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Oxazoline and Imidazoline Functionalization of a C_{60} Dimer via the Reaction of $C_{60}HBn$ and Aromatic Nitriles with a Bifunctional Hydroxide

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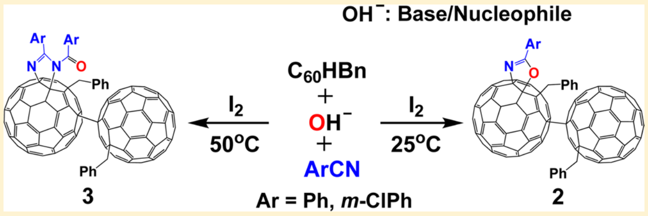
Supporting Information



ABSTRACT: Oxazoline and imidazoline functionalization of a singly bonded C_{60} dimer is achieved via a one-pot reaction of $C_{60}HBn$ with OH^- and aromatic nitriles, where the OH^- not only functions as a Brønsted base that deprotonates $C_{60}HBn$ but also as a nucleophile that initiates the nucleophilic addition to the fullerene cage. The structures of the obtained oxazolinated and imidazolinated C_{60} dimeric compounds have been established by HRMS, UV−vis, and ^1H, ^{13}C, and HMBC NMR characterizations and computational calculations. The reaction mechanism is studied with the in situ vis−near-IR spectra, which shows that the use of I_2 is crucial for the functionalization of the C_{60} dimer, indicating that it is likely the dimeric molecule rather than the fragment of the dimer that is involved in the reaction.

■ INTRODUCTION

As a strong nucleophile, hydroxide (OH^-) reacts with fullerenes and aromatic nitriles to form fullerene oxazolines[1] or imidazolines[2] under different temperature conditions. The reactions are also applicable to fullerene derivatives such as 1,4-R_2C_{60}, where the C_{60} cage is oxazolinated with a distinctive regioselectivity with respect to the existing addends.[3] It would be of interest to extend the work to the acidic organo(hydro)[60]fullerenes ($C_{60}HR$),[4] since $C_{60}HR$ would not only be deprotonated by strong bases[4−6] to form the singly bonded C_{60} dimers via subsequent oxidation,[6] but should also be capable of undergoing the OH^--initiated heterocyclic additions engaging aromatic nitriles,[1−3] which may constitute a novel approach for the derivatization of fullerene dimers.

Fullerene dimers are an important class of compounds,[7] which have exhibited enhanced performance for charge separation,[8] molecular anchoring,[9] energy harvesting,[10] and photovoltaic power generation[11] because of the presence of two fullerene units in one molecule. The singly bonded C_{60} dimers are of particular interest due to the facile preparation and the rich structural variations brought by the addends.[6,12] However, the presence of two carbon cages in one molecule lowers the solubility of the fullerene dimers,[7] which may hinder the potential applications of the materials. Derivatization is an effective approach to improve the solubility of fullerenes,[13] and it is expected to be also effective for improving the solubility of fullerene dimers. However, despite the rapid development of fullerene chemistry,[13] the progress for derivatizing fullerene dimers is rather slow,[14] likely due to the structural complications and the instability of the dimer molecules. Intriguingly, a "cleavage−recombination" approach has been recently proposed to achieve the derivatization of the singly bonded $RC_{60}−C_{60}R$ dimers under high temperature, where the $RC_{60}−C_{60}R$ dimers are cleaved first for derivatization, followed by a recombination of the subunits to form the derivatized dimer molecules.[15] Such a result has posed a question as to whether "cleavage−recombination" is a general mechanism for derivatizing the singly bonded $RC_{60}−C_{60}R$ dimers. Herein, we report a multicomponent reaction of $C_{60}HBn$ (1,2-H($PhCH_2$)-C_{60}) with OH^- and aromatic nitriles in the presence of I_2. Interestingly, oxazolinated and imidazolinated $RC_{60}−C_{60}R$ dimer derivatives are obtained, which shows that it is possible that the derivatization of $RC_{60}−C_{60}R$ dimer can take place via an alternative pathway, where the dimeric molecule is directly functionalized.

The structures of dimeric compounds **1**−**3** studied in the current work are illustrated in Scheme 1. Compound **1** is the underivatized singly bonded C_{60} dimer, while compounds **2** and **3** are the oxazolinated and imidazolinated products of **1** with only one of the two C_{60} cages being derivatized. Notably, all of the compounds are composed of the meso and racemic isomers due to the 1,4-configuration between the benzyl and the pivot bond connecting the other C_{60} cage.[6,15]

■ RESULTS AND DISCUSSION

The reaction conditions and substrate scope were screened, and the results are given in Table 1. Benzonitrile (PhCN) was first examined to establish suitable conditions. When a 1:1 molar ratio of OH^- to $C_{60}HBn$ was used, the major product obtained was **1** regardless of whether the reaction was carried out at 25

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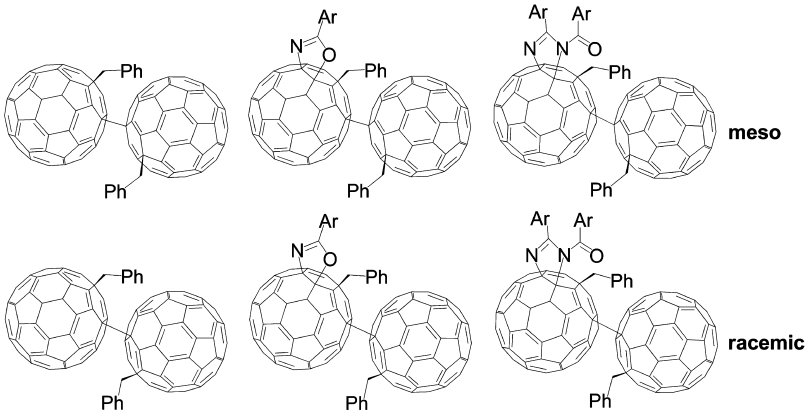
Scheme 1. Illustrated Structures of Compounds 1−3 Obtained in This Work



1

2
2a: Ar = Ph
2b: Ar = *m*-ClPh

3
3a: Ar = Ph
3b: Ar = *m*-ClPh

Table 1. Screening of the Reaction Conditions and the Substrate Scope[a]

entry	Ar (ArCN)	n_{OH^-}:$n_{C_{60}HBn}$	*T* (°C)	time[b] (h)	products (amt (%))[c]
1	Ph	1:1	25	1	**1** (84), **2a** (trace)
2	Ph	2.5:1	25	1	**1** (7), **2a** (29), **3a** (4)
3	Ph	2.5:1	25	4	**1** (6), **2a** (28), **3a** (4)
4	Ph	5:1	25	1	mixture
5	Ph	1:1	50	1	**1** (74), **3a** (6)
6	Ph	2.5:1	50	1	**1** (3), **2a** (6), **3a** (30)
7	Ph	2.5:1	50	4	**1** (3), **2a** (5), **3a** (30)
8	Ph	5:1	50	1	mixture
9	*m*-ClPh	2.5:1	25	1	**1** (85)
10	*m*-ClPh	2.5:1	25	4	**1** (3), **2b** (33), **3b** (4)
11	*m*-ClPh	2.5:1	50	4	**1** (4), **2b** (5), **3b** (35)
12	*m*-MeOPh	2.5:1	25	4	**1** (87)
13	*m*-MeOPh	2.5:1	50	4	**1** (86)
14	*p*-MeOPh	2.5:1	25	4	**1** (90)
15	*p*-MeOPh	2.5:1	50	4	**1** (87)

