Selective Functionalization on [60]Fullerene Governed by Tether Length

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Abstract: In order to accomplish the selective synthesis of [60]fullerene bisadducts, the reactions of [60]fullerene with compounds in which two α,α′-dibromo-*o*-xylene moieties were connected by an oligomethylene chain (n = 2−5) were investigated. By this method, only two isomers (*cis*-2- and *cis*-3-isomers) were selectively obtained when $n = 2$ and 3, while another isomer (*e*-isomer) was obtained when $n = 5$. When $n = 4$, a complex mixture of bisadducts was formed and has not been separated so far. *cis*-2-Bisadducts have been, for the first time, selectively obtained in the fullerene chemistry. The structures of bisadducts were determined on the basis of ^{1}H, ^{13}C NMR, IR, UV−vis, and mass spectroscopies. According to the NMR experiments, the symmetries of *cis*-2-, *cis*-3-, and *e*-isomers were concluded to be C_s, C_2, and C_1, respectively. Chiral *cis*-3- and *e*-bisadducts were successfully resolved into the respective enantiomers on a chiral HPLC column, although *cis*-2-bisadducts only gave a single peak. The UV−vis spectra of *cis*-2-, *cis*-3-, and *e*-bisadducts were remarkably different from one another. Specifically, the *e*-bisadducts showed a characteristic absorption peak around 420 nm. The cleavage of the oligomethylene chain produced the corresponding [60]fullerene derivatives possessing two phenol moieties. These compounds are applicable to further functionalization.

Introduction

As many functionalizations on [60]fullerene have been reported,[1] the research is now strongly directed toward selective multifunctionalization.[2] Hirsch and his co-workers reported the reactivity of a mono-cyclopropanated fullerene on the second cyclopropanation by an α-bromocarbanion generated from diethyl bromomalonate:[2a,c] i.e., the second addition is apt to occur in the order of *e*, *trans*-3, and *trans*-2 or *cis*-3.[3] Therefore, under kinetically controlled conditions, *e*-bisadducts can be obtained as major products, due to the bulkiness of reagents and the reactivities of [6,6] junctions, although the selectivity is not always high. For instance, when an *o*-quinodimethane homologue was used for the modification of [60]fullerene, bisadducts turned out to be a complex mixture which could not be separated by a simple column chromatographic technique.[4,5]

Diederich and his co-workers[6] invented a sophisticated method, the so-called tether-directed remote functionalization. They used tandem carbenoid and diene additions; i.e., one [6,6] junction of fullerene was first modified by cyclopropanation, and then two sites around the equator were selectively modified by the Diels−Alder addition of the dienes attached at the end of the two tethers stretched from the cyclopropane ring. They exclusively got a headphone-shaped trisadduct.[7]

We are interested in a one-step tandem bisaddition occurring within one hemisphere of [60]fullerene, using the tether-caused constraint. Then a question arises. What tether should be chosen in order to obtain a specific bisadduct selectively?

For the selective bisaddition, we designed α,ω-bis(3,4-bis-(bromomethyl)phenoxy)alkanes **1**, which generate *o*-quinodimethane species at both ends in situ by 1,4-elimination.[2d] These reactive intermediates are expected to add stepwise to two [6,6] junctions of fullerene and give specific bisadducts depending on the tether length. In practice, we have successfully achieved the selective addition of two *o*-quinodimethane species by changing the tether length. In this paper, we would like to report the selectivity, structural analysis, optical resolution, and removal of the tether to afford fullerene derivatives possessing phenolic hydroxy groups.

Results and Discussion

Synthesis of Precursors 1. The tether length (n) of **1** is limited between 2 and 5, so that the bisaddition can occur within one hemisphere of [60]fullerene, leading to *cis*-2-, *cis*-3-, and *e*-bisaddition.[8]

The synthesis of precursor **1** was first attempted by the reaction of *N*-bromosuccinimide (NBS) and compound **2**, which

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(1) (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685. (b) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138. (c) Olah, G. A.; Bucsi, I.; Aniszfeld, R.; Prakash, G. K. S. *Carbon* **1992**, *30*, 1203. (d) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 293. (e) Tago, T.; Minowa, T.; Okada, Y.; Nishimura, J. *Tetrahedron Lett.* **1993**, *34*, 8461. (f) Hirsch, A. *Synthesis* **1995**, 895.

(2) (a) Hirsch, A.; Lamparth, I.; Grösser, T. *J. Am. Chem. Soc.* **1994**, *116*, 9385. (b) Henderson, C. C.; Rohlfing, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786. (c) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437. (d) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78. (e) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296. (f) Kräutler, B.; Maynollo, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 87.

(3) We use Hirsch's edge labeling throughout this paper because of the popularity, although we developed our own edge labeling. Our labeling can express isomers more precisely than theirs, so that occasionally we apply ours for the stereochemical descriptions of compounds in footnotes; see: Nakamura, Y.; Taki, M.; Nishimura, J. *Chem. Lett.* **1995**, 703.

(4) Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351.

(5) Nakamura, Y.; Minowa, T.; Hayashida, Y.; Tobita, S.; Shizuka, H.; Nishimura J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 377.

(6) Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339.

(7) (A,2V)-Trisadduct (see ref 3).

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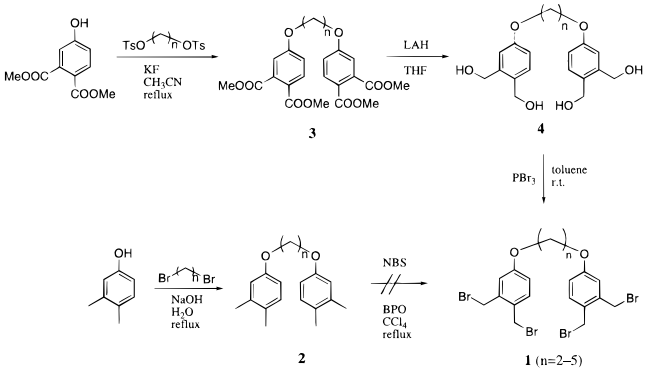
Scheme 1



was readily prepared from 3,4-dimethylphenol by the Williamson ether synthesis, as shown in Scheme 1. However, the radical bromination of **2** resulted in the meager yield of desired compound **1** with many byproducts.[9]

Thus, we took another route. Tetraester **3**, prepared from dimethyl 4-hydroxyphthalate, was reduced into tetraol **4** by lithium aluminum hydride (LAH). The bromination of **4** by phosphorous tribromide successfully afforded the desired compound **1**.

Product Distribution. Precursors **1** and [60]fullerene were refluxed in toluene overnight under high-dilution conditions (ca. 10^{-4} M), in order to prevent two fullerene molecules from being bridged by the tether of **1**. When $n = 2$, 3, and 5, major products were easily isolated by column chromatography (silica gel, benzene/hexane), and their purities were monitored by TLC. On the other hand, in the case of $n = 4$, many products were detected, each in a small amount, and could not be separated by the simple procedure mentioned above.

