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Synthesis and Regiochemistry of [60]Fullerenyl 2-Methylmalonate Bisadducts and their Facile Electron-Accepting Properties

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Abstract

A simple one-pot reaction using *in situ* chemically generated Na-naphthalenide as an electron reductant in the preferential generation of C_{60}^{2-} is described. Trapping of C_{60}^{2-} intermediate with two molar equivalents of sterically hindered 2-bromo-2-methylmalonate ester afforded two singly bonded fullerenyl bisadducts $C_{60}[-CMe(CO_2Et)_2]_2$ in 35 and 7% yield, respectively. The regiochemistry of these two products were determined to be 1,4- and 1,16-bisadducts, respectively, by NMR, UV-Vis-NIR, LCMS, and X-ray single crystal structural analysis. The minor 1,16-bisadduct **2** exhibits long wavelength absorption bands in near-IR region and the prominent electron-accepting characteristics as compared with those of the major 1,4-bisadduct and pristine C_{60} . As revealed by DFT calculation, we propose that the origin of these unusual characters of **2** arises from the moiety of [18 π]-trannulene, in close resemblance to that of the highly symmetrical emerald green 1,16,29,38,43,60-hexaadduct of C_{60} , EF-6MC_n. Accordingly, we anticipate a fast progressive formation of plausible 1,16-bisadduct-like intermediate moieties on a C_{60} cage as the precursor structure leading to the formation of EF-6MC_n, by taking the corresponding regiochemistry and electronic properties into account.

Introduction

Effective methods for fullerene functionalization have been investigated over the past decade¹ aiming at the enhancement of solubility and compatibility of C_{60} with the secondary system. Chemical modification of C_{60} also broadens the scope of its participation in the electronic and optoelectronic processes for materials utilities, *e.g.* photovoltaic cell, organic electroluminescence, and nonlinear optical photonics.² Thus, the high interest in searching simple, characterizable methods for the preparation of novel well-defined fullerene derivatives persists.

Direct reduction of C_{60} was achieved by transferring one or multiple electrons from the metal or organic donors leading to the generation of corresponding C_{60}^{n-} intermediates,³

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Supporting Information Available: APPI-LCMS, MALDI-TOF-HRMS, and ¹H and ¹³C NMR spectra of bisadducts **1** and **2**, HPLC charts for the reaction of bisadduct **1**, ORTEP drawing of **1** (other view), the CIF file, and Cartesian coordinates for the calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

including C_{60}^{2-} , which is a strong electron donor nucleophile in reaction with electrophiles.⁴ Such reaction may result in the product of fullereryl bisadducts. The mechanism of their formation was proposed to follow a sequence of stepwise pathways⁵ with an initial step reaction involving C_{60}^{2-} and one alkyl halide molecule, giving the monoalkyl adduct anion, RC_{60}^- , via single electron transfer followed by radical coupling. The second step involved the S_N2 reaction of RC_{60}^- with the second primary or secondary alkyl halide molecule to afford the corresponding bisadduct derivatives. Chemical generation of C_{60}^{2-} by the thiol donor reduction was plausible in reported methods using either *n*-propanethiol- K_2CO_3 or sodium alkanethiolate RS^-Na^+ ($R = Me, n\text{-}Pr, n\text{-}Bu$) as the reagents.^{4c,e,7}

Recently we reported the reaction of multi-anionic C intermediate (up to C_{60}^{6-})⁸ with di(*t*-butyl) 2-bromo-2-methylmalonate to produce a new class of emerald green fullerenes,⁹ giving an example of singly bonded hexaadduct $C_{60}[-CMe(CO_2\text{-}t\text{-}Bu)_2]_6$ (EF-6MC_{4t}). Here we report the use of sodium naphthalenide as an electron reducing agent for the generation of C_{60}^{2-} , followed by its trapping with diethyl 2-bromo-2-methylmalonate to afford novel fullereryl 1,4-bisadduct **1**, $C_{60}[-CMe(CO_2Et)_2]_2$, in a common 1,4-addition manner along with a minor quantity of 1,16-bisadduct **2** (as a racemic mixture with its enantiomeric 1,29-bisadduct) in an unusual 1,6-addition manner,¹⁰ as shown in Scheme 1. The latter minor bisadduct showed a C_2 -symmetry in the molecular structure consistent with 1,16-substituted fullereryl sp³ carbon positions that bears a close similarity in regiochemistry, as an adjacent pair of two substituents (1,16 or 1,38), to a partial structure of 1,16,29,38,43,60-hexaadduct EF-6MC_n, although the latter C_s -symmetrical 1,38-bisadduct was absent in the same reaction.

