

Xiao-Yu Yang,<sup>†</sup> Hao-Sheng Lin,<sup>‡</sup> Il Jeon,<sup>‡</sup> and Yutaka Matsuo<sup>\*,†,‡</sup>

<sup>†</sup>Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, China

<sup>‡</sup>Department of Mechanical Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

**S** Supporting Information

**ABSTRACT:** Aryl[60] fullerenyl cations  $(ArC_{60}^{+})$ , which were generated by heating aryl[60]fullerenyl dimers (ArC<sub>60</sub>-C<sub>60</sub>Ar) to generate aryl[60] fullerenyl radicals  $(ArC_{60}^{\bullet})$  followed by oxidation using Cu(II) salts (Cu( $BF_4$ )<sub>2</sub>(aq)), were reacted with various functionalized aryl boronic acids to produce functionalized 1,4-diaryl[60]fullerenes. This protocol tolerated various



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functional groups, such as OH, NH<sub>2</sub>, COCH<sub>3</sub>, and Cl substituents, with yields reaching 93%.  $C_{60}Ar^{1}Ar^{2}$  (Ar<sup>2</sup> = p-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) was used as a dopant in a photoactive CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer of a perovskite solar cell.

Functionalization of fullerenes has enabled their use in various practical applications, including energy conversion devices<sup>1</sup> and biomaterials.<sup>2</sup> Because of the excellent electron affinity of fullerenes,<sup>3</sup> typical fullerene modification reactions proceed via addition of nucleophilic moieties to fullerene,<sup>4</sup> such as azomethine ylides (Prato reaction),<sup>5</sup> malonates (Bingel-Hirsch reaction),<sup>6</sup> and organometallic nucleophiles.<sup>7</sup> However, such reactions generally involve fullerene anion intermediates, which cause problems with functional group tolerance. Although ester and ketone groups in substrates have been used in such nucleophilic reactions,8 there was lower tolerance for more reactive functional groups such as hydroxy and amino groups due to protonation of fullerene anion intermediates and so on. In general, installation of organic groups containing a hydroxy group onto fullerene has been achieved by using protection/deprotection strategies.9 Otherwise, reactive functional groups will take part in the reaction.<sup>10</sup>

We have previously reported the unique reactivity of fullerene cation intermediates for intramolecular migration and cyclization.<sup>11,12</sup> For example, thermal cleavage of alkylfullerenyl dimer  $RC_{60}-C_{60}R$  produces alkylfullerenyl radical Me<sub>3</sub>SiCH<sub>2</sub>C<sub>60</sub>,  $^{13,14}$  which can then be oxidized to alkylfullerenyl cation,  $Me_3SiCH_2C_{60}^+$ . This cation undergoes cyclization to produce dihydromethano[60]fullerene  $(C_{61}H_2)$ ,<sup>11a</sup> which is an important intermediate in the synthesis of methanoindene-fullerene,  $C_{60}(CH_2)$ (indene), which is a high-performance electron acceptor used in organic solar cells.<sup>11c,d</sup> Another example is demethylative cyclization of an arylfullerenyl cation bearing an o-methoxy group on the aryl group.<sup>12d</sup>  $\operatorname{ArC}_{60^+}$  (Ar =  $o - \operatorname{MeOC}_6H_4$ ) produces dihydrobenzofurano 60 fullerene and related compounds with fullerene-oxygen bond formation occurring through intramolecular interaction between the fullerene cation and the oxygen atom of the aryl group. In this way, the use of fullerene

cations marks a frontier in the chemistry of fullerenes for their synthetic modification. The abstraction of one electron from organofullerenyl anions to produce organofullerenyl radicals and the subsequent removal of one more electron to generate organofullerenyl cations can be regarded as abstraction of two electrons from the highest occupied molecular orbital (HOMO), which forms a new lowest unoccupied molecular orbital (LUMO) offering nontraditional reactivity for new fullerene modification reactions (Figure 1).



Figure 1. Concept of this work. The newly generated LUMO has unique reactivity. For example, weak nucleophiles such as aryl boronic acids can react with the newly formed LUMO.