In fact, when $n = 2$, two products, major **5a** and minor **6a**, were isolated in 10% and 8% yields, respectively, as shown in Scheme 2. The crude reaction mixture was analyzed by ^{1}H NMR spectroscopy, and there were no significant products other than the isolated materials.

In the same manner, two products were isolated when $n = 3$. In this case, major product **5b** was obtained in rather high 20% isolated yield as well as minor **6b** in 9% yield. Again we could not detect any other significant isomers in the crude reaction mixture by ^{1}H NMR spectroscopy.

Only one product **7** was isolated in 30% yield when $n = 5$. There were several products in the crude reaction mixture, but their total yield did not exceed two or three percent.

The linkages of all bisadducts could be cleaved quantitatively by the treatment of excess boron tribromide in benzene at room temperature,[10] to give the corresponding bisphenols. Note that two cyclic bisadducts **5a** and **5b** gave the identical bisphenol **8**, and bisadducts **6a** and **6b** another single product **9**, according to NMR, IR, and mass spectroscopy, as described below. Moreover, product **7** was also transformed into the third bisphenol **10**.

Characterization of Bisadducts. Products **5**−**10** gave correct molecular ion peaks in mass spectroscopy. In the IR spectra, we could not find any peaks characteristic of a certain isomer. Among the spectroscopic methods employed in this work, ^{1}H NMR, ^{13}C NMR, and UV−vis spectroscopy gave decisive evidence on the structural determination.

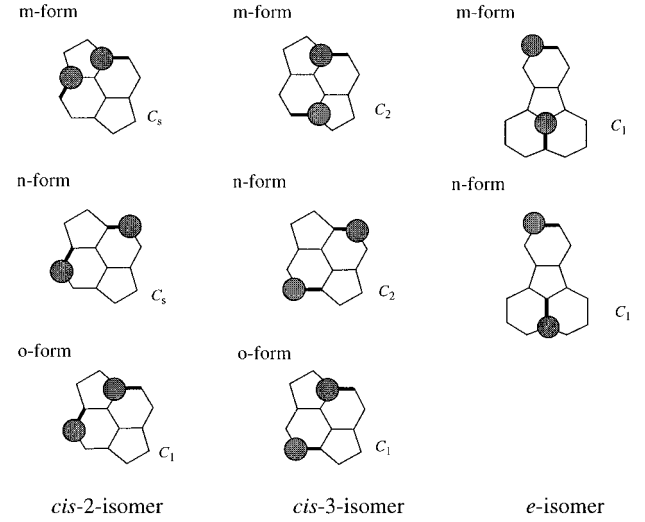
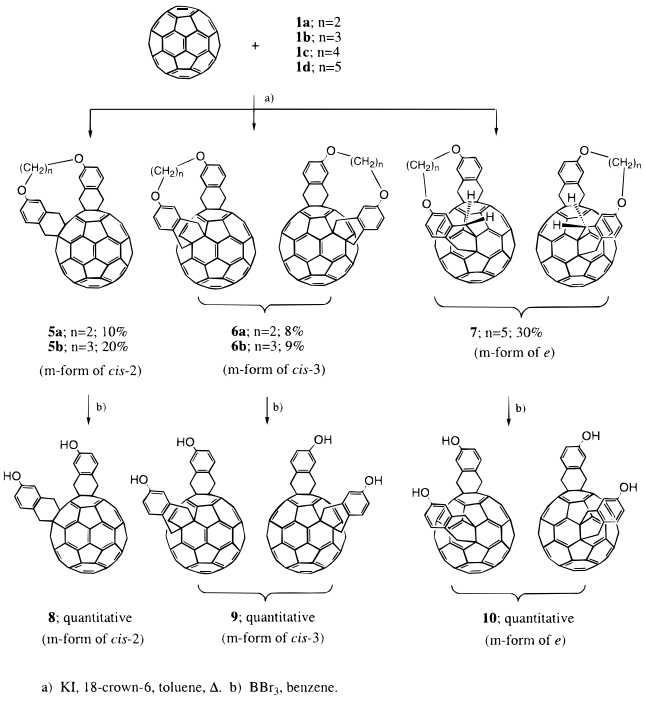


Figure 1. Possible isomers for *cis*-2-, *cis*-3-, and *e*-bisadducts. Bold lines and circles mean addition sites and positions of the oxygen-functional group, respectively.

Scheme 2



a) KI, 18-crown-6, toluene, Δ. b) BBr_3, benzene.

There are eight patterns with respect to the positions of bisaddition at [6,6] junctions of [60]fullerene. Among them, only three (*cis*-2, *cis*-3, and *e*) seem to be possible for **5**−**10** because of the tether length. For each of the three bisadditions, two or three isomers are possible in principle, due to the presence of a substituent (alkoxy group) on the benzene rings. Three isomers (m-, n-, and o-forms),[11] in which the two substituents are together, apart, and mixed, respectively, are possible for *cis*-2-bisadducts, as schematically illustrated in Figure 1. In a similar way, there are three isomers (m-, n-, and o-forms)[11] for *cis*-3-bisadducts and two isomers (m- and n-forms)[11] for *e*-bisadducts.

(8) It is hard to believe that *cis*-1-bisaddition takes place, because of the severe steric interaction between two benzocyclohexene moieties. Therefore, the addition was not taken into consideration.

(9) In this reaction, the bromination is considered to take place not only at the benzyl positions but also on the tethers and benzene rings, due to the presence of an electron-donating alkoxy group.

(10) Iyoda, M.; Sultana, F.; Sasaki, S.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1929.

(11) According to our nomenclature, the m-, n-, and o-forms of *cis*-2-bisadducts are systematically and precisely described as (A_1,C_{11}), (A_1, C^u_{12}), and (A_1,C^u_{11r}), the m-, n-, and o-forms of *cis*-3-bisadducts as (A_1,D^u_{11r}), (A_1, D_{12r}), and (A_1,D_{11r}), and the m- and n-forms of *e*-bisadducts as (A_1,H^r_1) and (A_1, H^r_2) (see ref 3).

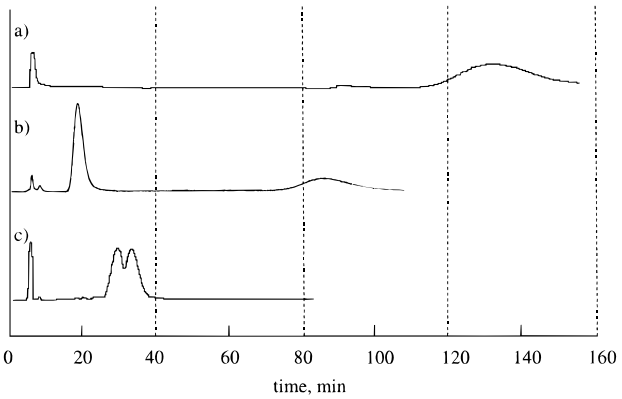


Figure 2. Optical resolution of (a) **5a**, (b) **6a**, and (c) **7** by chiral HPLC. See Table 1 for their optical rotation. Conditions: stationary phase, CHIRALCEL OD; eluent, hexane/2-propanol (9:1 (v/v)); flow rate, 1.0 mL/min.

