# Methoxylation of Singly Bonded 1,4−1′,4′-BnC60−C60Bn Dimer: Preferential Formation of 1,4-C60 Adduct with Sterically Less Demanding Addends and Stability Difference between 1,2- and 1,4-OMe(Bn)C60

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S *Supporting Information*

ABSTRACT: Methoxylation of the singly bonded 1,4−1′,4′-BnC60−C60Bn dimer afforded 1,4-OMe(Bn)C60, a 1,4-C60 adduct with sterically less demanding addends, as the major adduct. The situation was different from that of direct functionalization of C60, where 1,2-OMe(Bn)C60 was obtained as the major product. The reaction was studied with in situ vis-NIR spectroscopy and computational calculations to obtain a better understanding of this unusual regioselectivity. The stability difference between 1,2- and 1,4-OMe(Bn)C60 was studied.
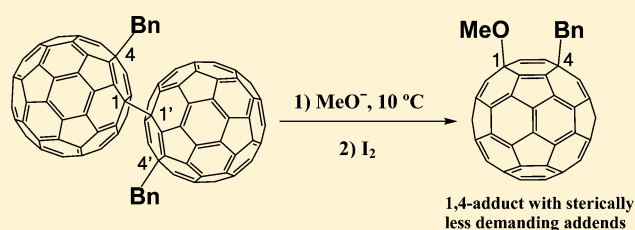
We have recently reported the methoxylation of C60 followed by benzylation, where 1,2-OMe(Bn)C60 (**1**, Scheme 1) was obtained as the major product and 1,4-

Scheme 1. Illustrated Structures of Compounds 1−3
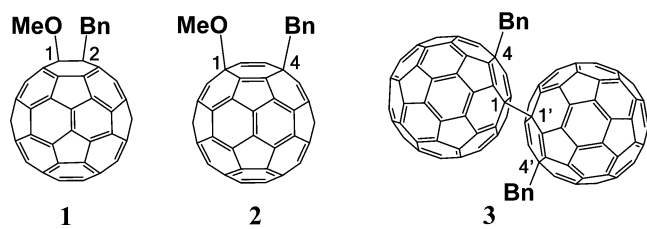
OMe(Bn)C60 (**2**, Scheme 1) was obtained only as a minor fraction.[1] The result is consistent with the literature in that the 1,2-adducts preferentially form over the 1,4-adducts when sterically less demanding addends are involved.[2,3] The 1,2-adducts of C60 are the electronically favored products, which retain the electronic structure of the pristine C60. On the contrary, the 1,4-adducts are the sterically favored products, as an electronically unfavored [5,6]-double bond is introduced with a predicted 8.5 kcal/mol energy increase,[4] which can be compensated for by a decrease in steric hindrance when the bulky addends are positioned with 1,4-addition pattern. In fact, the 1,2-C60 adducts with bulky addends[5] or 1,4-C60 adducts with sterically less demanding addends[6] are rare. One exception is the synthesis of 1,4-fullerenols (C60ArOH) via 1,2-C60Ar-(NO2) reported by Wang and co-workers,[7] where the 1,4-adducts bearing a small hydroxyl group are formed exclusively even though the 1,2-counterparts are facilely obtained by the

Lewis acid-assisted nucleophilic substitution of C60 epoxide[8] and are expected to be more stable, suggesting that it is possible to achieve regiocontrol of 1,2- and 1,4-addition for C60 functionalization.