Here, we report an intermolecular coupling reaction between arylfullerenyl cations and various functionalized aryl boronic acids to produce functionalized 1,4-diaryl[60]fullerenes, C<sub>60</sub>Ar-(Ar-FG) (FG = functional groups, including reactive OH and NH<sub>2</sub> groups). The diaryl[60]fullerenes, C<sub>60</sub>År<sub>2</sub>, are simple and robust scaffolds with a 1,4-addition pattern of fullerene derivatization, accessible using various synthetic methodologies.<sup>15–19</sup> An advantage of the present reaction is functional

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<sup>*a*</sup>Unless otherwise specified, all reactions were conducted at 120 °C for 16 h with a 1:5:4 molar ratio of dimer/boronic acid/oxidant. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Values in parentheses are based on the use of the oxidant CuBr<sub>2</sub> instead of Cu(BF<sub>4</sub>)<sub>2</sub>(aq). <sup>*d*</sup>Isolated yield when using Cu(BF<sub>4</sub>)<sub>2</sub>(aq) in the presence of molecular sieves 4 A.

group and water tolerance due to the use of fullerenyl cation intermediates, which are not reactive toward them. Importantly, this reaction features novel reactivity of the newly generated LUMO of the fullerene cations toward aryl boronic acids bearing a partial negative charge. Furthermore, this reaction can utilize the commercial availability of various functionalized aryl boronic acids. We anticipate that this reaction can contribute to further understanding of cation-mediated fullerene functionalization reactions and can provide a route to various functionalized fullerene derivatives for a wide range of applied research, without requiring the use of protection/deprotection protocols.

The present reaction starts from an organofullerenyl dimer, which can be synthesized in high yield and isolated simply by silica gel column chromatography.<sup>14</sup> Arylfullerenyl dimers (**2a** and **2b** for Ar = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> and p-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>, respectively) were readily prepared by I<sub>2</sub>-mediated single-electron oxidation of arylfullerenyl anions (ArC<sub>60</sub><sup>-</sup>) obtained by deprotonation of C<sub>60</sub>ArH with <sup>t</sup>BuOK.<sup>12d</sup> Upon heating, the singly bonded dimer **1** underwent homolytic cleavage of the single bond to give an

arylfullerenyl radical  $(ArC_{60}^{\bullet})$  which was then oxidized by a Cu(II) salt to generate an arylfullerenyl cation  $(ArC_{60}^{+})$ . Subsequently, the arylfullerenyl cation generated in situ participated in an intermolecular coupling reaction in the presence of various aryl boronic acids. Thus, 1, hydroxyphenyl boronic acid 3a (5 equiv), and aqueous  $Cu(BF_4)_2$  (4 equiv) were heated in o-dichlorobenzene (o-DCB) at 120 °C under an inert atmosphere, producing coupling product 1-(4-methoxyphenyl)-4-(4-hydroxyphenyl)[60]fullerene 4a in 78% isolated yield (Table 1, entry 1). Note that the use of  $Cu(BF_4)_2$  (aq) was superior to the use of CuBr<sub>2</sub> in terms of both ease of operation and product yield. A certain amount of an aqueous solution of  $Cu(BF_4)_2$  can be taken by pipetting without weighing, utilizing the water-tolerance of this reaction due to the use of fullerene cation intermediates that are stable against water. In a reaction with CuBr<sub>2</sub> previously investigated in our laboratory, Cu(II) oxidant gave 51% isolated yield, which can be ascribed to the poor solubility of CuBr<sub>2</sub> in o-DCB.

After optimization of the reaction conditions, we further investigated the scope and limitations of this reaction. Amino

group functionalized boronic acid **3b** reacted with the fullerenyl cation to produce derivative **4b** in 50% and 53% yields in the presence of  $Cu(BF_4)_2(aq)$  and  $CuBr_2$ , respectively, without the use of protecting groups (Table 1, entry 2). Notably, the acetyl and chloro groups were also tolerated in this reaction to produce **4c** and **4d**, respectively, in the presence of  $Cu(BF_4)_2(aq)$  as the oxidant (entries 3 and 4). The benzofuran and thiophene functional groups also could be installed by using benzofuranyl and thienyl boronic acids to produce **4e** and **4f** in 89% and 75% yields, respectively (entries 5 and 6). Other organic substituents (entries 7–10) on the aryl groups could be used to obtain diaryl[60]fullerenes **4g**–**j**, with the highest yield reaching 93%.

Meanwhile, dimer 2 bearing a 'Bu group could be used for this reaction to obtain corresponding diaryl[60]fullerenes 5a-dunder the same reaction conditions (Supporting Information, SI). We also examined the use of boronic acid pinacol esters instead of boronic acids and found that they similarly generated the desired products in satisfactory yield (SI). Generally, the products 5a-d with the 'Bu group had better solubility than compounds 4a-j, and all of the products 4 could be easily separated by silica gel column chromatography, owing to the polarity of the MeO group.