Results and Discussion

Experimentally, the reducing agent was prepared by the treatment of naphthalene (78 mg, 0.61 mmol) with sodium metal (>14 mg, 0.61 mmol) in freshly distilled THF (50 mL) at ambient temperature under N_2 or Ar atmosphere. The solution was stirred until the color changed to dark green. The resulting Na-naphthalenide solution was transferred slowly into the deoxygenated solution of C_{60} (200 mg, 0.28 mmol) in dry toluene (100 mL). The mixture was allowed to stir for 4.0 h at room temperature, followed by the addition of diethyl 2-bromo-2-methylmalonate (281 mg, 1.11 mmol). The reaction was continued for an additional 1.0 h. At the end of reaction, the solvent was removed under reduced pressure and the residue was purified on a silica gel column using toluene-THF (98:2) as the eluent to afford a mixture of $C_{60}[-CMe(CO_2Et)_2]_2$ **1** and **2** as brown solids in a total yield of 42% and a ratio of *ca.* 5:1 based on the HPLC peak area count (5-PBB column, toluene, UV 310 nm). The unreacted C_{60} as confirmed by LCMS was recovered in 20% yield. Further isolation of **1** and **2** was made by using a preparative HPLC equipped with a Buckyprep column with toluene/2-propanol (6:4) as the eluent to afford two products in a yield of 35 and 7%, respectively.

Reaction conditions were roughly optimized as shown in Table 1. To generate the dianion of C_{60} efficiently, 2.2 equiv of naphthalene relative to C_{60} was used. When a nearly equal molar quantity of 2-bromo-2-methylmalonate (2.0 equiv) was used, both the conversion and the yield of bisadducts **1/2** remained low (55 and 6%, respectively). By employing an excess amount of malonate (10 equiv), the conversion was increased up to *ca.* 80% and the yield was moderately increased (35–40%). In these conditions, tetraadducts were also obtained along with bisadducts and unreacted C_{60} that may provide the reason of more than 4.0 equiv of malonate necessary to give the highest yield (45%) and conversion rate. When an excess amount of naphthalene (10 equiv) was applied, the conversion was further increased up to 94 and 100% within the reaction period of 1.0 and 12 h, respectively. However, due to the significant increase of multiadducts, the observed yield of **1/2** was reduced to 15 and 0%,

respectively. At the end of the reaction period (12 h) under this condition, the greenish hexaadduct, EF-6MC₂, was isolated in more than 25% yield.

Structural characterization of **1** and **2** was achieved by various spectroscopic measurements. APPI-LCMS spectra of bisadducts **1** and **2** both showed a weak peak at m/z 1066, corresponding to the molecular mass ion of C₇₆H₂₆O₈, and two clear mass fragmentation peaks at m/z 721 and 893 corresponding to the loss of a CMe(CO₂Et)₂ and a [CMe(CO₂Et)₂]₂ moiety, respectively, from the molecular mass ion, however, in different relative peak intensity. In the case of HRMS (MALDI-TOF), the spectrum showed only fragmentation peaks at m/z 720 and 893 (see Supporting Information). ¹H NMR spectrum of **1** in CDCl₃ basically showed three aliphatic peaks at δ 4.3 (q) and 1.3 (t) for the ethyl group and 2.4 (s) for the methyl group, which was assigned to the diethyl 2-methylmalonate moiety. In more details, the spectrum also displayed two sets of triplet at δ 1.31 and 1.34 (6H, J = 7.3 Hz) and two sets of doublet–quartet at δ 4.31 and 4.32 (2H, J = 14.5 and 7.3 Hz) overlapped with one quartet at δ 4.30 (4H, J = 7.3 Hz). The pattern implies the presence of two sets of carboethoxy group, indicating the different chemical environment between these two sets out of four ethyl groups, consistent with the plausible C_s or C₂ symmetry. The complex coupling pattern of the peak at δ ~4.3 suggested that one of the sets of carboethoxy group is suffered from the steric hindrance caused by the neighboring fullerene moiety while the other carboethoxy group is in a rather far position capable of the free-rotation. In the case of the minor bisadduct **2**, the corresponding peaks in its ¹H MMR spectrum were essentially the same but slightly shifted to the lower field for the ethyl group and to the higher field for the methyl group, as compared to those of **1**.

More importantly, ¹³C NMR spectrum of **1**, as shown in Figure 1, exhibited 30 carbon signals (1 peak of 4C, 25 peaks of 2C, and 4 peaks of 1C) in the range of δ 138–154 for the fullereryl sp² carbons. Two chemical shifts at δ 170.2 and 170.1 were assigned to peaks of two sets of carbonyl carbons. Chemical shift of a tertiary methyl carbon (sp³) of 2-methylmalonate moiety was found to be 20.9 ppm, based on its peak intensity in a half to that of the terminal ethoxy carbon peak at δ 13.9. One carbon peak at δ 60.4 can be easily assigned to the quaternary carbon of 2-methylmalonate group due to its low peak intensity. The number of fullereryl carbon peaks revealed a symmetry plane (σ_v) dissecting the molecule with four sp² carbons located on the plane. Peaks of these four carbons, each in a reduced signal intensity, were assigned to the chemical shift at δ 140.2, 142.8, 143.0, and 144.3, consistent with the C_s symmetrical structure of 1,4-bisadduct. On the other hand, ¹³C NMR spectrum of **2**, as shown in Figure 2, showed the similar spectrum to that of **1** except for the aromatic region: the spectrum exhibited 29 carbon signals with almost the same intensity in the range of δ 136–160 for the fullereryl sp² carbons, indicating a C₂ symmetrical structure for this minor 1,16-bisadduct. It is noted that the lowest fielded aromatic peak located apart at δ 159.8 was assigned by DFT simulation as 6 and 15-position carbons which are adjacent to 2-methylmalonate substituted sp³ carbon carbons at the [5,6]-bond.