The singly bonded fullerene dimers 1,4−1′,4′-RC60−C60R are a special type of C60 derivative in which the two C60 cages are positioned in a 1,4-pattern with respect to the R group due to the bulky size of the C60 cage.[9] The covalent bond that directly connects the two C60 cages is weak and easily cleaved,[9c,10] consistent with the elongated bond length (1.576−1.645 Å)[9b−d,10] compared with the typical C−C bond length (1.541 Å).[11] In addition, the 1,4-positioned addends in the 1,4−1′,4′-RC60−C60R dimers may act as the directing groups in controlling the reaction site for the subsequent nucleophilic addition with the formation of a stable type of 1,4,15-R3C60− intermediate bearing the 10π indenyl anion resonance structure, similar to the cases of 1,4-R2C60 derivatives,[1,12−14] making 1,4−1′,4′-RC60−C60R an interesting starting material for fullerene functionalization. Here, we report the methoxylation of 1,4−1′,4′-BnC60−C60Bn (**3**, Scheme 1), which exhibits different regiocontrol compared with that of functionalizing C60 directly.
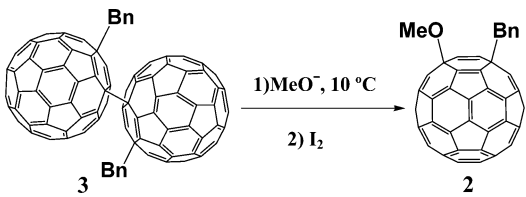
Compound **3** was generated following procedures reported previously, and the identity of the compound was confirmed by spectroscopic characterization.[9d] Compound **3** was then subjected to a reaction with MeO− in *o*-dichlorobenzene (*o*-DCB) under argon, followed by quenching with I2. The reaction afforded compound **2**, which was confirmed by

spectroscopic characterizations,[1] and recovered starting material 3 with no compound 1 being produced (see Figure S1 for HPLC trace). In addition, the reaction resulted in some toluene-insoluble materials, which were difficult to purify and remained unidentified. Table 1 lists the screening of the

Table 1. Screening of the Reaction Conditions for Preparing 2 Starting with 3[a]

| entry	molar ratio[b]	source of MeO⁻	temp (°C)[c]	yield (%)[d]
1	1:3:0.5	MeONa	10	trace
2	1:3:0.5	MeONa/TBABr	10	trace
3	1:1:0.5	TBAOH/MeOH	10	18.3 (25)
4	1:2:0.5	TBAOH/MeOH	10	30.2 (40.2)
5	1:3:0.5	TBAOH/MeOH	10	33.0 (43.0)
6	1:5:0.5	TBAOH/MeOH	10	17.8 (22.9)
7	1:3:1	TBAOH/MeOH	10	30.5 (36.1)
8	1:3:2	TBAOH/MeOH	10	21.4 (25.6)
9	1:3:5	TBAOH/MeOH	10	19.9 (24.3)
10	1:3:0.5	TBAOH/MeOH	30	15.8
11	1:3:0.5	TBAOH/MeOH	0	8.7

[a]Unless otherwise specified, the reaction was performed by putting 30 mg (18.5 μmol) of 1,4−1′,4′-BnC$_{60}$−C$_{60}$Bn into 10 mL of o-DCB, followed by adding MeO⁻ and reacting for 1 h. The reaction was quenched with I$_2$, and the whole process was kept under argon. [b]Molar ratio of 3:MeO⁻:I$_2$. [c]Temperature for the reaction of 3 with MeO⁻. [d]Isolated yield; the values in parentheses are based on consumed 3.

reaction. It shows that the source of MeO⁻ is important for the reaction. Only a trace amount of compound 2 was produced when MeONa was used even with the use of phase transfer agent tetra-n-butyl ammonium bromide (TBABr), likely due to the low solubility of MeONa in the less polar o-DCB solvent (entries 1 and 2). The reaction was improved when a solution of MeOH containing 1.0 M tetra-n-butyl ammonium hydroxide (TBAOH) was used as the MeO⁻ source. A molar ratio of 3:1 between MeO⁻ and 3 seemed to be appropriate for the reaction (entry 5), where compound 2 was obtained with 33.0% yield (43.0% based on consumed 3) with no 1,2-adduct being produced. The use of less MeO⁻ (entries 3 and 4) resulted in a lower yield of 2 likely due to the incompleteness of the reaction, while the use of more MeO⁻ (entry 6) also resulted in a lower yield of 2 with the formation of more toluene-insoluble materials. The use of more I$_2$ (entry 7−9) resulted in more fractions that are difficult to purify for characterization and more toluene-insoluble materials, suggesting that I$_2$ may not only function as the oxidizing agent to remove the negative charge from the reaction intermediates but may also be involved in other reactions with fullerenes. The reaction was sensitive toward temperature as the yield for 2 decreased when the temperature was changed to 30 or 0 °C (entries 10 and 11), respectively.

