-mean-square (RMS) surface roughness of OC was 5.8 nm, which was comparable to that of PCBM films (6.1 nm) and slightly larger than that of ICBA films (3.6 nm). All results suggested that the morphology of OC films is similar to those of PCBM and ICBA.

Considering the basicity of the pyridyl group in OC, the author checked possible protonation by NMR measurement using a mixture of OC and FAI in DMSO- $d_6$  solution (Figure. S4). No peak shift was detected, suggesting that Brønsted–Lowry acid–base reactions are unlikely in the solution.<sup>33</sup> The author then carried out X-ray photoelectron

spectroscopy (XPS) characterization to check the passivation effect of OC on the Snbased perovskite layer. The negligible peak shifts in Sn  $3d_{5/2}$  (Figure S5) suggested very limited interaction between PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> and OC. Stronger interactions were perhaps inhibited by the steric hindrance from the *tert*-butyl group in OC.



**Figure. 2** (a) UV-vis absorption spectra of PCBM, OC, and ICBA (50  $\mu$ M). (b) Cyclic voltammograms (CV) of PCBM, OC, and ICBA in ODCB (1.0 mM). (c) CV for spin-coated PCBM, OC, and ICBA films in acetonitrile. (d) Energy level diagrams of PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> and PCBM, OC, and ICBA films. PVSK denotes PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> perovskites.

After confirming that OC is suitable to be used as the ETM for Sn-based PSCs in terms of the energy levels and the film-forming ability, inverted Sn-based PSCs with the structure ITO/PEDOT:PSS/PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub>/OC/BCP/Ag was fabricated. ITO is indium tin oxide, PEDOT:PSS is poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) and BCP is bathocuproine (Figure 3a). Similar devices using PCBM or ICBA as ETMs were



**Figure. 3** (a) Schematic illustration and cross-section SEM images of devices (scale bar is 200 nm). (b) *J-V* curves of champion devices based on 2D/3D PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> perovskite with PCBM, OC, and ICBA. Forward ( $J_{SC}$  to  $V_{OC}$ ) and reverse ( $V_{OC}$  to  $J_{SC}$ ), scans are shown with solid and dashed lines, respectively. (c) EQE spectra of the devices with PCBM, OC, and ICBA. (d) Distributions of the  $V_{OC}$  values from the cells. (e) *J-V* curves of champion devices based on 3D FA<sub>0.75</sub>MA<sub>0.25</sub>SnI<sub>3</sub> perovskite with OC. F and R denote forward and reverse scans, shown with solid and dashed lines, respectively. (f)  $V_{OC}$  as a function of illumination intensity for the devices based on PCBM, OC, and ICBA (*k* is Boltzmann's constant, *T* is 298 K, and *q* is the unit of electronic charge).

fabricated as benchmarks. The current density-voltage (*J-V*) curves evaluated under the simulated solar illumination (AM 1.5G, 100 mW cm<sup>-2</sup>) are shown in Figure 3b, and the corresponding device parameters are summarized in Table S1 and Figure S6. The control devices with PCBM as ETM had PCE of up to 5.3%, short-circuit current density (*J*<sub>SC</sub>) of 17.7 mA cm<sup>-2</sup>, *V*<sub>OC</sub> value of 0.57 V, and fill factor (FF) of 0.52. The ICBA-based device delivered PCE of up to 11.6% with *J*<sub>SC</sub> of 20.7 mA cm<sup>-2</sup>, *V*<sub>OC</sub> value of 0.82 V, and FF of 0.69. Meanwhile, the OC-based device exhibited a PCE of 9.6%, with a *J*<sub>SC</sub> of 19.6 mA cm<sup>-2</sup>, *V*<sub>OC</sub> value of 0.72 V, and FF of 0.68. As shown in Figure 3c, the integrated *J*<sub>SC</sub> estimated from external quantum efficiency (EQE) spectra was 17.9, 19.1, and 20.2 mA cm<sup>-2</sup> for the devices based on PCBM, OC, and ICBA, respectively, in close agreement with the values obtained from the *J-V* curves. Notably, the trend in the *V*<sub>OC</sub> values of the devices. To

verify the universality of OC in Sn-based PSCs, OC was also used as ETM in 3D  $FA_{0.75}MA_{0.25}SnI_3$ -based PSCs (MA: methylammonium). The devices showed PCE of 9.4% ( $J_{sc} = 20.6 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.69 \text{ V}$ , and FF = 0.66) (Figure 3e), which is comparable with the 2D/3D Sn-based PSCs (PEA\_{0.15}FA\_{0.85}SnI\_3) described above.