[a] Conditions: 30 mg of $C_{60}HBn$ (37 μmol) was added to a mixture of ArCN (10 mL) and ODCB (*o*-dichlorobenzene, 20 mL). The mixture was stirred for 15 min at the preset temperature under argon. Then a suitable amount of tetra-*n*-butylammonium hydroxide (TBAOH, 1.0 M in MeOH) was added, and the mixture was stirred for 40 min before adding I_2 (2.5 equiv). The mixture was then stirred for 1 or 4 h. [b] The time after I_2 was added. [c] Isolated yield.

or 50 °C (entries 1 and 5), which is in agreement with previous results on the reaction of $C_{60}HR$ with a strong base.[6b,c] As the molar ratio of OH^- to $C_{60}HBn$ was increased to 2.5:1, a significant amount of **2a** was obtained when the reaction was carried out at 25 °C (entries 2 and 3), while a significant amount of **3a** was obtained if the reaction was carried out at 50 °C (entries 6 and 7), where different reaction times (1 or 4 h) were used. A further increase of the molar ratio of OH^- and $C_{60}HBn$ to 5:1 results in a complex mixture at either 25 or 50 °C (entries 4 and 8), likely containing further derivatized products which are inseparable under the experimental conditions. The yield of **2a** or **3a** was not significantly improved by prolongation of the reaction time (entries 3 and 7). It is interesting to note that $C_{60}HR$ and PhCN may be involved in a different reaction with the formation of imino C_{60} derivatives when KO^tBu and trimethylsilylmethyl triflate are present, where KO^tBu functions exclusively as a base to deprotonate $C_{60}HR$.[5b] The aromatic nitriles *m*-ClPhCN, *m*-MeOPhCN, and *p*-MeOPhCN were also examined under similar conditions for **2a** and **3a**. It was found that *m*-ClPhCN is capable of similar reactions for a prolonged reaction time by producing **2b** and **3b** with a yield comparable to that of **2a** and **3a** (entries 10 and 11). In contrast, no oxazolinated or imidazolinated dimeric product was obtained when *m*-MeOPhCN or *p*-MeOPhCN was used (entries 12−15), suggesting that aromatic nitriles with electron-withdrawing groups are favored for the reaction.

ESI (electrospray ionization) HRMS of **2a** and **3a** shows the protonated molecular ions ($[M + H]^+$) at *m*/*z* 1742.15437 and 1845.19286, respectively (Figures S2 and S14, Supporting Information), in agreement with the assigned structures (**2a**, $C_{141}H_{20}NO^+$ calcd *m*/*z* 1742.15394; **3a**, $C_{148}H_{25}N_2O^+$ calcd *m*/*z* 1845.19614). Figure 1 displays the expanded ^1H NMR spectra of **2a** and **3a**, where eight doublets arising from the methylene protons of the benzyls are shown for each compound. With the help of COSY and HMBC NMR (Figures S5 and S6 for **2a** and Figures S17 and S18 for **3a**; Supporting Information), the eight doublets can be grouped into four sets of AB quartets, as labeled in Figure 1. The appearance of eight doublets indicates the presence of eight diastereotopic methylene protons for **2a** and **3a**, respectively, suggesting that only one of the C_{60} cages in the dimer molecule is derivatized,

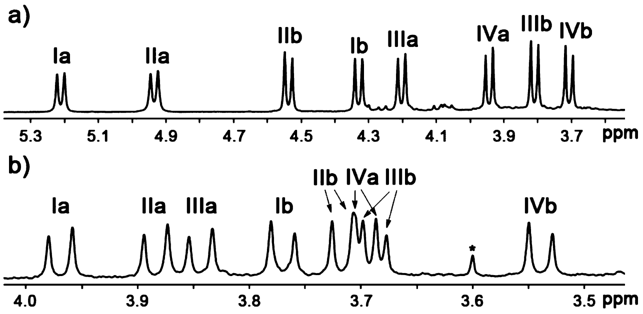


Figure 1. ^1H NMR (600 MHz) spectra of (a) **2a** and (b) **3a** recorded in CS_2 with DMSO-d_6 as the external lock. The peak labeled with an asterisk is due to an unknown impurity.

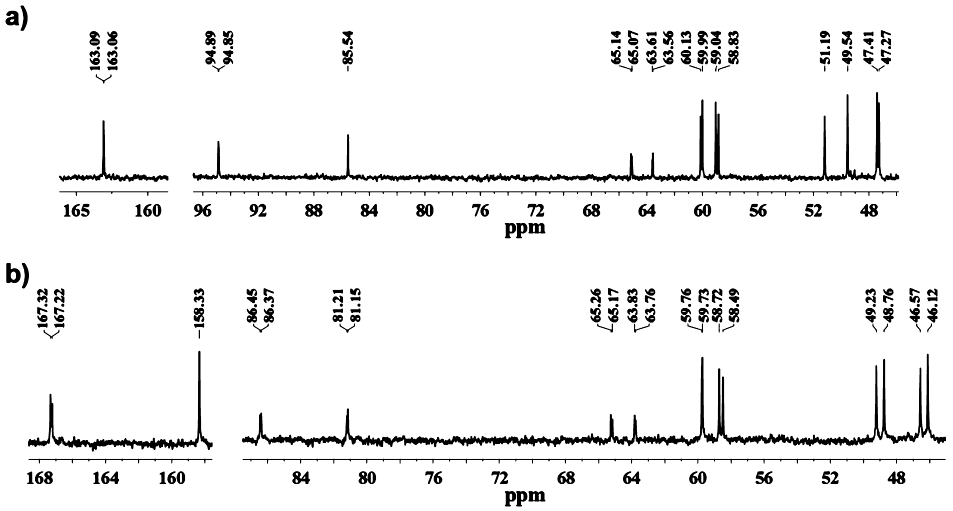


Figure 2. Expanded ^{13}C NMR spectra (150 MHz) showing the sp^3, C=O and C=N carbons for (a) **2a** and (b) **3a** recorded in CS_2 with DMSO-d_6 as the external lock.

as both **2a** and **3a** are composed of the meso and racemic regioisomers due to the 1,4-addition pattern of the dimers.[6,12]

Aromatic protons arising from the phenyls are also shown in the ^{1}H NMR spectra of **2a** and **3a** (Figures S3 and S15, Supporting Information). Typically for fullerene oxazolines and imidazolines, the phenyl ring of the heterocycle exhibits a doublet resonance in the most downfield region.[1−3] The appearance of two sets of closely positioned doublets (**2a**, 7.70 and 7.64 ppm; **3a**, 7.27 and 7.25 ppm) in the most downfield region of the respective ^{1}H NMR spectra confirms the presence of two regioisomers for each product, and the integrated area ratio of the phenyl protons to the methylene protons is 15:4 for **2a** and 20:4 for **3a**, demonstrating explicitly that only one of the carbon cages in each respective regioisomer is derivatized.