In order to determine the structures of **5**−**10**, their symmetries were examined first. The symmetries of [60]fullerene bisadducts are sensitively reflected by the number of signals in the ^{1}H and ^{13}C NMR spectra.[12] If a bisadduct has only C_1 symmetry, 6 signals for the aromatic protons and more than 60 signals for the fullerene and aromatic sp^2 carbons will be observed in the ^{1}H and ^{13}C NMR spectra, respectively. In a bisadduct with C_2 or C_s symmetry, however, each number will be decreased by about half.[13] The symmetries of the adducts are also associated with their chirality; bisadducts with C_1 or C_2 symmetry are chiral, while those with C_s symmetry are achiral. Thus, the optical resolution of the enantiomers seems to be possible for the former.

In practice, only one set (3 signals) of aromatic proton peaks was observed in the ^{1}H NMR spectra of bisadducts **5a**,**b** and **6a**,**b**. In the ^{13}C NMR spectra, these compounds gave 30−36 peaks for the sp^2 carbons of the fullerene moiety and the benzene rings. Therefore, both **5a**,**b** and **6a**,**b** were concluded to have C_s or C_2 symmetry. At this stage, four isomers (m- and n-forms of *cis*-2 (C_s) and *cis*-3 (C_2)) are candidates for **5a**,**b** and **6a**,**b**. The distinction between C_s and C_2 symmetry, however, could not be accomplished by the number of signals in the NMR spectra.[13]

The optical resolution of **5a**,**b** and **6a**,**b** was attempted on a chiral HPLC column (see the Experimental Section). As shown in Figure 2 and Table 1, adduct **6a** exhibited two peaks, which were found to correspond to a pair of enantiomers according to the sign and value of optical rotation.[14] These results apparently indicate that **6a** is chiral, i.e., a *cis*-3 isomer (m- or n-form) with C_2 symmetry. On the contrary, adduct **5a** afforded only one peak in the chromatogram. Even the front and tail parts of the peak did not give any optical rotation in the range of 200−800 nm. This evidence clearly suggests that **5a** is achiral, i.e., a *cis*-2 isomer (m- or n-form) with C_s symmetry. Adducts **5b** and **6b** provided results similar to those of **5a** and **6a**, respectively. A remarkable difference in retention for **5a**−**7** toward the chiral stationary phase (CHIRALCEL OD) consisting of cellulose tris(3,5-dimethylphenyl carbamate)-coated silica gel[15] is notable. The retention in chromatography is the consequence of the interaction between a solute and a stationary phase, and is sensitive to the structure of a solute. The arrangement of the two phenyl residues of **5a** must be highly suitable to induce its tight interaction with the chiral stationary.[16]

Table 1. Retention Time in HPLC and Optical Rotation $[\alpha]_D$ of Enantiomers of **6a**, **7**, **9**, and **10**

bisadducts	HPLC retention time (min)[a]	$[\alpha]_D$	concn (g/mL)
6a	19	5.5×10^3	1.0×10^{-4} [c]
	82	-5.8×10^3	9.0×10^{-5} [c]
7	31	5.7×10^2	6.5×10^{-5} [c]
	35	-5.2×10^2	1.2×10^{-4} [c]
9	47	5.2×10^3	1.3×10^{-4} [d]
	57	-5.6×10^3	1.1×10^{-4} [d]
10	36[b]	4.4×10^1	1.8×10^{-4} [d]
	78[b]	-7.4×10^1	4.1×10^{-5} [d]

[a] See conditions in Figure 2 unless otherwise noted. [b] Hexane/2-propanol (7:3 (v/v)). [c] Cyclohexane. [d] Cyclohexane/2-propanol (1:1 (v/v)).

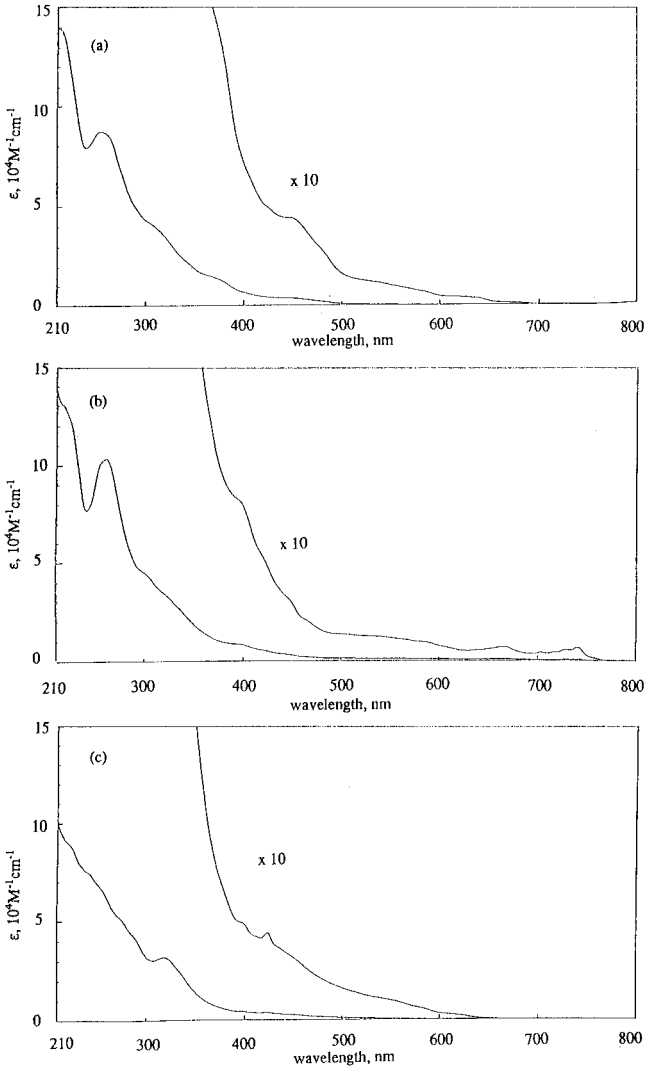


Figure 3. Absorption spectra of (a) **5a**, (b) **6a**, and (c) **7** in cyclohexane at room temperature.

The electronic absorption spectra of these adducts partially support the above assignments. As shown in Figure 3, the spectra of **5a** and **6a** are quite different from each other; the

(12) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 8926.

