One-pot Synthesis of Indolino[2′,3′:1,2][60]fullerenes from Fullerene Epoxide: Lewis Acid-assisted Nucleophilic Addition Followed by Intramolecular Cyclization

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An efficient one-pot method for the synthesis of indolino[2′,3′:1,2][60]fullerene derivatives was developed, in which the formation and cyclization of a β-amino alcohol intermediate by the nucleophilic reaction of fullerene epoxide with aromatic amines was promoted in the presence of aprotic heterogeneous catalysts.

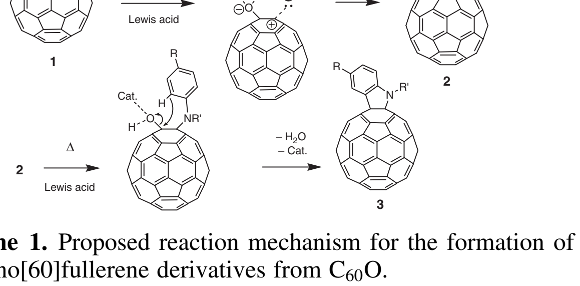
Fullerenes exhibit anomalous physicochemical properties by characteristics such as high electron affinity, widely expanded π-conjugation, rigid spherical skeleton, and steric limitations. To improve the availability of fullerenes for various applications, many effective methods for fullerene functionalization for preparing the intended fullerene derivatives have been reported.[1] The endowment of characteristics such as excellent solubility and controlled redox potentials enhances the commercial value of fullerenes. Such functionalization is worthy of consideration in advanced research toward industrial materials. The simplification of the synthesis procedures for fullerene derivatives is also required for reducing the manufacturing cost. In particular, the high regioselectivity of reaction sites onto fullerene cages by the addition of functional groups is extremely important. We recently observed the substitution of fullerene epoxides $C_{60}O_n$ from the viewpoint of regioselective functionalization. We reported that regioselective pure mono- or di-functionalized fullerenes could be transformed efficiently from the corresponding fullerene epoxides.[2] These results demonstrate that even poly-functionalized fullerene derivatives can be manufactured on a large scale.

A number of indoline compounds have been known to exhibit useful pharmaceutical,[3] and photovoltaic properties.[4] As a general rule, such organic functional compounds are required to be durable and stable. For instance, the indoline dyes in dye-sensitized organic solar cells (OSCs) require increased weathering durability. Indolino[60]fullerene derivatives in which a fullerene moiety is attached to an indoline ring are very stable. However, the direct formation of C_{60}-fused indoline compounds has been scarcely explored, and numerous cycloaddition reactions using amino compounds are utilized in the functionalization of fullerenes, including the Prato reaction.[5] Previously, we reported the reaction of carbonyl compounds with $C_{60}O$ (**1**) to give C_{60}-fused 1,3-dioxolane compounds in the presence of a Lewis acid catalyst. Therefore, in accordance with our previous results,[2] we hypothesized that the reaction of $C_{60}O$ with aniline would give anilinohydroxyl- and/or dianilino fullerene derivatives. However, the reaction between $C_{60}O$ and 4-dodecylaniline with Montmorillonite K10 as a Lewis acid catalyst in chlorobenzene unexpectedly gave a C_{60}-fused indoline compound. In this paper, we report the one-pot synthesis of C_{60}-fused indolines from $C_{60}O$ and various amine compounds. The reaction mechanism is also discussed in reference to characterization.

Our studies were initiated by heating a suspension of fullerene oxide, $C_{60}O$ (100 mg) and 4-dodecylaniline (355 mg) in chlorobenzene at 100 °C in the presence of Montmorillonite K10 (2.0 g). On processing, the reaction mixture afforded a product in 56.7% yield, which was characterized as 5′-dodecylindolino[2′,3′:1,2]-1,2-dihydro[60]fullerene (**3a**) (75 mg).

The product was characterized on the basis of spectroscopic data. The ^{1}H NMR spectrum of **3a** shows three peaks corresponding to aromatic protons, while the ^{13}C NMR spectrum shows thirty-six peaks corresponding to the sp^2 carbons of the fullerene cage and indoline moiety and two peaks corresponding to the two quaternary carbons of the fullerene cage. The atmospheric pressure photochemical ionization (APPI) mass spectrum of **3a** shows a molecular ion peak at m/z 979, which corresponds to $C_{60}O$ (MW 736) and 4-dodecylaniline (MW 261)–H_2O (MW 18). These results indicate that **3a** has an indoline moiety fused with the 6–6 bond of the C_{60} cage, and the fullerene cage of **3a** has quasi-C_s symmetry.

In order to elucidate the reaction mechanism, the progress of the reaction was followed by high-pressure liquid chromatography coupled with mass spectrometry. In this investigation, it was confirmed that the indolino[60]fullerene was formed as a result of two continuous steps. The first step was the formation of the intermediate, 1-anilino-2-hydroxy-1,2-dihydro[60]fullerenes (**2**) by the nucleophilic addition of anilines to **1** in the presence of a Lewis acid compound. The second step was the formation of an indoline moiety from **2**. We could directly observe the conversion from **2** to **3** (Figure S5, see Supporting Information).[8] This reaction is thought to be the Lewis acid-assisted intramolecular cyclization of **2** with the elimination of the –OH moiety. The molecular structure of **2a** was also characterized by the spectroscopic analyses. The ^{1}H NMR spectrum of **2a** shows peaks



Scheme 1. Proposed reaction mechanism for the formation of indolino[60]fullerene derivatives from $C_{60}O$.