The ^{13}C NMR spectrum of **2a** (Figure 2a) shows four resonances at 51.19, 49.54, 47.41, and 47.27 ppm for the methylene carbon atoms of the benzyls, four resonances at 60.13, 59.99, 59.04, and 58.83 ppm due to the sp^3 C_{60} carbons bonded to the benzyls, and four resonances at 65.14, 65.07, 63.61, and 63.56 ppm from the sp^3 C_{60} carbons bonded to the C_{60}Bn group. The exhibited chemical shifts are consistent with the signals reported for the respective carbon atoms of **1**.[6] In addition, two resonances due to the sp^3 C_{60} carbons bonded to the oxygen atom are shown at 94.89 and 94.85 ppm, consistent with the presence of the meso and racemic isomers, while only one signal is shown at 85.54 ppm for the sp^3 C_{60} carbons bonded to the nitrogen atom, probably due to the incidental overlapping of the signals for the meso and racemic isomers. Resonances due to the imine carbons of the oxazoline appear at 163.09 and 163.06 ppm, and a total of 135 peaks is shown for the sp^2 carbons of the C_{60} skeleton, consistent with the structural assignment of **2a**.[1,3,16]

Similar to the case for compound **2a**, the ^{13}C NMR spectrum of **3a** (Figure 2b) also shows four resonances for the methylene carbons at 49.23, 48.76, 46.57, and 46.12 ppm, four resonances at 59.76, 59.73, 58.72, and 58.49 ppm for the sp^3 C_{60} carbons bonded to the benzyls, and four resonances at 65.26, 65.17, 63.83, and 63.76 ppm for the sp^3 C_{60} carbon atoms bonded to the other C_{60} cage, suggesting the presence of meso and racemic isomers for compound **3a** and also similar addition patterns for **2a** and **3a**. Resonances due to the sp^3 C_{60} carbons bonded to heteroatoms appear at 86.45, 86.37, 81.21, and 81.15 ppm, which are significantly different from those of oxazoline heterocycles[1,3,16] but are similar to those of imidazoline heterocycles.[2,16d,17] Resonances arising from the carbonyls appear at 167.32 and 167.22 ppm, while the imine carbon atoms appear at 158.33 ppm. The results along with the ^{1}H NMR and HRMS therefore explicitly show that **3a** is a singly bonded C_{60} dimer in which one C_{60} cage is imidazolinated and consists of the meso and racemic regioisomers.

The structures of **2a** and **3a** were further examined with UV−vis spectroscopy, since the absorptions are quite sensitive toward the structure rather than the type of addend.[18] The spectra of **2a** and **3a** (Figures S7 and S19, Supporting Information) are very similar to those of 1,2,4,15-C_{60} adducts,[1,3,6b,19] suggesting that the addends are likely positioned with a 1,2,4,15-conformation in **2a** and **3a**, which is a favored configuration for C_{60} derivatives involving both 1,2- and 1,4-additions.[1,3,6b,19] The 1,2,4,15-configuration of **2a** is further supported by the chemical shifts of the sp^3 C_{60} carbons bonded to the oxygen and nitrogen atoms (~94.8 and 85.54 ppm), which are comparable to the values of the respective carbons for the C_{60} oxazoline compound with a 1,2,4,15-configuration (96.55 and 84.49 ppm)[3] but deviate greatly from the values of the respective carbons of a compound with a 1,2,3,4-configuration (98.0 and 91.5 ppm).[16a] In addition, as is shown in the HBMC NMR of **2a** and **3a** (Figures S6 and S18, Supporting Information), no correlation peak is observed for the methylene protons of the benzyls with any sp^3 C_{60} carbon atoms bonded to either the heteroatoms or C_{60} cages, consistent with the assigned structures of the compounds.

However, there are still questions regarding the location and the orientation of the heterocycle in **2a** and **3a**. Before probing further into such issues, it is necessary to first obtain a better understanding of the reaction mechanism. Figure 3 shows the in situ vis−near-IR spectra for the reaction of 1,2-H($PhCH_2$)-C_{60} with TBAOH, PhCN, and I_2. The brownish solution of 1,2-H($PhCH_2$)C_{60} turned dark green immediately after TBAOH (1.0 M in MeOH) was added, accompanied by the appearance of strong absorption bands at 659 and 995 nm (Figure 3), which are the typical absorptions for RC_{60}^-,[1,6a,22] indicating that $PhCH_2C_{60}^-$ was produced via the abstraction of a fullerenyl proton by OH^-. The spectral features of the mixture remained essentially unchanged before adding I_2, suggesting

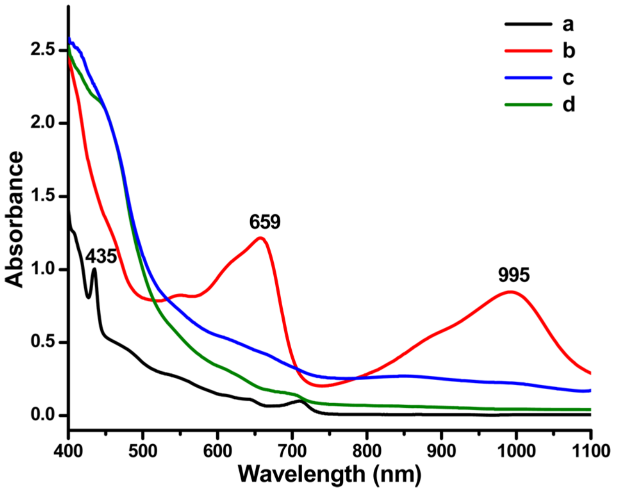


Figure 3. Vis−near-IR spectra of (a) 1,2-H($PhCH_2$)C_{60} (2.5 × 10^{-4} M), (b) reaction mixture of 1,2-H($PhCH_2$)C_{60} with TBAOH (2.5 equiv), (c) immediately after adding I_2 (2.5 equiv) into the mixture of 1,2-H($PhCH_2$)C_{60} with TBAOH, (d) after addition of I_2 for 1 h. The spectra were recorded in PhCN/ODCB (1/2 v/v) under deaerated conditions at 25 °C.

that $PhCH_2C_{60}^-$ is rather stable in the presence of OH^- and is unlikely to undergo an OH^--initiated nucleophilic addition reaction probably due to the electron-rich nature of the species. Instead, the absorption bands at 659 and 995 nm disappeared quickly after I_2 was added, accompanied by the formation of heterocyclic C_{60} derivatives, suggesting that compounds **2** and **3** are likely formed via the oxazolination and imidazolination of **1** directly, since **1** is formed with the removal of the negative charge from $(PhCH_2)C_{60}^-$ by I_2, and it would be unlikely to decompose into $PhCH_2C_{60}^\bullet$ fragments at relatively low temperature in the presence of I_2.[6]