The examination of non-radiative recombination in the devices was conducted by studying the light intensity dependence of the  $V_{OC}$  of the devices. As the devices adopt the same device structure except the ETM used, the difference in the obtained ideality factors ( $n_{id}$ ) would be governed by the recombination loss at the interface between perovskites and ETMs.<sup>34</sup> The  $n_{id}$  values are 1.84, 1,73, and 1.35 for the PEA<sub>0.15</sub>FA<sub>0.85</sub>SnI<sub>3</sub> devices using PCBM, OC, and ICBA as ETMs, respectively (Figure 3f). These results are in line with the  $V_{OC}$  values of the solar cells and confirm the suppressed charge recombination in the devices was also tracked, and they were stored in the dark in an N<sub>2</sub>-filled glovebox under open-circuit conditions. The OC-based devices maintained an average of 93% of their initial PCE for over 50 days of storage. On the contrary, those devices based on PCBM and ICBA retained 84% and 64% after the same storage conditions (Figure S7).

It is also worth noting that OC exhibited superior thermal stability compared with PCBM and ICBA. The thermogravimetric analysis (TGA) results in Figure 4a showed that OC started to lose weight at 450 °C and retained *ca.* 93% of its original weight (–7%) at 500 °C. For PCBM, it began to deplete its weight at 370 °C and only retained 88% of its original weight (–12%) at 500 °C. In sharp contrast, ICBA started to lose weight at a much lower temperature of 140 °C and experienced a substantial 25% weight loss at 300 °C. Considering all results, the author and the collaborators attempted to deposit the



**Figure 4.** (a) TGA results of PCBM, OC, and ICBA with the weight loss. (b) J-V curves of champion devices (3D FA<sub>0.75</sub>MA<sub>0.25</sub>SnI<sub>3</sub> perovskite) with OC deposited via thermal evaporation. (c) HPLC charts of OC before and after sublimation.

OC as ETM films by vacuum deposition. This device exhibited a maximum PCE of 7.6%, with  $J_{SC}$  of 21.8 mA cm<sup>-2</sup>,  $V_{OC}$  of 0.70 V, and FF of 0.50 (Figure 4b). These results were a huge leap forward compared with the previously reported results using vacuum-deposited fullerene derivatives as ETMs in PSCs,<sup>35,36</sup> in which PCBM showed severe decomposition during evaporation. The cause of the relatively low FF of 0.50 may be related to the purity of the sublimed OC. As shown in Figure 4c, HPLC analysis suggested 75% OC in pure form and 7% C<sub>60</sub> and 18% unknown impurities (+ solvent peak) in the deposited thin films. These impurities likely stem from the partial decomposition of OC during vacuum deposition and may have hindered electron extraction in the device.

#### Conclusion

In conclusion, the author and the collaborators applied an open-cage bis[60]fulleroid as the ETL in the Sn-based PSCs. This compound exhibited a higher LUMO energy level than that of PCBM and is comparable to that of ICBA. The mitigated energy levels offset between the Sn-based PSCs and the ETMs resulted in improved electron extractions and suppressed non-radiative recombination in the devices. Consequently, the devices with OC achieved PCEs of nearly 10% for both 3D and 2D/3D Sn-based PSCs with improved stability. Meanwhile, OC exhibited excellent thermal stability compared with commonly used PCBM and ICBA. These findings addressed the gaps in applying open-cage C<sub>60</sub> fullerene derivatives for PSCs.