Although the calculated ¹³C NMR pattern in the aromatic region for some bisadduct isomers, based on the DFT calculation, have predicted the structure of major bisadduct as C_s-symmetrical 1,4- or 1,38-bisadducts,¹¹ influence of the stereoelectronic effect of substituents as well as the solvent effect may be ignored to obtain the sufficient prediction. Therefore, we carried out the preparation of a single crystal for the X-ray crystal structural analysis. When a mixture of cyclohexane and hexane was used as crystallization co-solvents, we obtained pure single crystals in sufficiently good quality and succeeded in collecting the crystallographic data at 123 K (Figure 3). The crystal included a molecule of cyclohexane in a lattice of the bisadduct. Subsequent structural analysis confirmed this region-isomer as the 1,4-bisadduct **1**, consistent with the ¹H and ¹³C NMR spectroscopic

data. The C_S symmetrical structure at the fullerene moiety has a bisected mirror plane as indicated by its ^{13}C NMR spectrum. However, due to the high steric hindrance at the sp^3 fullerenyl carbon (C_F) region with a very limited degree of freedom for the $\text{C}_F\text{--C}(\text{CH}_3)$ bond rotation, the configuration of 2-methylmalonate moieties was found to be oriented in a different C_2 symmetry, not the same C_S symmetry. This interesting feature may make the symmetry prediction complicated for fullerenyl bisadducts having a 2-methylmalonate moiety. Accordingly, two addends of **1** were separated from each other having the closest H–H and O–O interspacing in a short distance of 2.580 and 2.831 Å, respectively.

Several attempts on the crystallization of the minor bisadduct **2** were conducted without success due to its poor crystallinity that may be related to its good solubility as compared with those of **1**. Thus, the regiochemistry of the isomer **2** was determined by the comparison of UV-Vis-NIR spectrum with those of reported structurally-known bisadducts reported. The UV-Vis spectrum of **1** in THF exhibited four broad absorptions with λ_{max} at 252, 294, 328, and 445 nm (Figure 4). Since the UV spectrum of the 1,4-bisadduct, regardless of the type of addends, typically shows a broad peak around 443–445 nm, optical absorptions of **1** are consistent with this regio-isomeric structure.^{4e,12}

On the other hand, the UV-Vis-NIR spectrum of **2** in THF showed the disappearance of a broad peak at 445 nm and the extended absorption to longer wavelengths. As shown in the inset of Figure 4, several absorption bands in weak intensity were observed at 706, 806, and 900 nm in the NIR region. Such a characteristic feature is closely similar to the reported spectrum of the 1,16-bisadduct, where peaks are reported to be 256, 292, 400, 454, 484, 520, 712, 813, and 912 nm,^{10c} even though the possibility of the 1,38-bisadduct regio-isomer cannot be fully ruled out. Observation of extended absorption up to more than 900 nm for this 1,16-bisadduct **2** is rather rare among many reported [60]fullerene derivatives (including pristine C_{60} as shown in Figure 4 as a comparison), whereas the 1,16,29,38,43,60-hexaadduct (EF-6MC_n) also showed a strong absorption at 850 nm as shown in Figure 4.9a Since the substituted positions at C(1) and C(16) are common between the structure of **2** and EF-6MC_n, the all-*trans* [18 π]-trannulene moiety existing in these fullerene derivatives may give the reason for the characteristics similarity in their NIR-absorption characteristics (Figure 5).^{13,14}

Structural characterization for the minor bisadduct **2** was also carried out by the comparison of its relative energy stabilization with other regio-isomers via semiempirical computational technique. Accordingly, the heat of formation, ΔH_f , of plausible 1,2-, 1,4-, 1,16-, and 1,38-bisadducts were calculated using the MOPAC PM3 method (Figure 6). Among these four regio-isomers, the most stable one was found to be the 1,4-bisadduct (1947.4 kJ mol⁻¹; the major product **1**) with the second for the 1,16-bisadduct (1976.3 kJ mol⁻¹; the minor product **2**). The energy difference, $\Delta\Delta H_f$, between 1,4- and 1,16-bisadducts is 28.9 kJ mol⁻¹ that is much smaller than $\Delta\Delta H_f$ values calculated for the 1,2- (128.0) and 1,38-bisadduct (726.5). Therefore, our proposed structure of **2** as the 1,16-bisadduct is quite reasonable in addition to the similarity argument of the NIR spectrum, stated above.