Previous work on the OH^--initiated oxazolination of 1,4-$(PhCH_2)_2C_{60}$ has shown that the 1,2,4,15-adduct is formed by first undergoing a nucleophilic addition of OH^- at the *para* carbon with respect to the existing benzyl, since it would form a stable 10π indenyl anion intermediate;[3,20] this is then followed by a charge-mediated nitrogen/oxygen rearrangement,[3,21] retaining the same 10π indenyl anion configuration and resulting in the nitrogen atom bonded to the *para* carbon atom with respect to the existing benzyl in the final product. As for the imidazolination reaction of fullerenes, this reaction also proceeds by a nucleophilic addition pathway, but no rearrangement of the heterocycle occurs as only monoanionic intermediates are involved, where the anionic charge is located at the imine carbon atom and the imine nitrogen atom is therefore bonded to the carbon atom of the initial attack.[2] It is therefore rational that the same regioselectivity should be followed for the oxazolination and imidazolination of **1**, since **1** can be considered as a 1,4-adduct of C_{60} with benzyl and $C_{60}Bn$ as the addends. However, in principle, there should exist two different *para* carbons (C1 and C30 in Figure 4) with respect to the existing benzyl and $C_{60}Bn$ addends, while in fact only one carbon atom is selected for the reaction, as the results indicate. Due to the nature of nucleophilic additions, the amount of positive charge at the *para* carbon atom with respect to the existing addends is of importance for the regioselectivity. A NBO (natural bond orbital) charge analysis at the HF (Hartree-Fock)/6-311G(d) level predicts that the *para* carbon atom with respect to the benzyl in **1** (C1) has a much greater positive charge than the counterpart carbon atom with respect to the $C_{60}Bn$ addend (C30), with a value of 0.032 vs 0.008 for the meso isomer and 0.030 vs 0.012 for the racemic isomer, as shown in Figure 4 (see Figure S25 in Supporting Information for the full NBO charge distribution), implying that the *para* carbon with respect to the benzyl group is likely the preferable site for the nucleophilic additions that eventually result in the oxazolinated and imidazolinated products of **1**. Consequently, C1 in Figure 4 should be the carbon atom bonded to the nitrogen atom via the nitrogen/oxygen rearrangement in **2**,[3] and it should also be the carbon atom bonded to the imine nitrogen in **3** with the structures shown in Scheme 1. In a similar way, the structures of **2b** and **3b** have also been established, even though the signals of the sp^3 carbons bonded to the heteroatoms and C_{60} for **3b** are missing in the ^{13}C NMR probably due to the weak nature of such signals.[2]

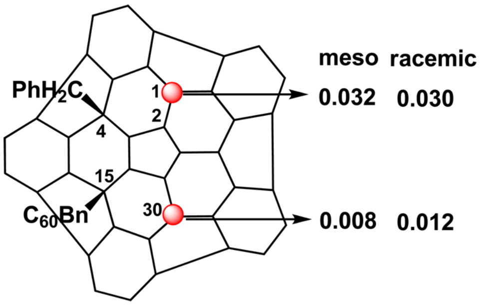


Figure 4. NBO charge distributions for the *para* carbons with respect to the existing addends in dimer **1**. The *para* carbon atom with respect to the benzyl has a much greater positive charge than the counterpart carbon atom with respect to the $C_{60}Bn$ addend.

The exhibited regioselectivities for compounds **2** and **3** are consistent with a recent report on the regioselective [2 + 2] cycloaddition of $RC_{60}-C_{60}R$ dimers with alkynes, where only one of the two C_{60} cages is derivatized with a specific 1,2,4,15-configuration[15] and the cyclobutene is located selectively on the side of the small R group, rather than on the side of the bulky C_{60} group. Notably, a "cleavage−recombination" mechanism has been proposed to account for the reaction of $RC_{60}-C_{60}R$ with alkynes,[15] as the reaction was carried out at high temperature, which may induce the decomposition of the dimer molecule into $RC_{60}^\bullet$.[12d] As for the current work, since it was carried out at a relatively low temperature, it is possible that the dimeric molecule remained intact during the oxazolination and imidazolination reaction, especially when I_2 was present. A control experiment was therefore performed following procedures similar to those when 1,2-H($PhCH_2$)C_{60} was used, except **1** was used as the starting material. Impressively, a much lower yield of **2a** was obtained (7%). Such a difference is probably caused by the poor solubility of the fullerene dimer that has been isolated from the solution and the relatively good solubility for the in situ generated $PhCH_2C_{60}-C_{60}CH_2Ph$ dimer, similar to the situation for other fullerene derivatives.[23] No such problem would be encountered if $RC_{60}^\bullet$ were involved, since $RC_{60}^\bullet$ is expected to have a much better solubility than $PhCH_2C_{60}-C_{60}CH_2Ph$, due to the presence of only one C_{60} cage in the species. The results therefore indicate that it is $PhCH_2C_{60}-C_{60}CH_2Ph$ rather than the $PhCH_2C_{60}^\bullet$ fragment that is involved in the oxazolination or imidazolination reaction.

NBO calculations at the HF/6-311G(d) level with Gaussian09 further support that $PhCH_2C_{60}^\bullet$ is not involved in the reaction. The results predict that the *ortho* carbon ([6,6]-bond) possesses a greater positive charge (0.086) than the *para* carbon (0.024) with respect to the benzyl (Figure 5; see Figure S26 in the Supporting Information for a full NBO analysis), suggesting that the oxazolination would likely engage the *ortho* carbon if $PhCH_2C_{60}^{\bullet}$ were involved. Since the placing of the oxazolino heterocycle next to the benzyl group is feasible, as evidenced by the formation of 1,4-dibenzyl-2,3-oxazolino C_{60} with the *cis*-**1** configuration,[16a] the absence of such a configuration confirms that $PhCH_2C_{60}^{\bullet}$ is unlikely to be engaged in the derivatization reaction of **1** under the conditions of the current work.

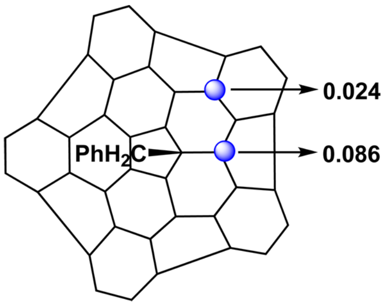


Figure 5. NBO charge distribution for the *ortho* ([6,6]-bond) and *para* carbons with respect to the benzyls in $PhCH_2C_{60}^{\bullet}$. The *ortho* carbon possesses a greater positive charge than the *para* carbon with respect to the benzyl.