### **Experimental section**

Materials. Formamidinium iodide (FAI, 99.99%) and bathocuproine (BCP) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Ammonium thiocyanate (NH<sub>4</sub>SCN, 99.99% trace metals basis), tin(II) fluoride (SnF<sub>2</sub>, 99%), and tin(II) iodide 99.99%, trace metals basis), ethane-1,2-diammonium iodide (SnI<sub>2</sub>, beads, (ethylenediammonium diiodide, EDAI<sub>2</sub>, ≥98%), and 1-chloronaphthalene (1-ClNp) were Co., Ltd. Sigma-Aldrich purchased from (Sigma-Aldrich). Poly (3, 4ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) aqueous solution (Clevious PVP AI 4083) was purchased from Heraeus Co., Ltd. Fullerene C<sub>60</sub> (sublimed, 99.99%) was purchased from ATR Company and Fullerene C<sub>60</sub> (95%) for synthesis was purchased from SES Research Co. Phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and Indene-C<sub>60</sub> bisadduct (ICBA) was purchased from Ossila. Dehydrated dimethyl sulfoxide (DMSO, super dehydrated), dehydrated orthodichlorobenzene (ODCB), carbon disulfide (CS<sub>2</sub>), dehydrated 1,2,4-trichlorobenzene (TCB), and acetonitrile were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. Dimethylformamide (DMF), toluene, and chlorobenzene were purchased from Kanto Chemical. Co., Inc. Hexane and toluene were purchased from Nacalai Tesque, Inc. All of these solvents that were used for the fabrication of devices were degassed by Ar gas bubbling for 1 h and further dried with molecular sieves (3 Å) in an Ar-filled glove box (H<sub>2</sub>O, O<sub>2</sub> <0.1 ppm) before use. Opencage bis60fulleroid (OC) was synthesized according to the literature.<sup>31</sup> Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. All reactions were carried out under an Ar atmosphere. All the materials were used as received.

#### Preparation of perovskite films.

**PEA**<sub>0.15</sub>**FA**<sub>0.85</sub>**SnI**<sub>3</sub>. 0.8 M PEA<sub>0.15</sub>**FA**<sub>0.85</sub>**SnI**<sub>3</sub> perovskite solution was prepared by dissolving PEAI (30.0 mg, 0.12 mmol), FAI (116.9 mg, 0.68 mmol), SnI<sub>2</sub> (298.0 mg, 0.8 mmol) SnF<sub>2</sub> (9.4 mg, 0.06 mmol) and NH<sub>4</sub>SCN (3.0 mg, 0.04 mmol) in a mixed solvent of 0.8 mL DMF and 0.2 mL DMSO. The precursor solution was stirred at 70 °C for 1 h and filtered through a 0.20  $\mu$ m PTFE filter before spin-coating. After the precursor solution was cooled down to room temperature, 100  $\mu$ L of the precursor solution was spin-coated at 5000 rpm for 50 s with an acceleration of 1000 rpm s<sup>-1</sup> (total time for spin-coating is 55 s). 500  $\mu$ L of toluene antisolvent was dripped onto the surface of the spinning substrate at 52 s during the spinning. Then, the substrate was immediately annealed on a 70 °C hot plate for 10 min. All the steps above were conducted in an Ar-filled glove box (H<sub>2</sub>O, O<sub>2</sub> < 0.1 ppm).

**FA0.75MA0.25SnI3.** 1.0 M FA0.75MA0.25SnI3 perovskite solution was prepared by dissolving FAI (129.0 mg, 0.75 mmol), MAI (39.8 mg, 0.25 mmol), SnI<sub>2</sub> (372.6 mg, 1.0 mmol) and SnF<sub>2</sub> (15.7 mg, 0.1 mmol) in 1.0 mL DMSO. The precursor solution was stirred at 45 °C for 1.5 h and filtered through a 0.20 µm PTFE filter before spin-coating. After the precursor solution was cooled down to room temperature, 200 µL of the precursor solution was spin-coated at 5000 rpm for 60 s with an acceleration of 1000 rpm s<sup>-1</sup>. 300 µL chlorobenzene (preheated to 65 °C) was used as antisolvent and dripped slowly onto the surface of spinning substrate at 2 s during the spin-coating step. The substrate was immediately annealed at 65 °C for over 10 min and then 100 °C for 10 min. All the steps above were conducted in an Ar-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm).