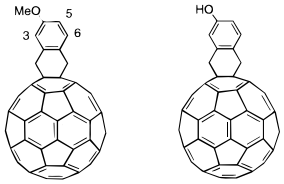
(13) Theoretically, the total number of sp^2 carbon signals of the fullerene moiety and the benzene rings should be different in the case of C_2 (34 signals) and C_s (36 signals) symmetry. Furthermore, all the fullerene sp^2 carbons should have the same intensity in bisadducts with C_2, while four fullerene sp^2 carbon signals should be half as intense as the others in bisadducts with C_s. It was, however, difficult to distinguish between C_2 and C_s for **5a**,**b** and **6a**,**b** due to the overlapping of some signals.

(14) Their mirror-imaged CD spectra have finally proved the enantiomeric relationship. These spectra will be reported elsewhere.

(15) Yashima, E.; Okamoto, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3289.

(16) Yashima, E.; Yamamoto, C.; Okamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4036.

Table 2. ^{1}H NMR Spectroscopic Data of Bisadducts **5**−**10** and Monoadducts **11** and **12** (Aromatic Part Only)[a]



11 **12**

adduct	at C3[b] (δ, d, J in Hz)[c]	at C5[b] (δ, dd, J in Hz)[c]	at C6[b] (δ, d, J in Hz)[c]
5a	7.84 (2.5)	7.02 (2.5, 7.9)	7.30 (7.9)
5b	7.44 (2.2)	6.96 (2.3, 8.1)	7.27 (8.2)
6a	6.94 (2.5)	7.02 (2.5, 8.0)	7.26 (8.0)
6b	6.85 (2.4)	6.99 (2.4, 8.0)	7.27 (7.6)
7	6.63 (2.8)	6.84 (2.6, 8.1)	7.27 (7.9)
	6.78 (2.8)	6.94 (2.7, 8.2)	7.35 (8.2)
11	7.22 (2.2)	7.06 (2.5, 8.3)	7.56 (8.2)
8	7.20 (2.1)	6.78 (2.3, 8.1)	7.18 (7.9)
9	6.88 (2.3)	6.85 (2.5, 8.0)	7.29 (8.0)
10	6.90 (2.4)	6.82 (2.5, 8.3)	7.33 (8.4)
	6.99 (2.4)	6.85 (2.6, 8.1)	7.34 (8.4)
12	6.70 (2.5)	6.57 (2.6, 8.1)	7.16 (8.3)

[a] Recorded at room temperature in $CDCl_3$ for **5a**, **6a**,**b**, and **7** in $CDCl_3/CS_2$ for **5b** and **11**, and at 75 °C in toluene-d_8 for **12**, and at 120 °C in DMSO-d_6 for the others. [b] Carbon positions are shown in structure **11**. [c] Coupling constants are listed in parentheses.

longest absorption band extends up to more than 750 nm in **6a**. Such a remarkable difference should be brought about by the difference in the addition sites rather than the difference in the positional relationship of the substituents; it seems unlikely that the three isomers of *cis*-2 or *cis*-3 exhibit quite different absorption spectra between them. These results are consistent with the above assignment that **5a**,**b** and **6a**,**b** are *cis*-2 and *cis*-3, respectively.

Further characterization of each bisadduct was carried out on the basis of ^{1}H NMR spectroscopy and MM2 calculations. ^{1}H NMR spectroscopic data are summarized in Table 2. It is noteworthy that bisadducts **5**−**7** recorded sharp peaks at room temperature in the ^{1}H NMR spectra, apparently indicating that the flipping motion around the cyclohexene rings is highly restricted by the tether. Such a situation enables the presence of three conformers (*syn*,*syn*, *syn*,*anti*, and *anti*,*anti*)[17] for each of the *cis*-2- and *cis*-3-bisadducts, and two (*syn* and *anti*) for each of the *e*-bisadduct, as depicted in Figure 4. The most stable conformation for each isomer of *cis*-2-, *cis*-3-, and *e*-bisadducts was calculated by the MM2 method. In all cases, the most stable conformation was found to be *syn*,*syn* or *syn*, whose steric energies are listed in Table 3. The value for the n-form of *e*-isomer was omitted due to the extremely large steric energy.

The determination of whether **5a**,**b** are the m- or n-form of *cis*-2 is as follows. The two protons at C3 (see structure **11** for numbering) of **5a**,**b** were resonated at lower fields than those of other bisadducts **6a**,**b** and **7** and monoadduct **11**, suggesting that the C3 protons in **5a**,**b** suffer from steric compression. Such interaction seems to be possible only in the m-form, as demonstrated by the MM2 calculations showing that the distance between the two C3 protons is 2.1−2.2 Å in this particular isomer. Therefore, products **5a**,**b** can be reasonably assigned as the m-form[11] of *cis*-2 as shown in Scheme 2. This assignment is also supported by the calculations of the steric energies. In

(17) The *syn* and *anti* conformations of bisadducts are defined as follows: when one cyclohexene ring attached at a [6,6] junction is directed toward another addition site, the stereochemical situation is defined as *syn*, and when it faces against another, this is defined as *anti*.

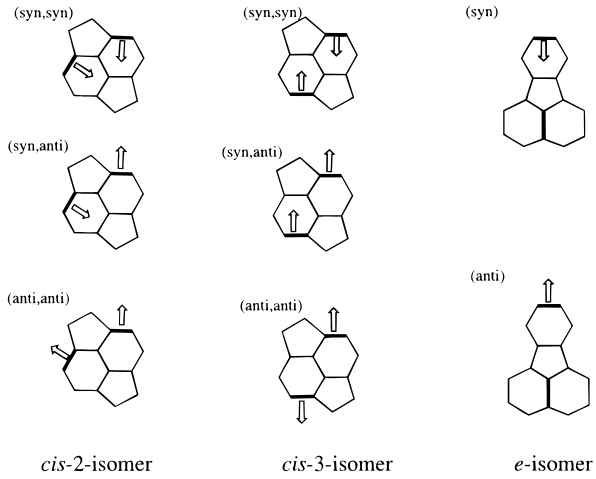


Figure 4. Possible conformers for each of the *cis*-2-, *cis*-3-, and *e*-bisadducts.

the case of $n = 2$ and 3, the steric energies of the m-form are less than those of the n-form, especially in $n = 2$ as shown in Table 3.

For **6a**,**b**, the distinction between the m- and n-form of *cis*-3 could not be achieved by NMR spectroscopy. The MM2 calculations, however, clearly indicate that the m-form[11] is much more favorable than the n-form by more than 30 kcal/mol. Therefore, bisadducts **6a**,**b** were concluded to be the m-form of *cis*-3 as depicted in Scheme 2.