Cyclic voltammetric (CV) profiles of **1**, **2**, and C_{60} collected in *o*-dichlorobenzene in the presence of tetra-*n*-butylammonium perchlorate (0.1 M) were shown in Figure 7. The electrochemical data for three reversible reduction waves of **1** and **2** measured between 0.0 and -2.0 V vs Ag/Ag⁺ were summarized in Table 2. Interestingly, while the first half-wave reduction potential $E_{\text{red}}^{1/2}$ of **1** (-0.92 V) was shifted to a negative potential by 0.12 V relative to that of the pristine C_{60} (-0.80 V), due to the reduction of π -conjugation from 60 π to 58 π electrons at the fullerenyl cage moiety, the $E_{\text{red}}^{1/2}$ value of **2** (-0.71 V) was found to be shifted to a positive potential by 0.09 V. Since 2-methylmalonate addends on **1** and **2** are the same alkyl groups, this increased electron accepting ability of **2** is not originated from

the electron-withdrawing nature of the addend. Such a tendency was also observed in the second ($E_{2\text{red}}^{1/2}$) and third ($E_{3\text{red}}^{1/2}$) half-wave reduction potentials.

In connection with the previous report that the structurally resembling 1,16-bisadducts may show a similar cyclic voltammogram.^{10c} Evidently, the regiochemistry-dependent π -conjugation on the C_{60} cage surface may play an important role in determining the electron-accepting ability of the regioisomer. Kadish et al. have reported that a difference in the first reductive potentials (100 mV) between 1,2-(PhCH₂)C₆₀ (−0.62 V vs SCE) and 1,4-(PhCH₂)C₆₀ (−0.52 V) was considered to be large.^{4f} In our cases, the observed difference in the potentials between the 1,4-bisadduct **1** and the 1,16-bisadduct **2** (210 mV) is much larger than that value, giving the implication of a unique π -conjugation structure of the latter. Moreover, unsymmetrical electron redox waves were observed with a current intensity for the $E_{2\text{red}}^p$ wave at −1.44 and −1.28 V in a doubly higher value than those of the corresponding $E_{2\text{ox}}$ waves in the redox cycle of **1** and **2**, respectively (Figure 7). This observation bore a close resemblance to a similar unsymmetrical CV profile with higher current intensity for $E_{2\text{red}}^p$ wave at −1.50 V (vs Fc/Fc⁺) reported for EF-6MC₂.^{9b} The phenomena were interpreted by the involvement of disproportionation of **1**^{2−} and (EF-6MC₂)^{2−} with the neutral **1** and EF-6MC₂, respectively, to produce two molecules of **1**[−] and (EF-6MC₂)[−] during the reductive cycle. That resulted in an accumulatively higher number of monoanionic intermediate species available for the second electron reduction in the reductive cycle. On the basis of this interpretation, the overall redox wave profiles agreed well with good reversibility and high stability of **1**^{n−} with $n \leq 3$.

Higher electron affinity of the 1,16-bisadduct **2** than those of the 1,4-bisadduct **1** and the pristine C_{60} revealed by their cyclic voltammetry was rationalized by the DFT calculation of the HOMO/LUMO energy at B3LYP/6-31G* level of the theory (Figure 8). Two model compounds 1,4- $C_{60}H_2$ and 1,16- $C_{60}H_2$ were used instead of **1** and **2**, respectively, in order to simplify electronic and steric factors of addends as well as to reduce the calculation time. The order of LUMO energy level in the sequence of 1,4- $C_{60}H_2$ (−3.13) > C_{60} (−3.23) > 1,16- $C_{60}H_2$ (−3.31 eV) is highly related to the order of the first reduction potentials $E_{1\text{red}}^{1/2}$ as shown in Table 1, in contrast to the order of the HOMO energy level in the sequence of 1,16- $C_{60}H_2$ (−5.36 eV) > 1,4- $C_{60}H_2$ (−5.69) > C_{60} (−5.99). The LUMO energy level of 1,16- $C_{60}H_2$ was 0.08 eV lower than that of C_{60} . The significantly decreased HOMO–LUMO energy gap of 1,16- $C_{60}H_2$ (2.05) as compared with those of 1,4- $C_{60}H_2$ (2.56) and C_{60} (2.76 eV) may be correlated to both analysis results from the NIR absorption spectrum and the nature of all-*trans* [18 π]-trannulene moiety¹⁴ of **2**, as discussed in Figure 5, leading to such remarkable electronic properties. Indeed, both calculated HOMO and LUMO energy levels of 1,16- $C_{60}H_2$, as depicted in Figure 8, are mostly located on the [18 π]-trannulene belt while those of 1,4- $C_{60}H_2$ and C_{60} are not.