A reaction mechanism is therefore proposed and is shown in Scheme 2. The key point is that the singly bonded dimer **1** is involved in the nucleophilic addition, rather than the $PhCH_2C_{60}^{\bullet}$ subunit. The use of I_2 is crucial, since it acts as an oxidant to remove the negative charge of $PhCH_2C_{60}^{-}$ to form **1**.[6,12] The mechanism for oxazolination or imidazolination of the individual carbon cage of the dimer is in general similar to that when monomeric fullerene species are used.[1−3] It is noteworthy for the oxazolination process that the possession of a negative charge on the fullerene carbon cage is crucial for the formation of the key reaction intermediate $^{-}O{-}BnC_{60}^{-}{-}C_{60}Bn$ (**A**), which is required to initiate the nucleophilic attack to the aromatic nitriles. However, previous work has shown that I_2 can readily remove the negative charge from the fullerene carbon cage;[1,3] the results therefore indicate that the formation of the $^{-}O{-}BnC_{60}^{-}{-}C_{60}Bn$ intermediate by the reaction of OH^{-} with dimer **1** is a very fast step, as is the subsequent attack of $^{-}O{-}BnC_{60}^{-}{-}C_{60}Bn$ at aromatic nitriles followed by a N/O rearrangement to form the open-structured dianionic C_{60} oxazoline intermediate, in comparison to electron removal from the carbon cage by I_2. As for the imidazolination reaction, since no anionic fullerene initiated nucleophilic reactions are required, it would not be necessary to require a fast rate for the reaction of amidine anion with dimer **1**. Instead, the removal of the negative charge from intermediate **B**, which is necessary for the subsequent ring-closure reaction, is achieved likely by the I_2 oxidation rather than charge transfer to the neutral fullerene counterpart, as is the case when there is no other oxidant.[2]

CONCLUSION

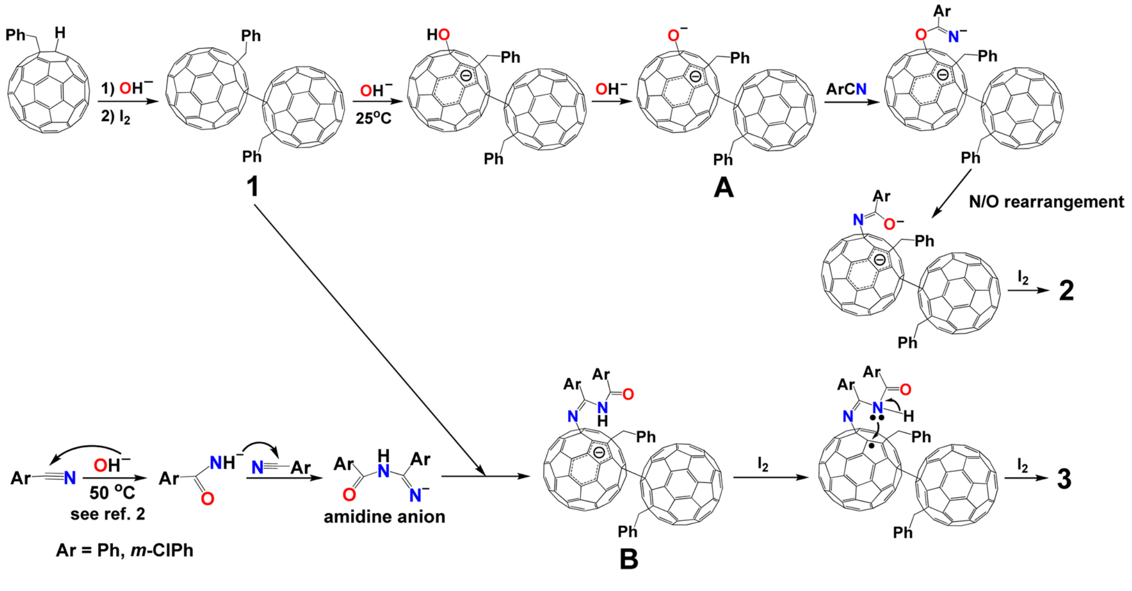
Derivatization of the singly bonded C_{60} dimers has been achieved via a one-pot reaction of $C_{60}HBn$ with OH^{-} and aromatic nitriles in the presence of I_2, where OH^{-} functions as both a Brønsted base and a nucleophile that initiates the heterocyclic addition to the fullerene cage. The result has demonstrated that C_{60} dimer derivatives can be obtained with the use of the more readily available $C_{60}HBn$ instead of the less available dimer compounds and offers a new approach for derivatization of fullerene dimers. In addition, the results indicate that, in addition to the "cleavage−recombination" mechanism, it is possible that the singly bonded fullerene dimer may be derivatized directly.

EXPERIMENTAL SECTION

General Methods. All reagents were obtained commercially and used without further purification, unless otherwise specified. PhCN was distilled over P_2O_5 under vacuum at 305 K prior to use. No data on the melting point of the products could be obtained, since the compounds decompose before reaching the melting point.

Preparation of Compound 2a with 1,2-H(PhCH$_2$)C$_{60}$. Typically, 30 mg of $1{,}2\text{-}H(PhCH_2)C_{60}$ (37 μmol) was added to a

Scheme 2. Proposed Mechanism for the Formation of 2 and 3 Starting from $C_{60}HBn$



mixture of PhCN (10 mL) and ODCB (20 mL), which was degassed with argon for 15 min with vigorous stirring at room temperature. Then 2.5 equiv of TBAOH (1.0 M in methanol, 92 μL) was added to the solution. The solution changed instantly from brown-yellow to dark green. Then 2.5 equiv of I_2 (23 mg, 92 μmol) was added after 40 min and the reaction was allowed to proceed for 1 h. The mixture was dried with a rotary evaporator under reduced pressure. The residue was washed with methanol to remove excess TBAOH and I_2. The crude product was put into toluene, and the soluble part was purified using a semipreparative Buckyprep column (10 mm × 250 mm) eluted with toluene at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compound **2a** was obtained as a solid with an isolated yield of 29% (9.3 mg), along with 2.0 mg of **1** and 1.2 mg of **3a**.

Control Experiment for Preparing 2a with $PhCH_2C_{60}$–$C_{60}CH_2Ph$. Typically, 20 mg of $PhCH_2C_{60}$–$C_{60}CH_2Ph$ (**1**) (12 μmol) was put into mixture of PhCN (8 mL) and ODCB (16 mL), which was degassed with argon for 15 min under vigorous stirring at room temperature. Then 2.5 equiv of I_2 (8 mg, 24 μmol) and 2.5 equiv of TBAOH (1.0 M in methanol, 37 μL) was added to the solution. The reaction was allowed to proceed for 4 h. The mixture was dried with a rotary evaporator under reduced pressure. The residue was washed with methanol to remove excessive TBAOH and I_2. The crude product was put into toluene, and the soluble part was purified using a semipreparative Buckyprep column (10 mm × 250 mm) eluted with toluene at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compound **2a** was obtained as a solid with an isolated yield of 7% (1.6 mg).

