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Regioselective Synthesis and Properties of Novel [60]Fullerene Bisadducts Containing a Dibenzocrown Ether Moiety

Yosuke Nakamura, Aya Asami, Toshio Ogawa, Seiichi Inokuma, and
Jun Nishimura*

*Contribution from the Department of Chemistry, Gunma University, Tenjin-cho,
Kiryu, Gunma 376-8515, Japan*

Received January 25, 2002

Abstract: The reactions of [60]fullerene with bis-*o*-quinodimethane precursors **3**, **4**, and **5** containing a dibenzo-18-crown-6, 24-crown-8 and 30-crown-10 moiety, respectively, were investigated. Both **3** and **4** provided *trans*-4 bisadducts **6a** and **7a**, respectively, as major product, though the selectivity in the latter was lower than that in the former. As minor product, **6b** (*cis*-2) was produced from **3**, while **7c** (*e*) as well as **7b** (*cis*-2) were produced from **4**. Precursor **5** exclusively afforded *e* bisadduct **8** without any other regioisomers. These bisadducts showed different ionophoric properties from one another; for instance, **6a** and **7b** exhibited a high complexing ability toward the K^+ ion, while **6b** hardly showed complexation with any alkali metal ions. The selectivity coefficients ($K_{\mathrm{Na,K}}^{\mathrm{pot}}$) of **6a** and **7b** toward K^+ over Na^+ ion, determined with an ion-selective electrode, were much higher than that of dibenzo-18-crown-6.

Introduction

Multiple adducts toward [60]fullerene have become of increasing interest from the viewpoints of spectroscopic,[1] electrochemical,[2] and chiroptical properties.[3] Even in the bisaddition reactions occurring exclusively at [6,6]-junctions, however, eight regioisomers are theoretically possible. Although a series of bisadduct regioisomers were successfully isolated and characterized for some typical reactions, such as Bingel reaction,[4] Prato reaction,[5] Diels−Alder reaction with *o*-quinodimethane,[6] and [2 + 2] cycloaddition by benzyne,[7] the second addition processes proceeded with insufficient regioselectivity. In combination with theoretical calculations, these reactions were found to be controlled kinetically rather than thermodynamically; the regioisomer distribution of bisadducts was qualitatively correlated with the coefficients of frontier orbitals in the corresponding monoadducts.[4]

To overcome such low regioselectivity, several research groups independently developed a synthetic methodology for controlling multiple additions efficiently, using tethers as covalent templates.[8] This method enabled the formation of bisadducts that would be difficult to obtain without suitable tethers. Diederich et al. achieved possible bisaddition patterns except for *cis*-1 by utilizing Bingel reaction.[9] We have succeeded in the regioselective synthesis of [60]fullerene−*o*-quinodimethane bisadducts modified within one hemisphere of [60]fullerene by connecting the two precursors with a single oligomethylene linkage; **1a** ($n = 2$) and **1b** ($n = 3$) provide the *cis*-2 and *cis*-3 isomers, while **1c** ($n = 5$) exclusively the *e* isomer.[10] This regioselectivity is apparently derived from the constrained distance between the two reactive species, governed by the oligomethylene linkage. Precursor **2** possessing a more flexible oligooxyethylene linkage than the pentamethylene linkage of

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* Corresponding author. E-mail: nisimura@chem.gunma-u.ac.jp.

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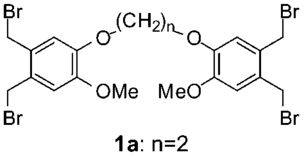
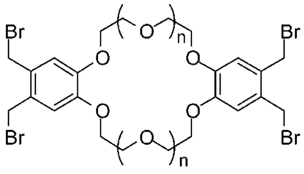
1c afforded *e* and *cis*-2 isomers.[11] The formation of the *cis*-2 isomer, which was not obtained from **1c**, is ascribed to the increased flexibility in bridging linkage of **2** due to the C−O ether bond.