Highly symmetrical molecular structure of EF-6MC_n, as shown in Figure 5, was well-resolved by the evidence of its X-ray single crystal structural analysis.^{9a} However, the formation mechanism for this unique hexaadduct regio-isomer retaining such a high symmetry remains unclear. One explanation for the formation of EF-6MC_n in a good yield (more than 25–30% when optimized) is to experience a faster kinetic rate of hindered malonate attachments on a C_{60} than the negative charge delocalization of $C_{60}^{n−}$, leading to nearly simultaneous multiple attachments of addends. It is reasonable to correlate this structural feature (the perpendicular relationship of all six addends with each other) to the relative position of all six anions of $C_{60}^{6−}$ in order to minimize the same negative charge repulsion on the cage surface. In principle, any stepwise reaction as those proposed for the formation of 1,2- and 1,4-bisadducts using the reaction of $C_{60}^{2−}$ and alkyl halides^{4–7} should result in a great number of unsymmetrical hexaadduct regio-isomers during the EF-6MC_n formation reaction.

Accordingly, it is of our interest in making the correlation of the mechanistic formation of **2** as a potential intermediate for the EF-6MC₂ chemistry since both bear a similar partial regio-structure in the first two addends. The assumption is plausible owing to the fact that the same reagents were used for the synthesis, except in a different stoichiometric amount. Consequently, both synthetic pathways should proceed through the similar mechanism, reactivity, and kinetics in the early stage of the reaction. Additionally, the 1,4-bisadduct **1** might also be an intermediate product for EF-6MC₂ if there is an involvement of rearrangement on the C_F–C(CH₃) bond in sigmatropic conjugation with fullereryl olefins. Based on these arguments, we carried out the similar reductive coupling reaction of bisadducts **1** and **2** with 2-bromo-2-methylmalonate in the presence of sodium naphthalenide under the similar condition. This step was intended to give hexaadducts for us to examine whether **1** or **2** can be correlated as the precursors to EF-6MC₂ (Scheme 2).

We applied a mixture of **1** and **2** instead of the isolated one due to the limit quantity of isolable minor product **2**. By monitoring with HPLC using 5-PBB column and toluene as the eluent, a mixture of bisadducts (**1/2** : 5/1) was completely disappeared after 30 min following the addition of the malonate with the appearance of several new peaks. They were assigned to the tetra- and hexaadduct by using the corresponding *R_f* value matching with that on a TLC plate [silica gel, *R_f* = 0.66 for the tetraadduct and 0.61 for the hexaadduct with toluene–THF (9:1) as the eluent], as shown in Figure 9. After a reaction period of 60 min, the HPLC peak of the hexaadduct was slightly increased, but remained unchanged even after 3.0 d. By placing the reaction mixture on the TLC plate, a greenish spot assigned to the material of EF-6MC₂ was overlapped with a brownish spot which is probably indicative of a mixture of other non-symmetrical regio-isomers of the hexaadduct. Nevertheless, the greenish compound EF-6MC₂ from this reaction was isolated by precipitation from the toluene solution upon the addition of hexane, as a poor solvent, and compared with the authentic sample. The yield of EF-6MC₂ was only 2.8% based on a mixture of **1/2** used and 17% based on the quantity of the minor bisadduct **2** fraction in the starting material. However, this yield is considerably low if the major bisadduct **1** is capable of undergoing sigmatropic rearrangement on the C_F–C(CH₃) bond¹⁵ and directly affords the final product of EF-6MC₂. Therefore, such fullereryl anion-induced rearrangement or trotting can be ruled out under the present condition. The direct yield correlation from the minor bisadduct **2** to the product EF-6MC₂ seems to be reasonable.

This hypothesis was also verified by the similar reaction employing the isolated bisadduct **1** under the same condition. In this case, no greenish compound EF-6MC₂ was detected through the same work-up procedure as in the case of a mixture of **1** and **2**. Only a brownish mixture of non-symmetrical regio-isomers of the hexaadduct was obtained along with a large amount of tetraadducts after 30–60 min reaction (see Supporting Information). These results implied clearly no structural correlation of **1** to EF-6MC₂ through a sequential addition reaction.

In order to examine further the third possibility of the thermally induced rearrangement pathway among different hexaadducts leading to EF-6MC₂ as a thermodynamically favorable product, we conducted the isomerization experiment by the treatment of a mixture of non-symmetrical hexaadduct regio-isomers with an excess of sodium naphthalenide (10 equiv) in toluene–THF at room temperature. After 1.0 h or even 3.0 d of reaction, the corresponding greenish spot of EF-6MC₂ was not observed on TLC, which supports the former observation on the difficulty in following the rearrangement pathway. It is also noted that a trace amount of the pristine C₆₀ was detected by HPLC, presumably, it was indicative of the reverse reaction from the plausible anionic bisadduct species.