Notably, the methoxylation of 1,4−1′,4′-BnC$_{60}$−C$_{60}$Bn exhibits a unique regioselectivity different from that of directly functionalizing C$_{60}$, where the 1,4-OMe(Bn)C$_{60}$ is more preferentially formed over the 1,2-counterpart.[1] The result is quite intriguing as the computational calculations with

Gaussian09 at B3LYP/3-21G predicted that 1,2-OMe(Bn)C$_{60}$ (1) is more stable than 1,4-OMe(Bn)C$_{60}$ (2) by 6.8 kcal/mol, consistent with previous work on the energy difference between the 1,2- and 1,4-adducts of C$_{60}$ brought by the unfavorable [5,6]-double bond (8.5 kcal/mol).[4]

The reaction was followed by in situ vis-NIR spectroscopy to obtain a better understanding of the mechanism. Figure 1
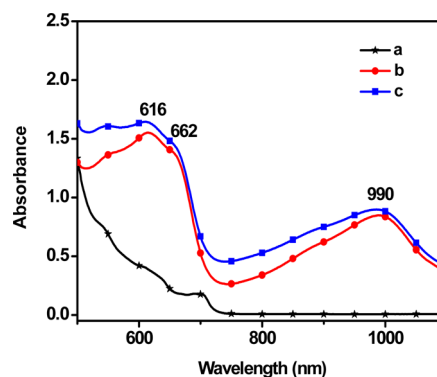
Figure 1. (a) Compound 2 (2.0 × 10⁻⁴ M), (b) after adding 3 equiv of MeO⁻ to 2 immediately, (c) after adding 3 equiv of MeO⁻ to 2 for 15 min. The measurement was performed in o-DCB with a 1 cm cuvette.

shows the in situ vis-NIR spectrum of the reaction mixture. The brownish solution of 1,4−1′,4′-BnC$_{60}$−C$_{60}$Bn turned dark green immediately after 3 equiv of MeO⁻ (1.0 M TBAOH in MeOH) was added and was accompanied by the appearance of broad absorption bands at 616, 662, and 990 nm. The exhibited spectral feature is essentially identical to that of 1,4-(MeO)-BnC$_{60}$⁻ (613 and 991 nm),[15] suggesting the formation of 1,4-(MeO)BnC$_{60}$⁻ from the reaction. The appearance of the shoulder peak at 662 nm indicates the presence of BnC$_{60}$⁻ (658 and 993 nm) in the solution,[16] which is responsible for the green color of the reaction mixture and is caused by the partial decomposition of 1,4-(MeO)BnC$_{60}$⁻ due to its instability.[15]

Considering that 1,4,15-R$_3$C$_{60}$⁻ monoanionic intermediate with the 10π indenyl resonance subunit is typically formed when 1,4-R$_2$C$_{60}$ is subjected to nucleophilic addition,[1,12−14] it is rational to assume that anionic intermediate A with the 1,4,15-configuration (Figure 2) is formed via the methoxylation of 3, where the methoxy is positioned at the para site with respect to the benzyl group judging from the structure of 2. Figure 2a shows the optimized structure of intermediate A, and Figure 2b shows the HOMO distribution of the intermediate obtained with Gaussian09 at the B3LYP/3-21G level. The calculations
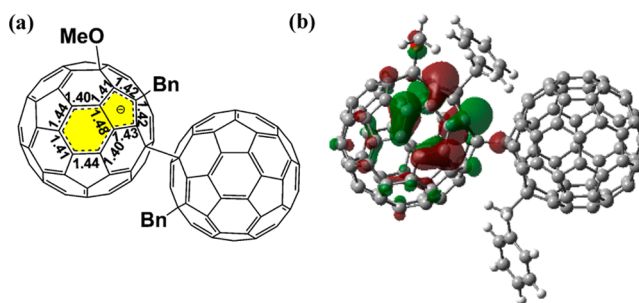
Figure 2. (a) Optimized structure of intermediate A with the labeling of the bond length (Å) for the 10π indenyl subunit and (b) HOMO distribution (0.028 isosurface) of intermediate A.