*Spectral Characterizations of Compound **2a**.* Positive ESI FT-ICR MS: m/z calculated for $C_{141}H_{20}NO^+$ $[M + H]^+$ 1742.15394, found 1742.15437. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6): δ 7.70 (d, 2H), 7.64 (d, 2H), 7.47 (d, 2H), 7.36 (d, 2H), 7.25–7.17 (m, 3H), 7.15 (t, 2H), 7.10 (t, 3H), 7.07–7.02 (m, 3H), 7.00 (d, 1H), 6.99–6.95 (m, 3H), 6.88–6.81 (m, 5H), 6.80 (d, 2H), 4.77 ($\Delta\nu$ = 528.6 Hz, J_{AB} = 12.6 Hz), 4.74 ($\Delta\nu$ = 238.2 Hz, J_{AB} = 13.2 Hz), 4.07 ($\Delta\nu$ = 235.8 Hz, J_{AB} = 13.2 Hz), 3.83 ($\Delta\nu$ = 141.6 Hz, J_{AB} = 13.2 Hz). ^{13}C NMR (150 MHz, CS_2/DMSO-d_6): δ 163.09 (C=N), 163.06 (C=N), 156.20, 155.82, 153.84, 153.60, 153.53, 153.37, 153.00, 151.61, 151.49, 151.46, 151.33, 151.02, 150.15, 150.01, 149.99, 149.28, 148.74, 148.70, 148.54, 148.52, 148.49, 148.23, 148.17, 148.07, 148.04, 148.00, 147.90, 147.87, 147.75, 147.59, 147.53, 147.50, 147.40, 147.37, 147.33, 147.03, 146.99, 146.98, 146.87, 146.81, 146.60, 146.57, 146.54, 146.46, 146.42, 146.38, 146.35, 146.30, 146.23, 146.09, 146.02, 145.91, 145.83, 145.70, 145.54, 145.45, 145.43, 145.39, 145.08, 145.01, 144.98, 144.94, 144.82, 144.74, 144.71, 144.68, 144.65, 144.52, 144.48, 144.41, 144.37, 144.34, 144.26, 144.21, 144.17, 144.07, 144.04, 143.99, 143.89, 143.83, 143.76, 143.71, 143.70, 143.66, 143.58, 143.54, 143.48, 143.42, 143.30, 143.26, 143.22, 143.15, 142.92, 142.84, 142.75, 142.67, 142.60, 142.57, 142.48, 142.40, 142.32, 142.23, 142.21, 142.06, 142.03, 141.94, 141.91, 141.80, 141.75, 141.57, 141.52, 141.45, 141.36, 141.32, 141.25, 141.23, 141.17, 141.08, 140.56, 140.39, 140.11, 140.06, 139.11, 138.96, 138.53, 138.45, 138.22, 138.18, 138.07, 137.76, 137.74, 137.39, 137.27, 136.65, 135.07, 134.57, 134.52, 134.35, 134.26, 134.12, 133.29, 133.24, 131.59, 130.53, 130.38, 130.30, 130.21, 128.46, 127.99, 127.94, 127.80, 127.19, 127.06, 126.74, 126.01, 125.92, 94.89 (1C, sp^3, C_{60}–O), 94.85 (1C, sp^3, C_{60}–O), 85.54 (2C, sp^3, C_{60}–N), 65.14 (1C, sp^3, C_{60}–C_{60}), 65.07 (1C, sp^3, C_{60}–C_{60}), 63.61 (1C, sp^3, C_{60}–C_{60}), 63.56 (1C, sp^3, C_{60}–C_{60}), 60.13 (1C, sp^3, C_{60}–CH_2), 59.99 (1C, sp^3, C_{60}–CH_2), 59.04 (1C, sp^3, C_{60}–CH_2), 58.83 (1C, sp^3, C_{60}–CH_2), 51.19 (1C, CH_2), 49.54 (1C, CH_2), 47.41 (1C, CH_2), 47.27 (1C, CH_2). UV–vis (hexane): λ_{max}/nm 253, 355, 450.

Preparation of Compound 2b. The procedures were similar to those for the preparation of **2a**, except *m*-ClPhCN (10 g) was used instead of PhCN and the reaction was allowed to proceed for 4 h after the addition of I_2. Compound **2b** was obtained as a solid with an isolated yield of 33% (10.8 mg), along with 1.1 mg of **3b**.

*Spectral Characterizations of Compound **2b**.* Positive ESI FT-ICR MS: m/z calculated for $C_{141}H_{19}ClNO^+$ $[M + H]^+$ 1776.11497, found 1776.11703. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6): δ 7.84 (s, 1H), 7.80 (s, 1H), 7.66 (d, 1H), 7.59 (d, 1H), 7.51 (d, 2H), 7.40 (d, 2H), 7.30 (d, 1H), 7.26 (d, 1H), 7.18 (t, 2H), 7.15–7.01 (m, 8H), 6.96–6.87 (m, 6H), 6.86–6.79 (m, 2H), 5.24 (d, 1H), 5.00 (d, 1H), 4.60 (d, 1H,), 4.38 (d, 1H), 4.26 (d, 1H), 3.98 (d, 1H), 3.87 (d, 1H), 3.74 (d, 1H). ^{13}C NMR (150 MHz, CS_2/DMSO-d_6): δ 162.57 (C=N), 156.71, 156.32, 154.09, 154.00, 153.85, 153.73, 153.43, 152.07, 151.62, 151.43, 150.61, 150.52, 150.40, 149.85, 149.41, 149.28, 149.23, 149.11, 149.06, 148.96, 148.83, 148.73, 148.63, 148.59, 148.46, 148.43, 148.18, 148.01, 147.91, 147.85, 147.76, 147.54, 147.46, 147.40, 147.35, 147.17, 147.14, 147.10, 147.04, 146.94, 146.90, 146.84, 146.81, 146.79, 146.72, 146.66, 146.46, 146.36, 146.21, 146.12, 145.95, 145.91, 145.79, 145.69, 145.66, 145.61, 145.58, 145.56, 145.51, 145.38, 145.32, 145.29, 145.21, 145.18, 145.13, 145.02, 144.97, 144.93, 144.84, 144.77, 144.67, 144.65, 144.57, 144.52, 144.41, 144.32, 144.19, 144.16, 144.12, 144.08, 143.96, 143.86, 143.76, 143.67, 143.60, 143.52, 143.40, 143.35, 143.10, 142.95, 142.87, 142.78, 142.60, 142.50, 142.46, 142.36, 142.28, 142.17, 142.07, 142.01, 141.89, 141.83, 141.67, 141.61, 141.45, 141.28, 141.25, 141.18, 140.68, 140.52, 140.23, 139.23, 139.06, 138.61, 138.56, 138.29, 138.20, 137.84, 137.44, 137.35, 136.73, 134.71, 134.64, 134.57, 134.50, 134.28, 133.92, 133.39, 133.31, 131.71, 130.72, 130.54, 130.34, 130.23, 129.23, 128.49, 128.42, 128.08, 128.04, 127.93, 127.88, 127.30, 127.17, 126.84, 126.51, 95.22 (1C, sp^3, C_{60}–O), 85.50 (2C, sp^3, C_{60}–N), 65.21 (1C, sp^3, C_{60}–C_{60}), 65.12 (1C, sp^3, C_{60}–C_{60}), 63.70 (1C, sp^3, C_{60}–C_{60}), 63.66 (1C, sp^3, C_{60}–C_{60}), 60.26 (1C, sp^3, C_{60}–CH_2), 60.14 (1C, sp^3, C_{60}–CH_2), 59.17 (1C, sp^3, C_{60}–CH_2), 58.94 (1C, sp^3, C_{60}–CH_2), 51.15 (1C, CH_2), 49.55 (1C, CH_2), 47.55 (1C, CH_2), 47.42 (1C, CH_2). UV–vis (toluene): λ_{max}/nm 450.