In contrast with **5a**,**b** and **6a**,**b**, product **7** gave 59 signals of sp^2 carbons of the fullerene moiety and the benzene rings in the ^{13}C NMR spectrum and two sets of aromatic signals (6 signals) in the ^{1}H NMR spectrum. Therefore, bisadduct **7** should have C_1 symmetry. This is also compatible with the fact that **7** was resolved into two peaks on the chiral HPLC (Figure 2c and Table 1). Among the four bisadducts (o-form of *cis*-2, o-form of *cis*-3, and m- and n-forms of *e*) with C_1 symmetry (Figure 1), an *e*-isomer (m- or n-form) seems to be the most appropriate for **7**, according to the absorption spectrum. As shown in Figure 3, the spectrum of **7** is obviously different from those of **5a** and **6a**, indicating that **7** should be neither *cis*-2 nor *cis*-3, but *e*-isomer. Furthermore, the rather sharp band around 420 nm in **7**, in agreement with that of the *e*-bisadducts reported by Diederich et al.,[6] supports the *e*-bisaddition. Among the two forms (m or n) of the *e*-isomer, the m-form is much more suitable than the n-form because of the extremely larger steric energy of the latter.

The two isomers (o-form of *cis*-2 and *cis*-3) that were excluded above according to the absorption spectra seem to be inappropriate also on the basis of the ^{1}H NMR spectra. Since the C3 and C6 protons of **7** hardly suffer from steric compression unlike **5a**,**b**, the o-form of the *cis*-2-isomer is not suitable for **7**. In the o-form of *cis*-3-isomer, there should be two methylene protons which face the opposite benzene ring and resonate at higher fields than the other methylene protons, as recognized in **6a**,**b** (at δ 3.40 and 3.49, compared with those of **5a**,**b** at δ 3.78 and 3.82). In fact, only one proton was found to be shifted to a considerably high field at δ 3.11, in agreement with the structure of the m-form of the *e*-isomer: i.e., the calculated structure of the m-form indicates that the proton is located just above the center of the benzene ring apart by ca. 4 Å (see structure **7** in Scheme 2). It suggests a high-field shift by the extent of 0.4 ppm.[18] Consequently, product **7** is concluded to be the m-form of the *e*-bisadduct, depicted in Scheme 2.

(18) Bovey, F. A.; Jelinski, L.; Mirau, P. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, 1988; p 110.

Table 3. Steric Energies (kcal/mol) in *syn*,*syn*- or *syn*-Conformation of Each Form of *cis*-2-, *cis*-3-, and *e*-Isomers Obtained by Addition of **1** ($n = 2-5$)[a]

	cis-2-isomer			*cis*-3-isomer			*e*-isomer
n	m-form (C_s)	n-form (C_s)	o-form (C_1)	m-form (C_2)	n-form (C_2)	o-form (C_1)	m-form (C_1)
2	233	258	242	230	269	240	242
3	229	236	239	227	261	240	242
4	236	238	236	232	253	235	234
5	238	245	240	235	255	234	234

[a] Steric energies for the most stable conformation. Values with lower steric energies are underlined.

Moreover, *e*-bisadducts seem to be kinetically much more accessible than the *cis*-3 ones, according to the experiments and calculations by Hirsch et al.[2c]

In contrast to the cyclic fullerene adducts **5a**,**b**, **6a**,**b**, and **7**, the ^{1}H NMR spectra of acyclic products **8**, **9**, and **10** were found to be extremely broadened at room temperature, indicating the flipping motion of the cyclohexene rings brought about by the loss of the chain, though the motion is relatively slow compared with the NMR time scale. Thus, their NMR spectra were measured above room temperature. At 120 °C in DMSO-d_6, both ^{1}H and ^{13}C NMR spectra gave sufficiently sharp signals. The number of signals in the ^{13}C NMR spectra of **8**, **9**, and **10** was almost the same as those of **5**, **6**, and **7**, respectively, except for the disappearance of the sp^3 carbons of the tether. This is also the case for the ^{1}H NMR spectra. Therefore, the symmetries in **5**−**7** are apparently maintained in **8**−**10**. The signals of the fullerene sp^2 carbons in **8**−**10** exhibited no appreciable shifts relative to those of **5**−**7**. These observations undoubtedly indicate that, in the transformation of **5**−**7** to **8**−**10**, only the cleavage of the tether took place without any rearrangement.

The absorption spectra of **8**, **9**, and **10** are in good agreement with those of **5**, **6**, and **7**, respectively, demonstrating the preservation of each fullerene skeleton. The formation of acyclic **8**−**10** was also confirmed by the appearance of a broad band around 3400 cm^{-1} in the IR spectra, corresponding to the O−H stretching. Naturally, the ^{1}H NMR, IR, and UV−vis spectra of **8** (or **9**) obtained from **5a** and **5b** (or **6a** and **6b**) with the different tether length were superimposable on each other, suggesting the formation of the identical compounds from different precursors.

Conclusion

The selective synthesis of [60]fullerene bisadducts was successfully carried out by the reaction of [60]fullerene and the compounds, where two α,α′-dibromo-*o*-xylene moieties were connected by an oligomethylene chain (−(CH$_2$)$_n$−, $n = 2-5$). By this method, *cis*-2- and *cis*-3-bisadducts were selectively obtained when $n = 2$ and 3 but only one *e*-bisadduct with $n = 5$. The selectivities are concluded to result from the subtle balance of stereochemical and electronic effects, because such high selectivity is usually not accomplished in the absence of the chain.[19] The cleavage of the oligomethylene chain in the obtained bisadducts gave the corresponding [60]fullerene derivatives possessing two phenol moieties. The structures of these [60]fullerene derivatives were determined by ^{1}H NMR, ^{13}C NMR, IR, UV−vis, and mass spectroscopy. The UV−vis spectra of *cis*-2-, *cis*-3-, and *e*-bisadducts were remarkably different from each other. Thus, the positions of bisaddition within one hemisphere are readily discernable, unless other large chromophores are attached to the fullerene.

Many chiral fullerene derivatives have been reported with chiral substituents.[20] There are, however, only a few examples of chiral derivatives with achiral substituents; i.e., Hawkins, Meyer, and Nambu reported chiral *trans*-2 and *trans*-3 osmium bisadducts with achiral ligands.[21] Recently, Nakamura and his co-workers reported the synthesis of one chiral *cis*-3-bisadduct enantiomer with an achiral substituent.[22] They reported its optical rotation of −1872°, which is as large as those of **6**. Further detailed comparison of circular dichroism spectra among independently synthesized chiral bisadducts can determine the absolute configuration of these interesting bisadducts.

These stereochemically well-defined [60]fullerene bisphenol adducts obtained are applicable to further transformations,[23] by taking advantage of their high reactivity. For example, it seems to be of great interest and importance to transform them into bioactive compounds,[24,25] electrolytes or functional dyes,[26] pearl-necklace shaped [60]fullerene polymers,[19] and so forth.