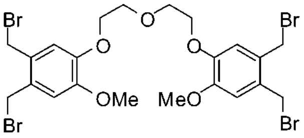
For the improvement of regioselectivity, we have also designed the reaction of dibenzocrown ether derivatives such as **3**−**5**. These macrocyclic moieties, which can serve as double bridging linkages connecting two *o*-quinodimethane precursors, are expected to control the relative arrangement as well as distance between the reactive species, probably leading to the preferential addition at two [6,6]-sites located almost in parallel. Furthermore, the resulting bisadducts appear to display ionophoric properties different from dibenzocrown ethers themselves. In the preliminary communication, we reported the regioselectivity resulting from **3** possessing an 18-crown-6 moiety and the intriguing complexation behavior of the bisadducts obtained.[11] We have further examined the bisaddition reactions using **4** and **5** with a larger macrocycle. In this paper, we disclose the regioselectivity resulting from these tethers and various properties including complexation, electrochemical, and fluorescence emissive behaviors of resulting bisadducts. These investigations are expected to provide a guide for preparing specific bisadducts.



1a: n=2
1b: n=3
1c: n=5



3: n=1
4: n=2
5: n=3



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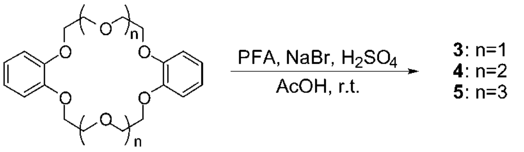

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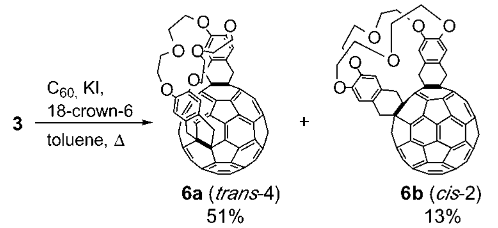

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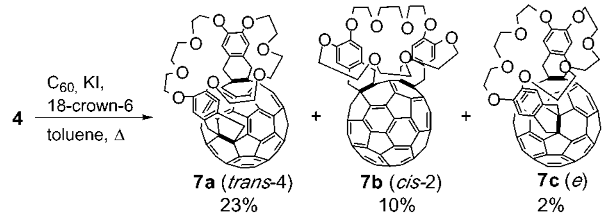

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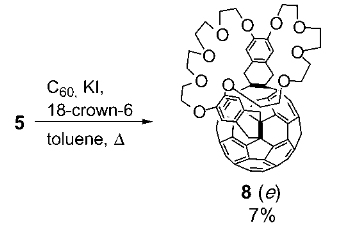

(4)

Results and Discussions

Preparation and Characterization of Bisadducts 6−8. Precursors **3**−**5** were prepared from commercially available corresponding dibenzocrown ethers by modifying the method in the literature (eq 1).[12]

Equimolar amounts of [60]fullerene and **3**−**5** were refluxed in toluene in the presence of KI and 18-crown-6 for 60 h under high-dilution conditions ($1-4 \times 10^{-4}$ M) (eqs 2−4). The color of the solution gradually changed from purple to brown, as the addition reaction toward [60]fullerene proceeded. In case of the reaction with **3**, purification of the reaction mixture by GPC (eluent; chloroform) gave an isomeric mixture of mainly two bisadducts **6a** and **6b** in 51 and 13% yields, respectively, which were successfully separated by preparative TLC (silica gel, chloroform/ethyl acetate). The reaction mixture obtained from **4** was purified by column chromatography (silica gel, chloroform/ethyl acetate), to give three bisadducts **7a**, **7b**, and **7c** in 23, 10, and 2% yields, respectively. Precursor **5** afforded a single bisadduct **8** in 7% yield, which was isolated by column chromatography. In all cases, insoluble oligomeric products were obtained besides the desired bisadducts and unreacted [60]fullerene, but they were not subjected to further purification and characterization.

The characterization of these bisadducts was established on the basis of mass, NMR, and UV−vis spectroscopies. Each of **6**−**8** indicated the molecular ion peak corresponding to the desired bisadduct in FAB- or APCI-mass spectra.

The ^{1}H NMR spectra of both **6a** and **6b** showed two aromatic proton peaks, apparently indicating C_2 or C_s symmetry. Their ^{13}C NMR spectra afford about 30 peaks of fullerene sp^2 carbons, supporting this symmetry. In the bisadducts obtainable from **3**−**5**, *cis*-3, *trans*-3, and *trans*-2 have C_2 symmetry, while *cis*-1, *cis*-2, *trans*-4 have C_s symmetry.[13] In **6b**, one of the aromatic proton peaks was resonated at much lower field (δ 7.58) than any aromatic protons in **6a**. Since this behavior is characteristic of *cis*-2 isomers due to steric compression as reported previously,[10] **6b** is reasonably assigned as the *cis*-2 isomer. The addition sites of **6a** could not be clarified by the NMR spectra alone. The UV−vis spectrum of **6a**, however, exhibits two broad maxima at 643 and 708 nm, which are characteristic of the *trans*-4 bisadduct as reported.[14] This addition pattern is compatible with the symmetry observed in the NMR spectra. The UV−vis spectrum of **6b**, similar to that of the *cis*-2 bisadduct from precursor **1a** or **1b**, supports the *cis*-2 bisaddition.