Preparation of Compound 3a. Typically, 30 mg of 1,2-$H(PhCH_2)C_{60}$ (37 μmol) was added to a mixture of PhCN (10 mL) and ODCB (20 mL), which was degassed with argon for 15 min with vigorous stirring at 50 °C. Then 2.5 equiv of TBAOH (1.0 M in methanol, 92 μL) was added to the solution. The solution changed instantly from brown-yellow to dark green, and then 2.5 equiv of I_2 (23 mg, 92 μmol) was added after 40 min and the reaction was allowed to proceed for 1 h. The mixture was dried with a rotary evaporator under reduced pressure. The residue was washed with methanol to remove excess TBAOH and I_2. The crude product was put into toluene, and the soluble part was purified using a semipreparative Buckyprep column (10 mm × 250 mm) eluted with toluene at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compound **3a** was obtained as a solid with an isolated yield of 30% (10.2 mg), along with 1.8 mg of **2a** and 1 mg of **1**.

*Spectral Characterizations of Compound **3a**.* Positive ESI FT-ICR MS: m/z calculated for $C_{148}H_{25}N_2O^+$ $[M + H]^+$ 1845.19614, found 1845.19286. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6): δ 7.27 (d, 2H), 7.25 (d, 2H), 7.16 (d, 2H), 7.14 (d, 2H), 7.06–7.02 (m, 3H), 7.01–6.86 (m, 24H), 6.82–6.77 (m, 5H), 3.87 ($\Delta\nu$ = 119.4 Hz, J_{AB} = 13.2 Hz), 3.80 ($\Delta\nu$ = 97.5 Hz, J_{AB} = 12.6 Hz), 3.76 ($\Delta\nu$ = 93.3 Hz, J_{AB} = 12.6 Hz), 3.62 ($\Delta\nu$ = 94.2 Hz, J_{AB} = 12.6 Hz). ^{13}C NMR (150 MHz, CS_2/DMSO-d_6): δ 167.32 (C=O), 167.22 (C=O), 158.33 (C=N), 156.35, 156.00, 154.53, 154.35, 152.80, 152.73, 152.63, 152.56, 151.73, 151.71, 151.54, 151.32, 150.71, 149.82, 149.44, 148.88, 148.70, 148.63, 148.50, 148.47, 148.09, 148.01, 147.93, 147.83, 147.78, 147.74, 147.72, 147.59, 147.49, 147.35, 147.17, 147.05, 146.87, 146.80, 146.65, 146.60, 146.46, 146.42, 146.34, 146.22, 146.21, 146.14, 146.11, 146.06, 145.88, 145.65, 145.62, 145.54, 145.48, 145.41, 145.33, 145.03, 144.99, 144.91, 144.85, 144.71, 144.64, 144.52, 144.29, 144.23, 144.20, 144.11, 144.06, 144.01, 143.92, 143.87, 143.84, 143.79, 143.72, 143.65, 143.61, 143.55, 143.48, 143.41, 143.37, 143.33, 143.27, 143.22, 143.15, 143.10, 143.06, 143.03, 142.98, 142.78, 142.68, 142.63, 142.57, 142.47, 142.39, 142.32, 142.25, 142.21, 142.13, 141.90, 141.87, 141.81, 141.75, 141.74, 141.63, 141.61, 141.47, 141.41, 141.19, 141.00, 140.71, 140.56, 140.23, 140.09, 140.03, 139.66, 139.56, 139.35, 139.22, 139.14, 138.84, 138.57, 137.76, 137.67, 136.77, 135.68, 135.66, 134.58, 134.57, 134.51, 134.41, 134.34, 134.02, 133.37, 133.16, 132.08, 131.82, 131.25, 131.13, 130.30, 130.21, 130.15, 130.01, 129.58, 128.73, 128.51, 127.91, 127.79, 127.73, 127.61, 127.44, 127.25, 126.82, 126.79, 126.72, 86.45 (1C, sp^3, C_{60}–N=), 86.37 (1C, sp^3, C_{60}–N=), 81.21 (1C, sp^3, C_{60}–N–), 81.15 (1C, sp^3, C_{60}–N–), 65.26 (1C, sp^3, C_{60}–C_{60}), 65.17 (1C, sp^3, C_{60}–C_{60}), 63.83 (1C, sp^3, C_{60}–C_{60}), 63.76 (1C, sp^3, C_{60}–C_{60}), 59.76 (1C, sp^3, C_{60}–CH_2), 59.73 (1C, sp^3, C_{60}–CH_2), 58.72 (1C, sp^3, C_{60}–CH_2), 58.49

(1C, sp^3, C_{60}−CH_2), 49.23 (1C, CH_2), 48.76 (1C, CH_2), 46.57 (1C, CH_2), 46.12 (1C, CH_2). UV−vis (hexane): λ_{max}/nm: 253, 355,450.

Preparation of Compound 3b. The procedures were similar to those for preparation of **3a**, except *m*-ClPhCN (10 g) was used instead of PhCN and the reaction was allowed to proceed for 4 h after the addition of I_2. Compound **3b** was obtained as a solid with an isolated yield of 35% (12.4 mg), along with 1.5 mg of **2b** and 1.2 mg of **1**.

*Spectral Characterizations of Compound **3b**.* Positive ESI FT-ICR MS: *m*/*z* calculated for $C_{148}H_{23}Cl_2N_2O^+$ [M + H]$^+$ 1913.11820, found 1913.11862. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6): δ 7.26 (s, 1H), 7.25 (s, 1H), 7.18−6.87 (m, 32H), 6.82−6.78 (m, 2H), 3.95 (d, 1H), 3.85 (d, 2H), 3.75 (d, 1H), 3.69 (d, 1H), 3.61 (d, 2H), 3.51 (d, 1H). ^{13}C NMR (125 MHz, CS_2/DMSO-d_6): δ 166.04 (C═O), 165.96 (C═O), 157.13 (C═N), 156.84, 156.51, 154.84, 154.66, 153.15, 153.11, 152.53, 152.33, 152.08, 152.04, 151.69, 151.06, 150.22, 150.03, 150.01, 149.47, 149.22, 149.13, 149.10, 149.07, 148.78, 148.68, 148.63, 148.59, 148.36, 148.28, 148.21, 148.17, 148.10, 148.02, 147.97, 147.77, 147.74, 147.71, 147.58, 147.34, 147.29, 147.22, 147.18, 147.12, 147.04, 146.99, 146.86, 146.83, 146.81, 146.76, 146.74, 146.72, 146.68, 146.63, 146.48, 146.45, 146.42, 146.16, 146.12, 146.09, 146.08, 146.00, 145.81, 145.73, 145.62, 145.57, 145.54, 145.51, 145.50, 145.44, 145.25, 145.14, 145.09, 145.07, 145.06, 144.84, 144.82, 144.79, 144.75, 144.57, 144.56, 144.44, 144.37, 144.27, 144.25, 144.21, 144.19, 144.17, 144.12, 144.03, 143.98, 143.96, 143.90, 143.76, 143.69, 143.67, 143.61, 143.59, 143.56, 143.38, 143.34, 143.28, 143.22, 143.20, 143.15, 143.04, 142.97, 142.93, 142.82, 142.80, 142.77, 142.71, 142.53, 142.50, 142.48, 142.44, 142.40, 142.34, 142.30, 142.27, 142.17, 142.09, 142.03, 141.95, 141.77, 141.62, 141.59, 141.32, 141.30, 141.27, 141.06, 140.82, 140.68, 140.62, 140.30, 139.98, 139.89, 139.60, 139.56, 139.46, 139.18, 138.24, 138.19, 138.13, 137.30, 136.41, 136.22, 136.19, 136.16, 135.10, 135.08, 134.90, 134.76, 134.68, 134.62, 134.50, 133.69, 133.46, 132.82, 132.56, 132.30, 131.86, 131.72, 130.79, 130.71, 130.68, 130.55, 130.35, 129.41, 129.27, 129.11, 129.05, 128.71, 128.39, 128.33, 128.16, 127.53, 127.48, 127.36, 127.30, 126.68, 126.48, 126.14, 126.11, 60.32 (1C, sp^3, C_{60}−CH_2), 60.28 (1C, sp^3, C_{60}−CH_2), 59.23 (1C, sp^3, C_{60}−CH_2), 59.00 (1C, sp^3, C_{60}−CH_2), 49.78 (1C, CH_2), 49.33 (1C, CH_2), 47.29 (1C, CH_2), 46.83 (1C, CH_2). UV−vis (toluene): λ_{max}/nm 450.