predicted the existence of the stable delocalized 10π indenyl resonance structure (highlighted by the yellow color) in **A** as evidenced by the bond length average of the related five- and six-membered rings and the localization of the HOMO at the same region, rationalizing the preferential 1,4-addition of the MeO$^-$ on 1,4−1′,4′-BnC$_{60}$−C$_{60}$Bn. In principle, the nucleophilic addition of MeO$^-$ to 1,4,1′,4′-BnC$_{60}$−C$_{60}$Bn might result in another anionic intermediate with the 1,4,15-configuration, where the methoxy is added at the carbon atom para to the C$_{60}$ cage (**A′**, Figure S5). However, such an addition is unlikely because of the strong steric hindrance brought by the C$_{60}$Bn functionality (Figure S6) even though the C$_{60}$ carbon atom para to the C$_{60}$Bn group is predicted to bear positive charge,[14b] consistent with previous work on functionalization of 1,4,1′,4′-RC$_{60}$−C$_{60}$R, where the derivatization occurred exclusively at the carbon atom para to the organic addend rather than the C$_{60}$R functionality.[10,14b]

Intermediate **A** would likely be subjected to further nucleophilic addition of MeO$^-$ at the other C$_{60}$ cage with the formation of intermediate **B** (Figure 3a) with methoxys para to
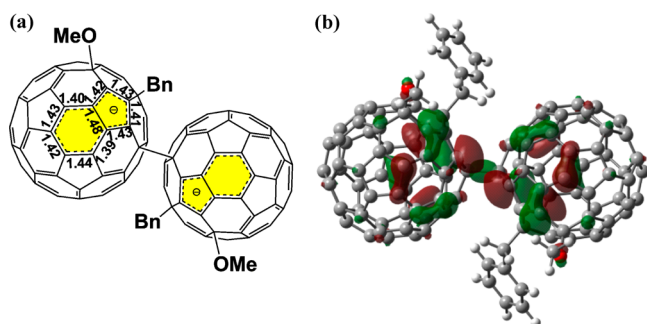
Figure 3. (a) Optimized structure of intermediate **B** with the labeling of the bond length (Å) for one of the identical 10π indenyl subunits and (b) HOMO distribution (0.028 isosurface) of **B**.

the benzyls driven by the force to form the 10π indenyl resonance subunits. Computational calculations indicate that such addition is likely because the C$_{60}$ carbon atom para to the benzyl group in the unmethoxylated carbon cage of **A** is predicted to bear a large positive charge (0.008, Figure S7), and intermediate **B** does possess two 10π indenyl resonance subunits (highlighted by the yellow color) as indicated by the bond length average and the localization of the HOMO at the same region (Figure 3b). The consumption of intermediate **A** is further supported by the benzylation experiment, which is capable of trapping the 1,4,15-R$_3$C$_{60}$$^-$ with no benzylated **A**

product (dimeric product) being obtained.[1] The resultant intermediate **B**, however, would likely decompose to 1,4-(OMe)BnC$_{60}$$^{-\bullet}$ (**2**$^{-\bullet}$) upon formation due to the repulsion of the two closely positioned negative charges on the neighboring carbon cages as indicated by the HOMO distribution in Figure 3b,[9b,d] consistent with the in situ vis-NIR spectrum of the reaction mixture. Notably, it is possible that intermediate **B′** (Figure S8) might form with the methoxy positioned para to the C$_{60}$ cage. However, such addition would be unlikely due to the significant steric hindrance brought by the BnC$_{60}$ functionality (Figure S7). A possible mechanism for the formation of **2** is proposed as shown in Scheme 2.