Table 1. Examination results of catalytic activities of selected compounds for the formation of **3a**

Catalyst	Time	Yield of **3a**/%[a]
Montmorillonite K10	6 h	56.7
Sepiolite	6 h	63.8
$BiCl_3$	2 h	50.3
p-TsOH	over 5 days	0 (C_{60} was given)
Amberlyst 15	over 5 days	trace (C_{60} was given)

[a]Isolated yields, estimated from HPLC areas.

corresponding to phenyl, amino, hydroxy, and alkyl protons,[8] while the APPI mass spectrum shows a molecular ion peak at m/z 998, which corresponds to the sum of the molecular weights of $C_{60}O$ (MW 736) and 4-dodecylaniline (MW 262). On the basis of these data, we proposed a possible reaction mechanism (Scheme 1). To the best of our knowledge, the one-pot synthesis of indoline derivatives from ordinal epoxides and aromatic amines has not yet been reported. To assist effective intramolecular cyclization (1) hydroxy and aniline groups can be fixed in the neighborhood and (2) fullerenes cannot be subjected to backside attack and bond rotation on the basis of their cage structures.

We examined the catalytic activity of several Lewis and Brønsted acids in this reaction under similar conditions.[8] The results are summarized in Table 1. The reactions with Sepiolite and $BiCl_3$ rapidly gave **3a** and in good yields. The reactions with Amberlyst 15 and *p*-toluenesulfonic acid (*p*-TsOH), which are Brønsted acids, gave pristine C_{60} with a trace amount of **3a**. We inferred that the protonation of Brønsted acids to anilines completely inhibited the nucleophilic addition to fullerene epoxide.

Reactions of **1** with various aromatic amines in the presence of Sepiolite were also carried out. Every reaction except for that with *N*-methyl-*p*-toluidine provides the corresponding indolino[60]fullerene derivatives in good yields (Table 2). For *N*-methyl-*p*-toluidine, the steric hindrance of the methyl group on the nitrogen atom may inhibit the nucleophilic addition to the fullerene cage.

The electrochemical behavior of **3** is similar to those of typical C_{60} derivatives. All indolino[60]fullerenes exhibited well-defined, reversible redox waves in *o*-dichlorobenzene solution containing 0.1 M $(n\text{-Bu})_4NPF_6$ on multicyclic voltammetry.[8] The first reduction potentials, $E^1{}_{\rm red}$, of C_{60}, **1**, and the series of indolino[60]fullerene derivatives were measured by differential pulse voltammetry, as shown in Table 3. The $E^1{}_{\rm red}$ data of indolino[60]fullerenes ranged from -1.127 to -1.145 V (vs. Fc/Fc$^+$). These values are lower than those of other fullerene derivatives. For the 1,2-substituted fullerenes, the electron-donating groups that are attached to the fullerene cage elevate their LUMO levels.[6] Thus, the lowering of the reduction potentials of indolino[60]fullerenes can be explained in terms of the electron-donating properties of the nitrogen atom. These electrochemical properties are attractive for OSCs. It has been proposed that the theoretical open circuit voltage, which is one of the most important parameters for developing a high-performance OSC, is closely related to the difference between the LUMO level of the accepter material and the HOMO level of the donor material.[7] Thus, the low reduction potentials of indolino[60]fullerenes are promising for application as good accepter materials in OSCs.

Table 2. Isolated yields of indolino[60]fullerenes

Aromatic amine	Product	R	R′	Yield/%[a]
4-Dodecylaniline	**3a**	$C_{12}H_{25}$	H	77.7
4-*n*-Butylaniline	**3b**	C_4H_9	H	64.1
p-Toluidine	**3c**	Me	H	84.0
4-Fluoroaniline	**3d**	F	H	75.7
Aniline	**3e**	H	H	78.9
N-Methyl-*p*-toluidine	**3f**	Me	Me	29.3

[a]Isolated yields, estimated from HPLC areas.

Table 3. First reduction potentials of indolino[60]fullerenes

Fullerenes	$E^1_{\rm red}$/V vs. Fc/Fc$^+$
C_{60}	-1.089
1	-1.052
3a	-1.143
3b	-1.135
3c	-1.138
3d	-1.127
3e	-1.141
3f	-1.145

In conclusion, we have demonstrated an effective preparation method for a series of indolino[60]fullerenes by reacting $C_{60}O$ with aromatic amines in the presence of Lewis acid compounds. We revealed that this reaction consisted of two steps via the formation of β-amino alcohol intermediate **2**. Reactions with various primary aromatic amines also give corresponding derivatives in good yields, except for **3f**, which has a bulky substituent on the nitrogen atom. The results of electrochemical measurements reveal that among all the fullerene derivatives, C_{60}-fused indoline compounds have relatively low reduction potentials and electrochemical stability.

This work was financially supported by the NEDO foundation (Grant for Practical Application of University R&D Results under the Matching Fund Method).

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