**Device fabrication.** Glass/ITO substrates (10  $\Omega$  sq<sup>-1</sup>, Geomatec Co., Ltd.) were etched with zinc powder and HCl (6 M in deionized water), then consecutively cleaned

with water, acetone, detergent solution (Semico Clean 56, Furuuchi chemical), water, and isopropyl alcohol with 15 min ultrasonic bath under each step. Before coating the PEDOT:PSS, plasma treatment was applied to clean the substrates. PEDOT:PSS aqueous dispersion was filtered through a 0.45 µm PTFE filter and then spin-coated on the ITO glass surface at 1000 rpm for 10 s and 4000 rpm for 30 s, and then annealed at 140 °C for 20 min under air. The substrates were transferred to an Ar-filled glove box (H<sub>2</sub>O,  $O_2 < 0.1$ ppm) and annealed at 140 °C for another 20 min. The perovskite layer was fabricated on PEDOT:PSS following the above-mentioned procedure. For EDAI<sub>2</sub> post-treatment, 1.0 mg EDAI<sub>2</sub> was added to 1.0 mL IPA and 1.0 mL toluene. The mixed solution was stirred at 70 °C for 3h and then filtered through a 0.20 µm PTFE filter before spin coating. After that, 150 µL solution was dynamically spin-coated onto perovskite films. The spin coating process was set as 4000 rpm for 20 s with an acceleration of 1333 rpm s<sup>-1</sup>. Following spin coating, the films were immediately annealed at 70 °C for around 5 min. Subsequently, 15 mg mL<sup>-1</sup> solution of PCBM, OC or ICBA in CB/CS<sub>2</sub>/TCB (10/5/1, v/v) was spincoated at 2000 rpm for 30 s, followed by annealing at 70 °C for 10 min. 8 nm of bathocuproine (0.01 nm s<sup>-1</sup>) was then deposited by thermal evaporation. Finally, 100 nm of Ag was deposited through a shadow mask to form the metal electrode. The deposition rate for Ag was set as 0.003 nm s<sup>-1</sup> until the thickness reached 5 nm, then 0.01 nm s<sup>-1</sup> until 20 nm, and finally 0.08 nm s<sup>-1</sup> until the target thickness was reached. The overlap area of the bottom ITO and the uppermost silver electrode of the devices was 0.15 cm<sup>2</sup>.

**Characterization.** Scanning electron microscopy (SEM) was performed with a Hitachi S8010 ultra-high-resolution scanning electron microscope (Hitachi High-Tech Corporation). Atomic force microscopy (AFM) was performed with a Picoscan Plus AFM instrument used in AC-mode with Nanoworld NCST probes. UV–vis absorption measurement was performed with a JASCO V-780 spectrophotometer.

Cyclic voltammetry (CV) of thin film was performed on an ALS/chi-620C electrochemical analyzer using a three-electrode cell with an ETMs-adsorbed ITO working electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The films of ETMs were spin-coated on a plasma-treated ITO surface (condition: 15 mg mL<sup>-1</sup> CB/CS<sub>2</sub>/TCB (10/5/1, v/v) solution of ETMs, 2000 rpm). The measurements were carried out using acetonitrile solution of 0.1 M tetrabutylammonium hexafluorophosphate (*n*Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. The area of the working electrode dipped into the electrolyte solution is 0.9 cm × 1.25 cm. The measurement of CV in solutions was

performed on an ALS/chi-620C electrochemical analyzer using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out using 1 mM solutions of ETMs and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) as a supporting electrolyte, and the potentials were calibrated with ferrocene used as an internal standard which was added after each measurement. The CV measurements were carried out under an argon atmosphere.