The reaction is initiated by the nucleophilic attack of MeO$^-$ on **3**, affording anionic intermediate **A** with the 10π indenyl resonance. Intermediate **A** undergoes further methoxylation with the formation of intermediate **B**, which would subsequently decompose into **2**$^{-\bullet}$. The generated **2**$^{-\bullet}$ would partially decompose into BnC$_{60}$$^-$,[15] which would produce **3** when quenching with I$_2$ via radical coupling, whereas the remaining **2**$^{-\bullet}$ would generate **2** by removing a negative charge with I$_2$. As shown in Scheme 2, the preferential formation of the intermediates with the 10π indenyl resonance is crucial for generating compound **2**, which overcomes the unfavorable electronic and steric factors when functionalizing C$_{60}$ directly.

Study of the isomeric effect of C$_{60}$ derivatives is important as it may reveal the intrinsic property of the electronic structure of fullerenes.[5b,17,18] We have recently reported the stability difference between the anionic species of 1,2- and 1,4-OMe(Bn)C$_{60}$ and found that the electronic factor is more important than the steric one in stabilizing the anionic species.[15] However, to the best of our knowledge, experimental study on the stability difference between the neutral 1,2- and 1,4-C$_{60}$ adducts is very limited with 1,4-H(t-Bu)C$_{60}$ being shown to be unstable for isolation.[6] Figure 4 shows the thermogravimetric analysis (TGA) traces of **1** and **2**. Compound **1** starts to decompose at around 216 °C, whereas compound **2** starts to decompose around a much lower temperature of 91 °C, indicating that the 1,4-OMe(Bn)C$_{60}$ is indeed less stable than the 1,2-counterpart. The decomposition traces of **1** and **2** are very similar after the temperature reaches above 320 °C, suggesting that the two compounds likely decompose into the same species at this temperature. A weight loss of approximately 5% is exhibited for the decomposition of **1** and **2** at 320 °C, which matches well with the weight loss of the methoxy group (3.7%), indicating that the methoxy group is the first to be removed from both **1** and **2**. A weight loss of 14.5% is achieved at around 590 °C for **1** and **2**, which matches

Scheme 2. Proposed Mechanism for the Formation of 2 from 1,4-1′,4′-BnC$_{60}$−C$_{60}$Bn
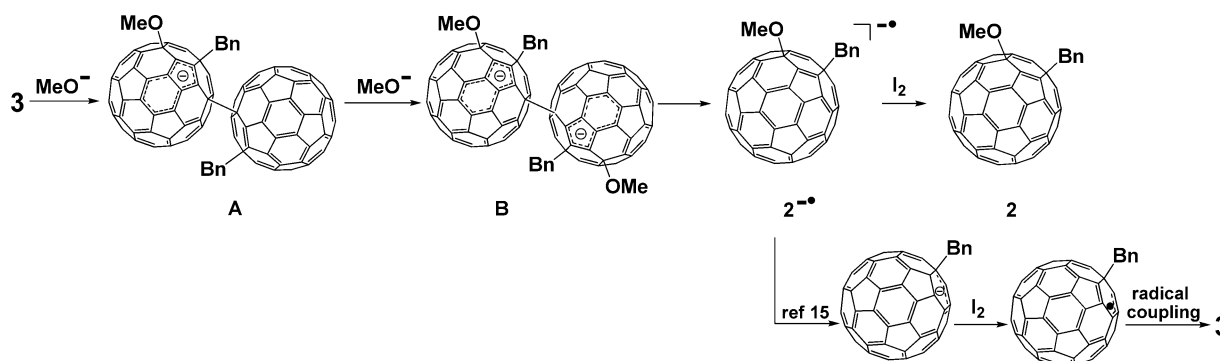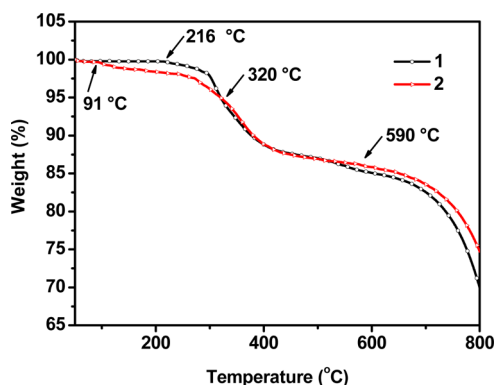
Figure 4. TGA traces of **1** and **2** with a heating rate of 10 °C/min under N_2.

well with the theoretical value for the loss of methoxy and benzyl groups (14.5%), suggesting that the removal of the benzyl addend from **1** and **2** has completed, and further decomposition at higher temperatures would involve only the C_{60} cage.