Another reason on the argument of **2** to serve as a suitable intermediate for the EF-6MC₂ formation is based on its high electronegativity, stated above. The compound **2** formed *in situ* in the reaction mixture should be more feasible to the electron reduction by sodium naphthalenide than other intermediate species. This would cause the fast kinetic rate in the disappearance of **2** that could reduce its yield, leading to only a minor product. In the same manner, the 1,38-bisadduct which was not obtained in the present reaction (Scheme 1) may also be possible to behave as a much short-lived intermediate toward the formation of EF-6MC₂ since the functionalized positions C(1) and C(38) are common between the 1,38-bisadduct and EF-6MC₂.¹⁶ However, this possibility is unlikely dominant in the view point of symmetry matching, as demonstrated in Figure 10. Assuming that the hexaadduct is formed by a repeating process of the preferential bisadduct formation, such as the C₂-symmetrical 1,16- or the C_S-symmetrical 1,38-bisadduct, we may consider two possible stepwise pathways in contest toward the formation of highly symmetrical 1,16,29,38,43,60-hexaadduct EF-6MC_n by focusing on the symmetry of regiochemistry. If the first and the second steps undergo the C_S symmetrical addition to give the 1,38-bisadduct and the subsequent 1,16,29,43-tetraadduct, the third step is required to undergo the C₂ symmetrical addition to attain the desired highly symmetrical regio-structure. In contrast to this unsymmetrical C_S-C_S-C₂ addition path, three repeating processes of the C₂ symmetrical addition giving a C₂-C₂-C₂ addition path can be made via the 1,16-bisadduct to afford the identical EF-6MC_n. Such a simple and highly symmetrical circumstance seems to match with the present stepwise mechanism.

As far as the reaction mechanism of C₆₀²⁻ is concerned, C₆₀ was known to undergo consecutive electron reductions up to C₆₀⁶⁻ with the reduction potentials of $E_{1\text{red}}^{1/2}$: -0.36 V vs SCE, $E_{2\text{red}}^{1/2}$: -0.83, $E_{3\text{red}}^{1/2}$: -1.42, $E_{4\text{red}}^{1/2}$: -2.01, and $E_{5\text{red}}^{1/2}$: -2.60.¹⁷ From the reported value for the reductive potential $E_{\text{red}}^{\text{p}}$ of naphthalene (Np → Np⁻) as -2.52 V vs SCE,¹⁸ C₆₀⁴⁻ (or partially C₆₀⁵⁻ as well) might be formed in the presence of an excess amount (>6.0 equiv) of sodium naphthalenide.¹⁹⁻²⁰ Thus, under the condition to give bisadducts using 2.2 equiv of sodium naphthalenide relative to C₆₀, it is obvious that C₆₀²⁻ is the main anion species formed *in situ*. The reaction mechanism of C₆₀²⁻ with alkyl halide, such as benzyl bromide, have been proposed by Fukuzumi and Kadish *et al.*⁵ to proceed an electron transfer from C₆₀²⁻ to alkyl halide in the first step followed by the radical coupling between C₆₀^{•-} and R[•] forming RC₆₀⁻. The same mechanism can be applied to the present reaction (Figure 11). The last step of the reaction may undergo the S_N2 substitution while it is difficult for the tertiary 2-bromo-2-methylmalonate.²¹ In this case, the second electron transfer can occur from RC₆₀⁻ to 2-bromo-2-methylmalonate as in the same manner from C₆₀²⁻ followed by a radical coupling process which gives a mixture of bisadducts.²² Based on this mechanism, the regio-isomer, 1,4- or 1,16-bisadduct, is determined at the final step; the S_N2 of RC₆₀⁻ with R-Br or the radical coupling process of RC₆₀[•] with R[•]. In either case, the 1,4-bisadduct is obviously electronically favorable, however, the 1,16-bisadduct is also formed due to the steric hindrance of the bulky addend.

Conclusions

In conclusion, we have demonstrated an efficient method for the preparation of novel fullereryl 1,4- and 1,16-bisadducts having 2-methylmalonate addends attached on a C₆₀ cage via the trapping of C₆₀²⁻ intermediate with highly reactive, sterically hindered 2-bromo-2-methylmalonate esters in the yield of 35 and 7%, respectively. The resulting minor 1,16-bisadduct **2** showed several unusual optical absorption bands in near-IR region up to 950 nm and the high electron-accepting ability ($E_{1\text{red}}^{1/2}$ = -0.71 V vs Ag/Ag⁺) as compared with those of the major 1,4-bisadduct (-0.92 V) and the pristine C₆₀ (-0.80 V). As revealed by DFT calculation, we propose that the origin of these unusual characters of **2** arises from the moiety of [18π]-trannulene, in close resemblance to that of the highly symmetrical

emerald green 1,16,29,38,43,60-hexaadduct of C₆₀, EF-6MC_n. Accordingly, we anticipate a fast progressive formation of plausible 1,16-bisadduct-like intermediate moieties on a C₆₀ cage as the precursor structure leading to the formation of EF-6MC_n, by taking the corresponding regiochemistry and electronic properties into account.