Experimental Section

General. FAB mass spectra were taken by a Jeol JMS-MStation. The elemental analysis was performed at the Technical Research Center of Instrumental Analysis, Gunma University. NMR spectra were recorded on a Jeol α-500 FT NMR spectrometer with tetramethylsilane as an internal standard. IR spectra were taken on a JASCO FT-IR 5300 spectrophotometer. Chiral HPLC was carried out by using a Shimadzu LC-6A HPLC apparatus (CHIRALCEL OD from Daicel Chemical Ind. Co., 15 μm, hexane/2-propanol). Absorption spectra were recorded on a JASCO Ubest-50 or a Hitachi U3210 spectrophotometer. The optical rotation $[\alpha]_D$ was measured by a JASCO DIP370 polarimeter. The MM2 calculation was performed by Chem3D. Benzene, toluene, and tetrahydrofuran (THF) were distilled over sodium after prolonged heating. Other materials and reagents were commercially available and used without further purification. Fullerene was isolated from soot and purified by the reported method.[27]

Preparation of Precursor 1b (General Procedure). A mixture of dimethyl 4-hydroxyphthalate (10.5 g, 50 mmol), 1,3-propanediol ditosylate[28] (6.5 g, 17 mmol), and potassium fluoride (3.1 g, 53 mmol) in acetonitrile (300 mL) was refluxed for a week under a nitrogen atmosphere. It was concentrated under reduced pressure to give a slurry residue, which was extracted with benzene. The benzene extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure. Purification by column chromatography (hexane/AcOEt = 2:1) gave 4.1 g (53% yield) of desired phenoxy ether **3b**.

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To a suspension of LAH (1.3 g, 34 mmol) in dry THF (400 mL) was added **3b** (1.8 g, 3.9 mmol) dissolved in dry THF (200 mL) under reflux. The mixture was refluxed overnight under a nitrogen atmosphere. After the mixture was cooled to 0 °C, ice water was carefully added dropwise. After gas evolution had ceased, the solution was poured onto iced 10% hydrochloric acid (200 mL) and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure, giving 1.1 g (78% yield) of white fine powdered 1,3-bis(3,4-bis(hydroxymethyl)phenoxy)-propane (**4b**), which was subjected to the next reaction without further purification.

Excess PBr_3 (2.2 mL, 23 mmol) in toluene (80 mL) was added dropwise to a solution of **4b** (0.50 g, 1.4 mmol) in toluene (180 mL) under a nitrogen atmosphere. The mixture was stirred overnight at room temperature, poured onto ice water (300 mL), and extracted with toluene. The toluene extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure to give 0.73 g (84% yield) of **1b** as a white powder, which was subjected to the next reaction without further purification.

Spectroscopic data of tetraols **4** and tetrabromides **1** are given below:

4a: ^{1}H NMR (acetone-d_6) δ 7.34 (2H, d, J = 8.2 Hz), 7.06 (2H, d, J = 2.8 Hz), 6.84 (2H, dd, J = 8.3 and 2.8 Hz), 4.67 (4H, s), 4.59 (4H, s), 4.36 (4H, s). Anal. Calcd for $C_{18}H_{22}O_4$: C, 64.66; H, 6.63. Found: C, 64.44; H, 6.65.

4b: ^{1}H NMR (DMSO-d_6) δ 7.22 (2H, d, J = 8 Hz), 6.99 (2H, d, J = 3 Hz), 6.77 (2H, dd, J = 8 and 3 Hz), 5.07 (2H, t, J = 5 Hz), 4.90 (2H, t, J = 5 Hz), 4.50 (4H, d, J = 5 Hz), 4.42 (4H, d, J = 5 Hz), 4.10 (4H, t, J = 6 Hz), 2.15 (2H, m). Anal. Calcd for $C_{19}H_{24}O_4$: C, 65.50; H, 6.94. Found: C, 65.50; H, 6.91.

4c: ^{1}H NMR (DMSO-d_6) δ 7.21 (2H, d, J = 8.2 Hz), 6.97 (2H, d, J = 2.8 Hz), 6.75 (2H, dd, J = 8.2 and 2.8 Hz), 5.06 (2H, t, J = 5 Hz), 4.91 (2H, t, J = 5 Hz), 4.51 (4H, d, J = 5 Hz), 4.42 (4H, d, J = 5 Hz), 4.00 (4H, m), 1.85 (4H, m). Anal. Calcd for $C_{20}H_{26}O_4 \cdot 0.25H_2O$: C, 65.51; H, 7.22. Found: C, 65.58; H, 7.28.

4d: ^{1}H NMR (DMSO-d_6) δ 7.21 (2H, d, J = 8 Hz), 6.96 (2H, d, J = 3 Hz), 6.74 (2H, dd, J = 8 and 3 Hz), 5.06 (2H, t, J = 5 Hz), 4.90 (2H, t, J = 5 Hz), 4.51 (4H, d, J = 5 Hz), 4.42 (4H, d, J = 5 Hz), 3.96 (4H, t, J = 6 Hz), 1.76 (4H, m), 1.55 (2H, m). Anal. Calcd for $C_{21}H_{28}O_4$: C, 67.00; H, 7.50. Found: C, 67.06; H, 7.37.

1a: ^{1}H NMR ($CDCl_3$) δ 7.30 (2H, d, J = 8 Hz), 6.96 (2H, d, J = 3 Hz), 6.87 (2H, dd, J = 8 and 3 Hz), 4.66 (4H, s), 4.62 (4H, s), 4.33 (4H, s); MS (m/z) 585 (M^+), 583, 508, 506, 504, 502.

1b: ^{1}H NMR ($CDCl_3$) δ 7.28 (2H, d, J = 8 Hz), 6.91 (2H, d, J = 3 Hz), 6.83 (2H, dd, J = 8 and 3 Hz), 4.65 (4H, s), 4.60 (4H, s), 4.16 (4H, t, J = 6), 2.26 (2H, m).

1c: ^{1}H NMR ($CDCl_3$) δ 7.28 (2H, d, J = 8 Hz), 6.89 (2H, d, J = 3 Hz), 6.81 (2H, dd, J = 8 and 3 Hz), 4.66 (4H, s), 4.61 (4H, s), 4.04 (4H, m), 1.97 (4H, m).

1d: ^{1}H NMR ($CDCl_3$) δ 7.27 (2H, d, J = 8 Hz), 6.90 (2H, d, J = 3 Hz), 6.81 (2H, dd, J = 8 and 3 Hz), 4.65 (4H, s), 4.61 (4H, s), 3.99 (4H, t, J = 6 Hz), 1.84 (4H, m), 1.65 (2H, m); MS (m/z) 550, 548, 546, 481, 469, 467, 465.

Formation of Bisadduct 7 (General Procedure). To a boiling toluene solution (350 mL) of [60]fullerene (0.145 g, 0.202 mmol), potassium iodide (0.33 g, 2.0 mmol), and 18-crown-6 (2.1 g, 7.9 mmol) was added dropwise **1d** (0.140 g, 0.223 mmol) dissolved in toluene (300 mL) under a nitrogen atmosphere. The mixture was refluxed for 15 h, cooled to room temperature, poured onto iced 10% NaOH aqueous solution (500 mL), and extracted with toluene. The extracts were washed with water and dried over sodium sulfate. After insoluble materials were removed by filtration, the solvent was removed under reduced pressure. The purification of the reaction mixture by column chromatography on silica gel (benzene/hexane) afforded desired bis-adduct **7** (61.5 mg, 30% isolated yield).