The lesser stability of compound **2** compared with that of compound **1** is consistent with the calculated energy difference between the two compounds and is further confirmed by the long time storage of the two compounds. No decomposition is observed for compound **1**, whereas a slight decomposition is observed for compound **2** in the HPLC traces of **1** and **2** after storing the compounds in solid form for five months in the dark at room temperature (Figure S9).

In summary, this work demonstrates that it is possible to overcome the unfavorable electronic and steric factors occurring in C_{60} functionalization and obtain the less stable 1,4-(OMe)BnC$_{60}$ as the major product by using the singly bonded 1,4,1′,4′-BnC$_{60}$–C$_{60}$Bn dimer. The preferential formation of the anionic intermediate with 1,4,15-configuration bearing the 10π indenyl resonance structure and the weak nature of the covalent bond that connects the two C_{60} cages are the key factors to achieve the synthesis. This work may shed light on exploring the synthetic application of the singly bonded C_{60} dimer for the synthesis of organofullerenes that are difficult to generated via direct functionalization of fullerenes.

■ EXPERIMENTAL SECTION

Synthesis of Compound 2. Typically, 30 mg of compound **3** (18.5 μmol) was added to 10 mL of *o*-DCB solution degassed with argon at 10 °C. Then, 3 equiv of TBAOH (1.0 M in methanol, 55 μL) was added to the solution, and the reaction was allowed to proceed for 60 min before being quenched with 0.5 equiv of I_2 (2.3 mg). The reaction mixture was dried with a rotary evaporator, and the residue was washed with methanol to remove excess TBAOH and I_2. The crude product was eluted with toluene over a semipreparative Buckyprep column (10 mm × 250 mm) at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm, which afforded **2** (dark brown powder) with 33.0% yield (10.3 mg) and recovered 6.9 mg of compound **3**. The identity of **2** was established by comparing with previously reported spectral data of the compound.[1]

Spectral Characterization of Compound 2. ^{1}H NMR (600 MHz, CS_2, DMSO-d_6 as the external lock solvent) δ ppm 7.28 (d, J = 7.6 Hz, 2H), 7.14 (t, J = 7.3 Hz, 2H), 7.08 (d, J = 7.7 Hz, 1H), 4.12 (d, J = 12.7 Hz, 1H), 4.03 (d, J = 12.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, CS_2, DMSO-d_6 as the external lock solvent, all 1C unless indicated) δ ppm 153.97, 153.23, 152.37, 148.95, 148.20, 147.70, 147.04, 147.00, 146.75, 146.50, 146.42, 146.28, 146.25, 146.16, 146.00, 145.86, 145.76, 145.03 (2C), 144.84, 144.29, 144.24, 143.93, 143.86,

143.77, 143.53, 144.51, 144.44, 143.35 (4C), 143.20, 142.71, 142.59 (3C), 142.53 (2C), 142.36, 142.21 (4C), 141.91 (4C), 141.62, 141.56, 141.41, 140.43, 140.27, 140.09, 139.28, 139.16, 138.03, 136.81, 134.60, 130.10 (2C), 127.87 (2C), 126.87, 80.47, 59.27, 53.70, 48.60; UV−vis (toluene) λ_{max}: 443 nm.

TGA Analysis. The measurement was performed under a nitrogen atmosphere with a heating rate of 10 °C/min.

Computational Methods. All calculations were performed with the Gaussian09 software package. The geometries of intermediates **A** and **B** and compounds **1**−**3** were optimized at the DFT B3LYP/3-21G level. The sum of electronic and zero-point energies for compounds **1** and **2** were obtained at the same level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01171.

HPLC traces, ^{1}H and ^{13}C NMR spectra of compound **2**, and calculation details (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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