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(13) Although the total number of the [60]fullerene sp^2 carbon peaks is theoretically different in the case of C_2 (28 signals) and C_s (30 signals) symmetry, it was difficult to distinguish between C_2 and C_s due to the overlapping of some peaks.

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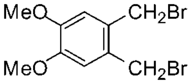
Table 1. Effect of Tethers on Regioselectivity



12

precursor	tether			bisadduct regioisomers obtained[c]	ref
	length[a]	flexibility[b]	framework		
1a	4	less	linear	*cis*-2 and *cis*-3	10
1b	5	less	linear	*cis*-2 and *cis*-3	10
1c	7	less	linear	*e*	10
2	7	more	linear	*e* and *cis*-2	11
3	7 × 2	more	cyclic (small)	*trans*-4 and *cis*-2	11 and this work
4	10 × 2	more	cyclic (medium)	*trans*-4, *cis*-2, and *e*	this work
5	13 × 2	more	cyclic (large)	*e*	this work
cf. **12**	∞	∞	none	*trans*-3, *e*, *trans*-2, *trans*-4, *cis*-2, *trans*-1, and *cis*-3	6

[a] Number of atoms constituting tether(s) between two *o*-quinodimethane moieties. [b] Flexibility of each tether is mentioned. [c] In the order of yields.

The regioisomers **7a**, **7b**, and **7c** with a 24-crown-8 moiety were identified in a manner similar to that mentioned above. The ^{1}H NMR spectral patterns of **7a** and **7b** were different from that of **7c**. The spectra of **7a** and **7b** showed two aromatic proton peaks that are resonated at fields similar to those for **6a** and **6b**, respectively, and that of **7c** showed four aromatic protons, indicating that **7a** and **7b** have C_2 or C_s and **7c** has C_1 symmetry. The symmetries in **7a** and **7b** were also confirmed by the ^{13}C NMR spectra, in which almost 30 peaks due to the fullerene sp^2 carbons are observed, although a well-defined ^{13}C NMR spectrum of **7c** was not obtained because of its poor yield and low symmetry. It is reasonable to assign **7c** as the *e* isomer because C_1 symmetry is accomplished only in the *e* isomer. In **7b**, the downfield shifted aromatic protons were again observed (δ 7.52), leading to the assignment as *cis*-2. The addition sites of **7a** were determined by its UV−vis spectrum; two characteristic broad bands were observed in the longer wavelength region similar to **6a**, resulting in the assignment as *trans*-4. The possibility of *trans*-3, *trans*-2, or *trans*-1 bisadducts was easily excluded, since these bisadducts are known to afford UV−vis spectra entirely different from that of **7a**, as reported from our group recently.[6] The UV−vis spectra of **7b** and **7c** also support the above assignments.

Bisadduct **8** bearing a further large dibenzo-30-crown-10 moiety was readily assigned as *e*, since the ^{1}H NMR spectrum reveals C_1 symmetry similar to **7c**. Its UV−vis spectrum is also characteristic of *e*-bisadducts.

The preferential formation of *trans*-4 bisadduct **6a** from **3**, in remarkable contrast with the formation of *e* bisadduct from **1c** or **2**, is quite reasonable, since the dibenzo-18-crown-6 moiety of **3** is expected to force the two *o*-quinodimethane precursors to be almost parallel. The two addition sites of *trans*-4 isomers are located almost parallel, whereas those of *e* isomers are perpendicular to each other. Thus, the *e*-bisaddition would significantly distort the crown ether moiety, becoming unfavorable relative to *trans*-4. According to the molecular mechanics calculations (MM2), the *e* isomer derived from **3** has a steric energy higher than the *trans*-4 isomer **6a** by more than 20 kcal/mol. Such a difference led to the selectivity for *trans*-4, though the *e* sites are known to be generally more reactive than the *trans*-4 sites.[4] Thus, the use of a crown ether unit as double bridging linkages proved to be effective for the regulation of relative arrangement of the two reactive species. The formation of *cis*-2 isomer **6b**, not the *cis*-3 isomer, is a seemingly unexpected result. The steric energy of the *cis*-3 isomer is as low as that of the *cis*-2 isomer and the two addition sites of *cis*-3 are situated almost parallel in contrast with the *cis*-2 isomer. The selectivity for the *cis*-2 isomer is probably derived from the higher reactivity at the *cis*-2 site than the *cis*-3 site in the second addition step; this reactivity is evidenced by the higher LUMO coefficients in typical [60]fullerene monoadduct determined by the MO calculations.[4]