We noticed that when the reaction system contained methanol methoxy products  $C_{60}Ar^1(OMe)$  were produced, as characterized by NMR and HRMS. In addition, when we added water to the reaction systems in the absence of boronic acid substrates, we obtained the known aryl(hydroxy)fullerene  $C_{60}Ar^1OH$ .<sup>17</sup> These results indicate that the intermediate is an arylfullerenyl cation  $Ar^1C_{60}^+$ , which can react with methanol and water to give  $C_{60}Ar^1(OMe)$  and  $C_{60}Ar^1OH$ , respectively. The present reaction to diarylfullerenes can take place in the presence of water from  $Cu(BF_4)_2(aq)$ , indicating that  $C_{60}Ar^1OH$  is equivalent to the arylfullerenyl cation in the presence of a Cu(II) ion.

Bearing in mind the above observations, we next investigated the limitations of this reaction. When we used an aryl boronic acid with an alcohol group  $HOCH_2C_6H_4B(OH)_2$  instead of a phenolic group like in **3a**, we could not obtain the desired diarylfullerene, even after considerable experimentation. Both the alcohol and boronic acid groups in the substrate reacted with the fullerenyl cation intermediate to give a complex mixture. Although phenolic OH groups are well tolerated in this reaction, alcoholic OH groups cannot be used. This is a limitation of the present reaction.

Another limitation can be seen from the low chemical yield of **4c**. This was due to the low nucleophilicity of the substrate with an electron-withdrawing acetyl group toward the fullerene cation electrophile. Interestingly, we obtained a hydroxyfullerene ( $C_{60}Ar^1OH$ ) as a side product from this reaction. This was attributed to competition between the boronic acid ( $Ar^{1(\delta-)}B$ -(OH)<sub>2</sub>) and water ( $O^{(\delta-)}H_2$ ), both of which act as weak nucleophiles. When we added molecular sieves 4 A to this reaction system with  $Cu(BF_4)_2$  (aq), the yield was improved from 22% to 35%. Overall, we consider this intermolecular reaction to be competitive, and the reactivity of the arylfullerenyl cation is in the order alcohol > aryl boronic acids > water; the electronic properties of the boronic acids slightly affect this order.

Based on our results, and a review of the literature, we propose a plausible mechanism for this fullerenyl-cationmediated coupling reaction. In general, Suzuki–Miyaura cross-coupling reactions with boronic acids occur under basic conditions, and hydroxide attacks the boron atom to generate tetracoordinated borate  $Ar^2B(OH)_3^-$ , which participates in transmetalation to the Pd(II)Ar<sup>1</sup>(OH) species to give  $B(OH)_4^-$  and Pd(II)Ar<sup>1</sup>Ar<sup>2</sup>, which subsequently undergoes reductive elimination (Figure 2c). Similarly, we can surmise that a halide



**Figure 2.** Plausible reaction mechanism of the fullerene-cationmediated coupling reaction. (a) Nucleophilic attack of weakly electronegative aryl groups to the fullerenyl cation. (b) Transmetalation analogue between  $Ar^2$  and  $Br^-$  on  $Ar^1C_{60}^{-+}$ . (c) Transmetalation between  $Ar^2$  and  $OH^-$  on  $Pd^{2+}$ .

coordinates to the boron atom to produce a tetracoordinated species for exchanging an aryl group and a halide on a borate and a fullerene cation, respectively, to afford the product (Figure 2b). However, considering that the reaction proceeds in the presence of  $Cu(BF_4)_2$  (not only  $CuBr_2$ ), we propose a reaction mechanism involving unconventional nucleophilic attack of weakly electronegative  $(\delta -)$  aryl groups onto the fullerenyl cation to generate the product (Figure 2a). This reaction does not occur with the usual LUMO of neutral  $C_{60}$ and fullerene derivatives, but it can take place with the newly generated LUMO after removal of two electrons from organofullerenyl anions (Figure 1). By utilizing this new frontier orbital, we found a unique reaction that was previously inaccessible. From the viewpoint of organic chemistry, this reaction can be regarded as an elementary reaction analogous to transmetalation in the Suzuki-Miyaura coupling (Ar<sup>1</sup>–Pd-OH to  $Ar^1$ -Pd- $Ar^2$  vs  $Ar^1$ - $C_{60}$ -X to  $Ar^1$ - $C_{60}$ - $Ar^2$  with similarity of Pd<sup>2+</sup> and ArC<sub>60</sub><sup>+</sup>). Given the rich synthetic chemistry of transition-metal complexes, the analogous fullerene cations here could be promising reactants for the preparation of various unique fullerene derivatives.