Experimental Section

General Procedure for the Synthesis of 1,4-C₆₀[CMe(CO₂Et)₂]₂ (1) and 1,16-C₆₀[CMe(CO₂Et)₂]₂ (2)

Sodium metal (>14 mg, 0.61 mmol or excess) was added to a solution of naphthalene (78 mg, 0.61 mmol) in freshly distilled THF (50 mL) at room temperature under Ar bubbling. After the change of the solution color to dark green, the *in situ* generated sodium naphthalenide solution was transferred slowly into the deoxygenated solution of C₆₀ (200 mg, 0.28 mmol) in dry toluene (100 mL). The mixture was stirred for 4.0 h at room temperature, followed by the addition of diethyl 2-bromo-2-methylmalonate (281 mg, 1.11 mmol). After an additional 1.0 h, the solvent and the remaining diethyl 2-bromo-2-methylmalonate were removed under a reduced pressure. The residue was purified on a silica gel column using toluene–THF (98:2) as the eluent to afford a mixture of bisadducts. Preparative HPLC purification of products with a Buckyprep column (eluent: toluene–2-propanol/6:4, flow rate: 1 ml/min, UV: 310 nm) afforded the pure 1,4-C₆₀[CMe(CO₂Et)₂]₂ **1** as a dark brown solid (104 mg, 35% yield) and 1,16-C₆₀[CMe(CO₂Et)₂]₂ **2** as a dark brown solid (21 mg, 7% yield).

1,4-Bis(1',1'-di(carboethoxy)ethyl)-1,4-dihydro[60,*h*]_hfullerene (1,4-C₆₀[CMe(CO₂Et)₂]₂) (1)

¹H NMR (270 MHz, CDCl₃) δ 4.32 (dq, 2H, *J* = 14.5, 7.3 Hz), 4.31 (dq, 2H, *J* = 14.5, 7.3 Hz), 4.30 (q, 4H, *J* = 7.3 Hz), 2.42 (s, 6H), 1.34 (t, 6H, *J* = 7.3 Hz), and 1.31 (t, 6H, *J* = 7.3 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 170.19 (C=O), 170.05 (C=O), 153.96 (2C), 151.64 (2C), 148.84 (2C), 148.53 (2C), 147.41 (2C), 147.22 (2C), 147.08 (2C), 146.68 (2C), 146.01 (2C), 145.94 (2C), 145.69 (2C), 145.28 (2C), 144.93 (2C), 144.58 (2C), 144.33 (1C), 144.28 (2C), 144.00 (2C), 143.94 (2C), 143.43 (2C), 143.26 (4C), 143.16 (2C), 142.96 (1C), 142.83 (1C), 142.77 (2C), 142.70 (2C), 142.65 (2C), 141.17 (2C), 140.27 (1C), 138.31 (2C), 137.80 (2C), 62.25 (2C, 4°), 62.09 (2C), 62.00 (2C), 60.44 (2C, C₆₀), 20.90 (2C), and 13.89 (4C); UV-Vis (THF) λ_{max} 252, 294, 328, and 445 nm; MS (APPI-LCMS) *m/z* 1066 (M⁺), 893, and 721. Crystallographic data for this compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication# CCDC 772977. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data-request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44-1233336033.

1,16-Bis(1',1'-di(carboethoxy)ethyl)-1,16-dihydro[60,*h*]_hfullerene (1,16-C₆₀[CMe(CO₂Et)₂]₂) (2)

¹H NMR (270 MHz, CDCl₃) δ 4.43–4.22 (m, 8H), 2.25 (s, 6H), 1.33 (t, 6H, *J* = 7.3 Hz), and 1.29 (t, 6H, *J* = 7.3 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 170.03 (C=O), 169.83 (C=O), 159.83 (2C), 151.02 (2C), 149.50 (2C), 148.69 (2C), 148.00 (2C), 147.33 (2C), 146.74 (2C), 146.39 (2C), 146.07 (2C), 145.67 (2C), 145.59 (2C), 145.53 (2C), 145.30 (2C), 145.14 (2C), 144.75 (2C), 144.68 (2C), 144.65 (2C), 144.29 (2C), 142.90 (2C), 142.67 (2C), 142.06 (2C), 141.91 (2C), 141.80 (2C), 141.35 (2C), 141.23 (2C), 138.67 (2C), 138.58 (2C), 136.75 (2C), 136.43 (2C), 62.10 (4C), 61.36 (2C, 4°), 61.04 (2C, C₆₀), 19.97 (2C), and 13.96 (4C); UV-Vis-NIR (THF) λ_{max} 252, 287, 400, 510, 706, 806, and 900 nm; MS (APPI-LCMS) *m/z* 1066 (M⁺), 893, and 721.