Photocurrent–voltage (*J*–*V*) curves were measured in an N<sub>2</sub>-filled glove box (H<sub>2</sub>O,  $O_2 < 0.1$  ppm) with an OTENTO-SUN-P1G solar simulator (Bunkoukeiki Co., Ltd.). The light intensity of the illumination source was calibrated using a standard silicon photodiode. The active area of the devices was 0.0985 cm<sup>2</sup> as defined by the aperture of the shadow mask placed between the light source and test cells. Each device was measured with a 10-mV voltage step and a 100 ms time step (i.e., scan rate of 0.1 V s<sup>-1</sup>) using a Keithley 2400 source meter. External quantum efficiency (EQE) were measured with a Bunkoukeiki SMO-250III system equipped with a Bunkoukeiki SM-250 diffuse reflection unit (Bunkoukeiki Co., Ltd.). The incident light intensity was calibrated with a standard SiPD S1337-1010BQ silicon photodiode.

The <sup>1</sup>H measurements were carried out at room temperature (unless otherwise noted) with JEOL JNM ECA500 and Bruker Advance III 400 spectrometer. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of acetone- $d_6$  ( $\delta$  2.05 ppm in <sup>1</sup>H NMR,  $\delta$  29.84 ppm in <sup>13</sup>C NMR) and DMSO- $d_6$  ( $\delta$  2.50 ppm in <sup>1</sup>H NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (two directly connected columns; 250 mm in length, 20 mm in inner diameter) for preparative purpose. Column chromatography was performed using PSQ 60B (Fuji Silysia). XPS was recorded with a JPS-9010 (JEOLCo.,Ltd.) instrument, with an X-ray energy of 1.5 keV (Al K $\alpha$ ), a step of 0.1 eV, and a dwell time of 200 ms. The perovskite film samples were transferred to the XPS chamber through an Ar-filled transfer vessel in order to avoid oxygen contamination.

**Computational Methods.** Theoretical calculations were performed using the Gaussian 09 software package. Ground state structures were optimized at the B3LYP-D3/6-31G(d,p) level of theory without any symmetry assumptions and confirmed by frequency analyses at the same level of theory.



**Figure S1**. Top view SEM images of (a) PCBM, (b) OC, and (c) ICBA films grown on Sn-based perovskite layers (scale bar is  $2 \mu m$ ).



**Figure S2**. Cross section SEM images of (a) PCBM, (b) OC, and (c) ICBA films fabricated onto Sn-based perovskite layers (The scale bar is 500 nm). (d) The average thickness of the PCBM, OC and ICBA films estimated from SEM images.



**Figure S3**. (a) AFM images and (b) the root-mean-square roughness of PCBM, OC and ICBA-covered perovskite samples.



**Figure S4.** <sup>1</sup>H NMR spectra (500 MHz, DMSO- $d_6$ /CS<sub>2</sub>(2:1)) of OC, OC mixed with (FAI+SnI<sub>2</sub>+SnF<sub>2</sub>+PEAI), and mixture of (FAI+SnI<sub>2</sub>+SnF<sub>2</sub>+PEAI).



**Figure S5**. XPS spectra of the (a) Sn  $(3d_{3/2} \text{ and } 3d_{5/2})$ , (b) C 1*s*, (c) I  $(3d_{3/2} \text{ and } 3d_{5/2})$ , and (d) N 1*s* core levels for the bare perovskite films and perovskite films treated with OC.

Molecule for ETM	$J_{\rm SC}~({ m mA~cm^{-2}})^{ m a}$	$V_{\rm OC}  ({ m V})^{ m a}$	FF <sup>a</sup>	PCE (%) <sup>a</sup>
РСВМ	17.7	0.57	0.53	5.3
	$(18.4 \pm 1.3)$	$(0.48\pm0.04)$	$(0.48 \pm 0.03)$	$(4.3\pm0.5)$
OC	19.6	0.72	0.68	9.6
	$(18.9\pm0.7)$	$(0.69\pm0.06)$	$(0.65 \pm 0.04)$	$(8.5\pm0.8)$
ICBA	20.7	0.81	0.69	11.6
	$(20.3 \pm 0.4)$	$(0.76 \pm 0.05)$	$(0.67 \pm 0.03)$	$(10.4 \pm 0.7)$

**Table S1**. Champion and average PV parameters of PSCs from a single batch of six solar cells

<sup>a</sup> The average and standard deviation values are given in parentheses.