Spectroscopic data are given below:

5a: R_f 0.59 (benzene); ^{1}H NMR ($CDCl_3$) δ 7.84 (2H, d, J = 2.5 Hz), 7.30 (2H, d, J = 7.9 Hz), 7.02 (2H, dd, J = 7.9 and 2.5 Hz), 4.87 (2H, m), 4.62 (2H, d, J = 14.3 Hz), 4.31 (2H, m), 4.09 (2H, d, J = 13.2 Hz), 4.06 (2H, d, J = 13.4 Hz), 3.79 (2H, d, J = 13.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.98, 158.84, 158.79, 149.70, 149.34, 149.06, 147.67, 147.25, 147.16, 146.90, 146.47, 145.81, 145.78, 145.72, 145.35, 145.27, 145.21, 145.02, 144.97, 144.56, 144.42, 144.38, 143.59, 142.66, 141.68, 141.31, 139.27, 138.01, 133.53, 132.63, 132.03, 131.68, 128.68, 128.33, 118.92, 116.47, 70.05, 63.75, 63.01, 43.76, 43.38; FAB/FD MS (m/z) 986 (M^+), 987 ($M + H)^+$; UV−vis (cyclohexane, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 445.6 (4400), 372.4 (1400), 309.2 (40 000), 253.6 (87 000).

5b: R_f 0.48 (benzene); ^{1}H NMR ($CDCl_3/CS_2$) δ 7.44 (2H, d, J = 2.2 Hz), 7.27 (2H, d, J = 8.2 Hz), 6.96 (2H, dd, J = 8.1 and 2.3 Hz), 4.63 (2H, m), 4.61 (2H, d, J = 14.4 Hz), 4.33 (2H, m), 4.02 (2H, d, J = 14.3 Hz), 3.99 (2H, d, J = 14.7 Hz), 3.80 (2H, d, J = 14.0 Hz), 2.49 (1H, m), 1.90 (1H, m); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 160.64, 158.97, 156.80, 149.49, 149.15, 148.86, 147.51, 147.25, 147.16, 147.02, 146.72, 146.23, 145.86, 145.56, 145.53, 145.17, 145.03, 144.89, 144.80, 144.77, 144.55, 144.33, 144.24, 143.64, 142.58, 141.51, 141.19, 138.45, 138.43, 133.26, 132.56, 131.26, 130.24, 128.66, 117.89, 113.67, 65.28, 63.19, 62.40, 44.11, 43.50, 26.59; FAB/FD MS (m/z) 1000 (M^+), 1001 ($M + H)^+$.

6a: R_f 0.81 (benzene); ^{1}H NMR ($CDCl_3$) δ 7.26 (2H, d, J = 8.0 Hz), 7.02 (2H, dd, J = 8.0 and 2.5 Hz), 6.94 (2H, d, J = 2.5 Hz), 4.70 (2H, m), 4.60 (2H, m), 4.39 (2H, d, J = 13.4 Hz), 4.02 (2H, d, J = 13.4 Hz), 3.95 (2H, d, J = 13.3 Hz), 3.41 (2H, d, J = 13.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.01, 154.25, 150.87, 149.53, 149.18, 149.02, 148.60, 148.07, 147.46, 146.56, 146.19, 146.15, 145.94, 145.39, 144.86, 144.61, 143.09, 142.29, 141.96, 141.89, 141.72, 141.46, 140.00, 139.14, 138.08, 136.17, 135.02, 133.29, 131.46, 128.80 (bd), 128.42, 117.15 (bd), 114.66 (bd), 72.20, 65.11, 60.93, 43.72, 42.95; FAB MS (m/z) 986 (M^+), 987 ($M + H)^+$; UV−vis (cyclohexane, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 740.0 (680), 728.4 (580), 667.2 (730), 394.4 (8300), 260.4 (100 000).

6b: R_f 0.72 (benzene); ^{1}H NMR ($CDCl_3$) δ 7.27 (2H, d, J = 7.6 Hz), 6.99 (2H, dd, J = 8.0 and 2.4 Hz), 6.85 (2H, d, J = 2.4 Hz), 4.72 (2H, m), 4.34 (2H, d, J = 13.4 Hz), 4.11 (2H, m), 4.00 (2H, d, J = 13.7 Hz), 3.99 (2H, d, J = 13.7 Hz), 3.50 (2H, d, J = 13.7 Hz), 2.28 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.49, 154.39, 151.13, 149.55, 149.19, 148.74, 148.03, 146.23, 145.99, 145.52, 145.46, 144.98, 144.76, 142.29, 142.05, 141.92, 141.76, 141.15, 139.96, 138.91, 138.13, 136.44, 134.32, 130.17, 129.18, 128.77, 128.32, 117.93, 116.80, 112.40, 64.64, 63.13, 60.57, 43.47; FAB/FD MS (m/z) 1000 (M^+), 1001 ($M + H)^+$.

7: R_f 0.64 (benzene); ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, d, J = 8.2 Hz), 7.27 (1H, d, J = 7.9 Hz), 6.94 (1H, dd, J = 8.2 and 2.7 Hz), 6.84 (1H, dd, J = 8.1 and 2.6 Hz), 6.78 (1H, d, J = 2.8 Hz), 6.63 (1H, d, J = 2.8 Hz), 4.50 (1H, d, J = 12.8 Hz), 4.45 (1H, d, J = 12.8 Hz), 4.24 (2H, m), 4.20 (1H, d, J = 13.4 Hz), 4.17 (1H, d, J = 13.4 Hz), 4.07 (2H, m), 3.90 (1H, d, J = 13.1 Hz), 3.87 (1H, d, J = 13.4 Hz), 3.86 (1H, d, J = 12.8 Hz), 3.10 (1H, d, J = 13.4 Hz), 1.89 (1H, m), 1.76 (1H, m), 1.62 (1H, m), 1.25−1.48 (3H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.90, 160.65, 156.94, 156.57, 155.55, 155.09, 154.98, 154.70, 154.56, 154.25, 150.08, 149.11, 149.02, 148.32, 148.05, 147.94, 147.90, 147.78, 147.33, 147.12, 147.09, 146.41, 145.86, 145.78, 145.60, 145.44, 145.12, 144.79, 144.70, 144.55, 144.49, 144.43, 144.40, 144.06, 143.46, 143.39, 142.95, 142.90, 142.76, 142.48, 142.38, 142.03, 141.98, 141.95, 141.56, 141.04, 140.84, 140.13, 140.10, 139.93, 139.77, 139.28, 136.27, 136.13, 136.02, 135.68, 135.55, 130.38, 129.73, 129.70, 128.15, 116.80, 116.19, 110.77, 110.19, 66.92, 65.95, 65.76, 64.73, 64.43, 48.18, 45.99, 43.34, 42.24, 27.73, 25.69, 20.66; FAB MS (m/z) 1028 (M^+), 1029 ($M + H)^+$; UV−vis (cyclohexane, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 423.2 (4500), 396.4 (5000), 318.0 (32 000).