The present reaction can be compared with a palladiumcatalyzed fullerene modification reaction reported by Itami and co-workers.<sup>19b</sup> They synthesized  $C_{60}Ar_2$  from  $C_{60}ArH$  and aryl halides in the presence of a Pd(II) catalyst and a base. Because they used aryl halides and a base, their reaction mechanism involves a fullerenyl anion intermediate. In contrast, the present reaction mechanism involves a fullerenyl cation intermediate. This is advantageous for realizing functional group and water tolerance and avoiding the use of noble metal catalysts.

We conducted controlled experiments for further understanding of this reaction. We examined the reaction in air, in the absence of a Cu(II) reagent, and in the absence of a Cu(II) in air while using dimer 1 and boronic acid 3i. Under the standard conditions, in the presence of  $Cu(BF_4)_2(aq)$  in argon, HPLC yield and isolated yield were 98% and 88%, respectively (Figure S1). In air, the yields dropped somewhat to 84% and 63%, respectively (Figure S2). Without Cu(II) in argon, the target molecule also formed, but HPLC and isolated yields were 42% and 23%, respectively, and many unidentifiable products formed (Figure S3). Finally, the reaction in the absence of Cu(II) in air gave only 5% and 2% HPLC and isolated yields, respectively (Figure S4). From these data, Cu(II) is not mandatory, and the reaction can occur with a fullerenyl radical, but Cu(II) to generate a fullerenyl cation is necessary to obtain the desired products in high yield. Avoiding oxygen is preferable for cleaner reactions, even though a small amount of water does not affect the reaction.

Finally, we demonstrated the potential of our new fullerene derivatives in an organic electronic application. Fullerene application has played a crucial part in the field of perovskite solar cells (PSCs).<sup>20</sup> Accordingly, we fabricated PSCs and showcased the application of amine-functionalized compound (4b) as a photoactive layer dopant. It has been reported that the amine group can interact with CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> to form a Lewis acid adduct, passivating trapping sites.<sup>21</sup> In addition, fullerene derivatives inside the photoactive layer are reported to enhance photovoltaic performance.<sup>22</sup> Therefore, we fabricated inverted PSCs and introduced 4b according to the method in ref 22. The power conversion efficiency (PCE) of control device increased from 12.7% to 13.5% upon addition of 4b, owing to increased current density  $(I_{SC})$  (Figure S5). This demonstrates that fullerenes prepared by this reaction can function as a dopant in PSCs, and we are planning further analysis and more detailed investigations for our future research.

In summary, we found a unique intermolecular reaction by exposing new frontier orbitals of fullerene derivatives (i.e., a newly generated LUMO) to react with functionalized boronic acids producing functionalized fullerene derivatives without use of a protection/deprotection protocol. The key aspect of this reaction is that the organofullerenyl cation intermediate tolerates reactive functional groups, as well as water. In comparison with Suzuki-Miyaura coupling, the present reaction on ArC<sub>60</sub><sup>+</sup> is analogous to the elementary transmetalation reaction with boronic acids on Pd<sup>2+</sup>. Such reactivity cannot be accessed via the conventional LUMOs of neutral fullerene derivatives. The present reaction offers a new route to C-C bond formation for synthesizing various fullerene derivatives. Obtained fullerene derivatives with reactive functionalities are expected to be useful in various areas of research, such as energy-related studies, as shown in our demonstration of an amino-functionalized arylfullerene derivative as a dopant in a perovskite solar cell.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b01295.

Experimental section including <sup>1</sup>H and <sup>13</sup>C NMR spectra and HRMS (PDF)

## AUTHOR INFORMATION

### **Corresponding Author**

\*E-mail: matsuo@ustc.edu.cn, matsuo@photon.t.u-tokyo.ac.jp.

# ORCID 🔍

Il Jeon: 0000-0002-4220-8374

Yutaka Matsuo: 0000-0001-9084-9670

## Notes

The authors declare no competing financial interest.

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