Synthesis of 1,16,29,38,43,60-C₆₀[CMe(CO₂Et)₂]₆ (EF-6MC₂) from a mixture of 1,4- and 1,16-C₆₀[CMe(CO₂Et)₂]₂ (1/2 = 5:1)—Sodium metal (>13 mg, 0.56 mmol or excess) was added to a solution of naphthalene (71.8 mg, 0.56 mmol) in freshly distilled THF (10 mL) at room temperature under Ar bubbling. After the change of the solution color to dark green, the *in situ* generated sodium naphthalenide solution was transferred slowly into the deoxygenated solution of a mixture of C₆₀[CMe(CO₂Et)₂]₂ (59.7 mg, 0.056 mmol) in dry toluene (40 mL). The mixture was stirred for 4.0 h at room temperature, followed by the addition of diethyl 2-bromo-2-methylmalonate (425 mg, 1.68 mmol). After an additional 1.0 h, the solvent and the remaining diethyl 2-bromo-2-methylmalonate were removed under a reduced pressure and the residue was purified on a silica gel column using toluene–THF (95:5) as the eluent to afford a mixture of hexaadducts. The reprecipitation of the product was carried out by using a mixture of toluene–hexane followed by centrifugation to afford a pure 1,16,29,38,43,60-C₆₀[CMe(CO₂Et)₂]₆ as an emerald green solid (2.8 mg, 2.8% yield based on 1/2 and 17% based on 2).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
 ^{13}C NMR spectrum of the bisadduct **1**.

Figure 2.
 ^{13}C NMR spectrum of the bisadduct **2**.

Figure 3.
ORTEP drawing of the major 1,4-bisadduct **1**.

Figure 4.

UV-Vis-NIR spectra of the bisadducts **1** (dotted line), **2** (solid line), and EF-6MC₂ (chain line) in THF (0.1 mM). The spectrum of pristine C₆₀ (bold line) in toluene (0.1 mM) is also shown for a comparison. The inset is magnified NIR spectra of the minor bisadduct **2**, EF-6MC₂, and C₆₀.

Figure 5. Schlegel diagram of the 1,16,29,38,43,60-hexaadduct EF-6MC_n and **2**.

Figure 6.

Calculated heat of formation ΔH_f for several bisadduct regio-structures of $C_{60}[-CMe(CO_2Et)_2]_2$, optimized by the MOPAC PM3 method. The value in parentheses is $\Delta\Delta H_f$ relative to that of the 1,4-bisadduct.

Figure 7. Cyclic voltammograms of bisadducts, **1** (blue line) and **2** (red line), and C_{60} (purple dotted line).

Figure 8. Calculated HOMO and LUMO energy (eV) of C_{60} , 1,4- $C_{60}H_2$, and 1,16- $C_{60}H_2$ as the model compound of bisadducts **1** and **2** by the DFT method at B3LYP/6-31G* level of the theory.

Figure 9. HPLC profiles for the reaction of a mixture of bisadducts (0, 30, and 60 min) and the isolated EF-6MC₂ (5-PBB, toluene 100%, 1 mL/min, UV 310 nm).

Figure 10. Symmetry matching according to a stepwise mechanism for the formation of 1,16,29,38,43,60-hexaadduct EF-6MC_n.

Figure 11.
Proposed reaction mechanism for the formation of bisadduct C_{60}R_2 ($\text{R} = \text{CMe}(\text{CO}_2\text{Et})_2$).

Scheme 1.

Scheme 2.

Table 1

The reaction of C₆₀ with diethyl 2-bromo-2-methylmalonate under various conditions

Naphthalene /eq ^a	Anionization Time / h ^b	Malonate /eq ^a	Reaction Time / h ^c	Conv. / % ^d	Yield 1/2 / % ^{d, e}
2.2	4	2	72	55	6
2.2	4	10	1	81	35
2.2	2	10	4	76	40
2.2	4	4	1	80	45
10	4	10	1	94	15
10	4	10	12	100	0 (25) ^f

^aRelative to C₆₀ used (0.28 mmol). Sodium was used in excess than naphthalene.

^bBefore adding malonate.

^cAfter adding malonate.

^dDetermined by HPLC based on C₆₀ used.

^eCombined yield of **1** and **2**.

^fThe value in parentheses is the isolated yield of EF-6MC₂ hexaadduct.

Table 2Cyclic voltammetric data for **1**, **2**, and C₆₀

	$E^{1/2}$ (V) vs Ag/Ag ⁺		
	$E_{1\text{red}}$	$E_{2\text{red}}$	$E_{3\text{red}}$
1	-0.92	-1.29	-1.80
2	-0.71	-1.18	-1.66
C ₆₀	-0.80	-1.20	-1.66

^a In 1,2-dichlorobenzene (0.1 mM) in the presence of (*n*-Bu)₄N⁺(ClO₄)⁻ (0.1 M). Working electrode: Pt; counter electrode: Pt; scan rate: 0.1 V s⁻¹.