**Figure S6**. Distributions of (a) PCE, (b)  $J_{SC}$ , (c)  $V_{OC}$ , and (d) FF values derived for six devices with PCBM, OC, and ICBA. The data includes values derived from both forward and reverse J-V scans.



**Figure S7**. Shelf-stability of unencapsulated cells with PCBM, OC, and ICBA. For this test, devices were stored in the dark in an N<sub>2</sub>-filled glovebox. The error bars represent the standard deviation. The data includes values derived from both forward and reverse J-V scans of three devices for each ETM.

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# **List of Publications**

The content of this thesis is composed of following papers.

# Chapter 1

"An H<sub>2</sub>O<sub>2</sub> Molecule Stabilized inside Open-Cage C<sub>60</sub> Derivatives by a Hydroxy Stopper." <u>Guanglin Huang</u>, Shota Hasegawa, Yoshifumi Hashikawa, Yuki Ide, Takashi Hirose, Yasujiro Murata\*, *Chem. –Eur. J.* **2022**, *28*, e202103836. (Selected as Very Important Paper)

(Chapter 1 is the author's version of a submitted work that was subsequently accepted for publication in *Chemistry – A European Journal*, copyright © John Wiley & Sons, Inc. after peer review. To access the final edited and published work, see the following website: https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/chem.202103836)

# Chapter 2

"CH<sub>3</sub>CN@open-C<sub>60</sub>: An Effective Inner-Space Modification and Isotope Effect inside a Nano-Sized Flask."

<u>Guanglin Huang</u>, Yuki Ide, Yoshifumi Hashikawa, Takashi Hirose, Yasujiro Murata\*, *Chem. –Eur. J.* **2023**, *29*, e202301161. (Selected as Hot Paper and Cover Picture)

(Chapter 2 is the author's version of a submitted work that was subsequently accepted for publication in *Chemistry – A European Journal*, copyright © John Wiley & Sons, Inc. after peer review. To access the final edited and published work, see the following website: https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202301161)

#### Chapter 3

"Synthesis of an Open-Cage C<sub>60</sub> Derivative with a Double Stopper." <u>Guanglin Huang</u>, Yoshifumi Hashikawa, Yasujiro Murata\*, *ChemistrySelect* **2023**, *8*, e202304880. (Chapter 3 is the author's version of a submitted work that was subsequently accepted for publication in *ChemistrySelect*, copyright © John Wiley & Sons, Inc. after peer review. To access the final edited and published work, see the following website: https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/slct.202304880)

# Chapter 4

"Reactions of Diaminonaphthalenes with an Open-Cage C<sub>60</sub> Derivative." <u>Guanglin Huang</u>, Shumpei Sadai, Yoshifumi Hashikawa, Yasujiro Murata\*. *Under revision*.

# **Chapter 5**

"An Open-Cage Bis[60]fulleroid as an Efficient Electron Transport Material for Tin Halide Perovskite Solar Cells"

Wentao Liu,<sup>‡</sup> <u>Guanglin Huang</u>,<sup>‡</sup> Chien-Yu Chen,<sup>‡</sup> Tiancheng Tan, Fuyuki Harata, Shuaifeng Hu, Tomoya Nakamura, Minh Anh Truong, Richard Murdey, Yoshifumi Hashikawa, Yasujiro Murata\*, and Atsushi Wakamiya\*. (<sup>‡</sup>equally contributed first authors)

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(Chapter 5 is the author's version of a submitted work that was subsequently accepted for publication in *Chemical Communications*, copyright © Royal Society of Chemistry after peer review. To access the final edited and published work, see the following website: https://pubs.rsc.org/en/Content/ArticleLanding/2024/CC/D3CC05843C)

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