11: R_f 0.88 (benzene), 0.52 (benzene:hexane = 1:1); ^{1}H NMR ($CDCl_3/CS_2$) δ 7.56 (1H, d, J = 8.2 Hz), 7.22 (1H, bs, J = 2.2 Hz), 7.06 (1H, dd, J = 8.3 and 2.5 Hz), 4.80 (2H, d, broad), 4.76 (2H, d, broad), 4.38 (4H, d, broad), 3.95 (3H, s); ^{13}C NMR ($CDCl_3/CS_2$, 125 MHz) δ 159.40, 156.48 (broad), 147.58, 147.57, 146.39, 146.37, 146.14 (broad), 145.40 (broad), 145.36, 144.63, 144.61, 142.99, 142.49, 142.15, 142.11, 141.98 (broad), 141.60 (broad), 140.1 (broad), 139.11, 129.98, 128.74, 113.75, 112.95, 66.05, 65.69, 55.23, 45.41, 44.38; FAB MS (m/z) 854 (M^+).

Synthesis of 10 (General Procedure). Bisadduct **7** (61.5 mg, 0.0598 mmol) was dissolved in dry benzene (20 mL) in a flask, which was sealed with a septum under a nitrogen atmosphere. The system was allowed to stand at ice-bath temperature, and then excess boron tribromide (0.2 mL, 2.3 mmol) was added through the septum by a hypodermic syringe. The mixture was stirred overnight, brought from

0 °C to room temperature, and carefully quenched by the addition of 10 mL of ice water. It was then extracted with ethyl acetate. The extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure to give the target molecule **10** in quantitative yield.

Spectroscopic data are given below:

8: R_f 0.13 (benzene:AcOEt = 9:1); ^{1}H NMR (DMSO-d_6 at 120 °C) δ 7.20 (2H, d, J = 2.1 Hz), 7.18 (2H, d, J = 7.9 Hz), 6.78 (2H, dd, J = 8.1 and 2.3 Hz), 4.36 (4H, s, broad), 4.11 (2H, d, broad), 3.91 (2H, d, broad); ^{13}C NMR (DMSO-d_6 at 120 °C, 125 MHz) δ 161.06, 159.06, 156.16, 148.51, 148.17, 147.85, 147.60, 146.71, 146.29, 146.14, 145.79, 145.67, 145.27, 144.66, 144.49, 144.41, 144.17, 144.01, 143.73, 143.41, 143.35, 143.05, 142.79, 142.00, 140.67, 140.00, 137.25, 132.43, 131.69, 127.73, 127.55, 127.04, 115.13, 113.87, 63.07, 61.40, 42.84, 41.52; FD MS (m/z) 960 (M^+); UV−vis (cyclohexane:2-propanol = 1:1, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 445.2 (4200), 371.6 (11 000), 308.4 (30 000), 252.8 (67 000).

9: R_f 0.50 (benzene:AcOEt = 9:1); ^{1}H NMR (DMSO-d_6 at 120 °C) δ 7.29 (2H, d, J = 8.0 Hz), 6.88 (2H, d, J = 2.3 Hz), 6.85 (2H, dd, J = 8.0 and 2.5 Hz), 4.26 (2H, d, broad), 4.16 (2H, d, broad), 3.99 (2H, d, broad), 3.77 (2H, d, broad); ^{13}C NMR (DMSO-d_6 at 120 °C, 125 MHz) δ 156.95, 154.68, 152.28, 150.64, 149.46, 149.21, 148.71, 147.86, 147.46, 146.41, 146.05, 146.03, 145.87, 145.77, 145.61, 145.21, 145.18, 144.73, 142.36, 142.02, 141.72, 141.62, 141.22, 139.73, 138.63, 138.02, 136.73, 134.79, 133.49, 129.28, 128.75, 116.06, 114.79, 65.29, 61.07, 43.24, 42.85; FD MS (m/z) 960 (M^+); UV−vis (cyclohexane:2-propanol = 1:1, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 738.8 (460), 666.0 (570), 394.0 (7000), 260.0 (74 000).

10: R_f 0.28 (benzene:AcOEt = 9:1); ^{1}H NMR (DMSO-d_6 at 120 °C) δ 7.34 (1H, d, J = 8.4 Hz), 7.33 (1H, d, J = 8.4 Hz), 6.99 (1H, d, J = 2.4 Hz), 6.90 (1H, d, J = 2.4 Hz), 6.85 (1H, dd, J = 8.1 and 2.6 Hz), 6.82 (1H, dd, J = 8.3 and 2.5 Hz), 4.18 (6H, broad), 3.91 (2H, broad); ^{13}C NMR (DMSO-d_6 at 120 °C, 125 MHz) δ 161.63, 161.61, 156.28, 156.24, 155.66, 155.52, 155.38, 155.37, 155.31, 154.35, 154.25, 153.59, 149.48, 148.08, 148.06, 147.15, 147.13, 147.09, 147.04, 147.01, 146.26, 146.24, 145.94, 145.65, 145.63, 145.41, 144.86, 144.10, 143.88, 143.78, 143.73, 143.56, 143.50, 142.65, 141.95, 141.53, 140.79, 140.74, 140.45, 140.43, 139.98, 139.84, 139.82, 138.45, 137.97, 136.72, 136.66, 135.18, 135.16, 133.84, 133.80, 127.85, 127.76, 127.57, 114.41, 114.37, 113.88, 113.79, 64.68, 64.40, 64.24, 63.76, 46.16, 44.26, 43.79, 42.88, 42.52; FD MS (m/z) 960 (M^+); UV−vis (cyclohexane:2-propanol = 1:1, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 422.8 (3800), 396.0 (4500), 315.6 (27 000).

12: R_f 0.61 (benzene:AcOEt = 9:1), ^{1}H NMR (toluene-d_8 at 75 °C) δ 7.16 (1H, d, J = 8.3 Hz), 6.70 (1H, d, J = 2.5 Hz), 6.57 (1H, dd, J = 8.1 and 2.6 Hz), 4.18 (4H, broad); ^{13}C NMR (toluene-d_8 at 75 °C, 125 MHz) δ 157.05, 156.30, 148.02, 148.01, 146.84, 146.83, 146.59, 146.13, 145.81, 145.71 (broad), 145.08, 145.06, 143.48, 142.95, 142.66, 142.62, 142.43, 141.98, 140.54, 139.76, 130.36, ca.128, 115.46, 114.93, 66.63, 66.23, 45.59, 44.73; FAB MS (m/z) 840 (M^+).

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