Computational Methods. The geometries of **1** and $PhCH_2C_{60}^{\bullet}$ were optimized with Gaussian09 at the Hartree−Fock (HF) level with the 3-21G basis set, followed by harmonic frequency calculations at the same level to confirm them as the energy minima. The NBO charge distribution calculations were performed with Gaussian09 at the HF/6-311G(d) level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and tables giving HPLC traces, spectra of the new compounds, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chang, W.-W.; Li, Z.-J.; Yang, W.-W.; Gao, X. *Org. Lett.* **2012**, *14*, 2386−2389.

(2) Hou, H.-L.; Li, Z.-J.; Li, S.-H.; Chen, S.; Gao, X. *Org. Lett.* **2013**, *15*, 4646−4949.

(3) Li, Z.-J.; Li, F.-F.; Li, S.-H.; Chang, W.-W.; Yang, W.-W.; Gao, X. *Org. Lett.* **2012**, *14*, 3482−3485.

(4) (a) Niyazymbetov, M. E.; Evans, D. H.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093−13098. (b) Jousselme, B.; Sonmez, G.; Wudl, F. *J. Mater. Chem.* **2006**, *16*, 3478−3482.

(5) (a) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946−5952. (b) Matsuo, K.; Matsuo, Y.; Iwashita, A.; Nakamura, E. *Org. Lett.* **2009**, *11*, 4192−4194.

(6) (a) Yang, W.-W.; Li, Z.-J.; Gao, X. *J. Org. Chem.* **2011**, *76*, 6067−6074. (b) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086−8089. (c) Lu, S.; Jin, T.; Bao, M.; Yamamoto, Y. *Org. Lett.* **2012**, *14*, 3466−3469.

(7) Segura, J. L.; Martín, N. *Chem. Soc. Rev.* **2000**, *29*, 13−25.

(8) Sánchez, L.; Sierra, M.; Martín, N.; Guldi, D. M.; Wienk, M. W.; Janssen, R. A. J. *Org. Lett.* **2005**, *7*, 1691−1694.

(9) Martin, C. A.; Ding, D.; Sørensen, J. K.; Bjørnholm, T.; van Ruitenbeek, J. M.; van der Aznt, H. S. J. *J. Am. Chem. Soc.* **2008**, *130*, 13198−13199.

(10) Delgado, J. L.; Espíldora, E.; Liedtke, M.; Sperlich, A.; Rauh, D.; Baumann, A.; Deibel, C.; Dyakonov, V.; Martín, N. *Chem. Eur. J.* **2009**, *15*, 13474−13482.

(11) Liu, J.; Guo, X.; Qin, Y.; Liang, S.; Guo, Z.-X.; Li, Y. *J. Mater. Chem.* **2012**, *22*, 1758−1761.

(12) (a) Tanaka, T.; Komatsu, K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1671−1676. (b) Cheng, F.; Murata, Y.; Komatsu, K. *Org. Lett.* **2002**, *4*, 2541−2544. (c) Zhang, T.-H.; Lu, P.; Wang, F.; Wang, G.-W. *Org. Biomol. Chem.* **2003**, *1*, 4403−4407. (d) Wang, G.-W.; Wang, C. Z.; Zhu, S. E.; Murata, Y. *Chem. Commun.* **2011**, *47*, 6111−6113.

(13) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005.

(14) (a) Fujiwara, K.; Komatsu, K. *Chem. Commun.* **2001**, 1986−1987. (b) Komatsu, K.; Fujiwara, K.; Tanaka, T.; Murata, Y. *Carbon* **2000**, *38*, 1529−1534. (c) Knol, J.; Hummelen, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 3226−3227. (d) Fujiwara, K.; Komatsu, K.; Wang, G.-W.; Tanaka, T.; Hirata, K.; Yamamoto, K.; Saunders, M. *J. Am. Chem. Soc.* **2001**, *123*, 10715−10720.

(15) Xiao, Z.; Matsuo, Y.; Maruyama, M.; Nakamura, E. *Org. Lett.* **2013**, *15*, 2176−2178.

(16) (a) Zheng, M.; Li, F.-F.; Ni, L.; Yang, W.-W.; Gao, X. *J. Org. Chem.* **2008**, *73*, 3159−3168. (b) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417−6420. (c) Takeda, Y.; Enokijima, S.; Nagamachi, T.; Nakayama, K.; Minakata, S. *Asian J. Org. Chem.* **2013**, *2*, 91−97. (d) Yang, H.-T.; Liang, X. -C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650−4653.

(17) He, C.-L.; Liu, R.; Li, D.-D.; Zhu, S.-E.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 1532−1535.

(18) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492−5502.

(19) (a) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *122*, 563−570. (b) Nambo, M.; Wakamiya, A.; Yamaguchi, S.; Itami, K. *J. Am. Chem. Soc.* **2009**, *131*, 15112−15113.

(20) (a) Sawamura, M.; Toganoh, M.; Suzuki, K.; Hirai, A.; Iikura, H.; Nakamura, E. *Org. Lett.* **2000**, *2*, 1919−1921. (b) Toganoh, M.; Suzuki, K.; Udagawa, R.; Hirai, A.; Sawamura, M.; Nakamura, E. *Org. Biomol. Chem.* **2003**, *1*, 2604−2611.

(21) Ni, L.; Yang, W.-W.; Li, Z.-J.; Wu, D.; Gao, X. *J. Org. Chem.* **2012**, *77*, 7299−7306.

(22) (a) Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077−5090. (b) Liu, R.; Li, F.; Xiao, Y.; Li, D.-D.; He, C.-L.; Yang, W.-W.; Gao, X.; Wang, G.-W. *J. Org. Chem.* **2013**, *78*, 7093−7099.

(23) (a) Taylor, R. *J. Fluorine Chem.* **2004**, *125*, 359−368. (b) Darwish, A. D.; Birkett, P. R.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Fullerene Sci. Technol.* **1997**, *5*, 705−726.