The formation of **7a** and **7b** from **4** can be reasonably explained in a manner similar to that for **6a** and **6b**. However, the regioselectivity toward *trans*-4 over *cis*-2 is significantly low compared to that for **3**, though *trans*-4 still remains the major product. More surprisingly, a slight amount of *e* isomer **7c** was also produced. The reduced selectivity toward *trans*-4 is apparently attributed to the decrease in constraint between two *o*-quinodimethane species due to the enhancement of the crown ether ring; since the *cis*-2 and *e* sites are inherently more reactive than *trans*-4, the decreased constraint makes the formation of **7b** and **7c** relatively favorable. The observed isomer ratio seems to reflect the subtle balance between the reactivity of each [6,6]-junction and the steric effects resulting from bridging linkages.

Precursor **5** containing a dibenzo-30-crown-10 moiety led to the exclusive formation of *e* isomer **8** without other regioisomers. This selectivity resembles that provided by **1c** with a single linkage rather than **3** or **4** bearing a smaller crown ether moiety. Presumably, the crown ether ring of **5**, sufficiently large and flexible, operates as a single linkage, allowing the second addition to occur at the most reactive *e* position. The increase of size and flexibility in the crown ether moiety makes it difficult to regulate the relative arrangement of two reactive species and to control addition sites.

Table 1 summarizes the properties of tethers in **1**−**5** and the resulting regioselectivities. The result for the bisaddition without any tether, namely the reaction of [60]fullerene with 4,5-dimethoxy-*o*-quinodimethane generated from **12**,[6] is also listed for comparison. It is noteworthy that **3** and **4** afforded the *trans*-4 isomer, whose population would be rather low without appropriate tethers, as the major product.

Properties of Bisadducts 6−8

1. Complexation behavior: ESI-MS and Ion-Selective Electrode. The complexation of **6a**, **6b**, **7a**, or **7b** with alkali metal ions was investigated by ESI-MS in a positive ion mode.

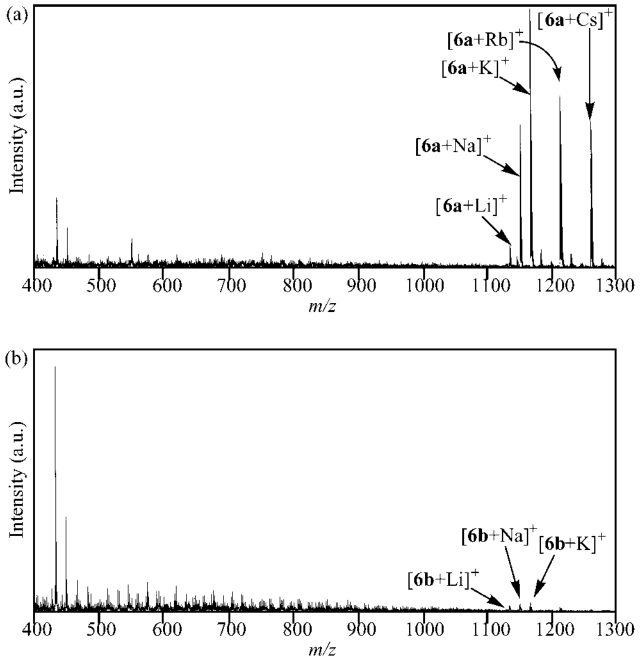


Figure 1. ESI-mass spectra of (a) **6a** and (b) **6b** in the presence of alkali metal ions. Solvent: $CHCl_3$/MeOH (1:1 (v/v)). Concentration: [**6**] = [Li^+] = [Na^+] = [K^+] = [Rb^+] = [Cs^+] = 0.1 mM.

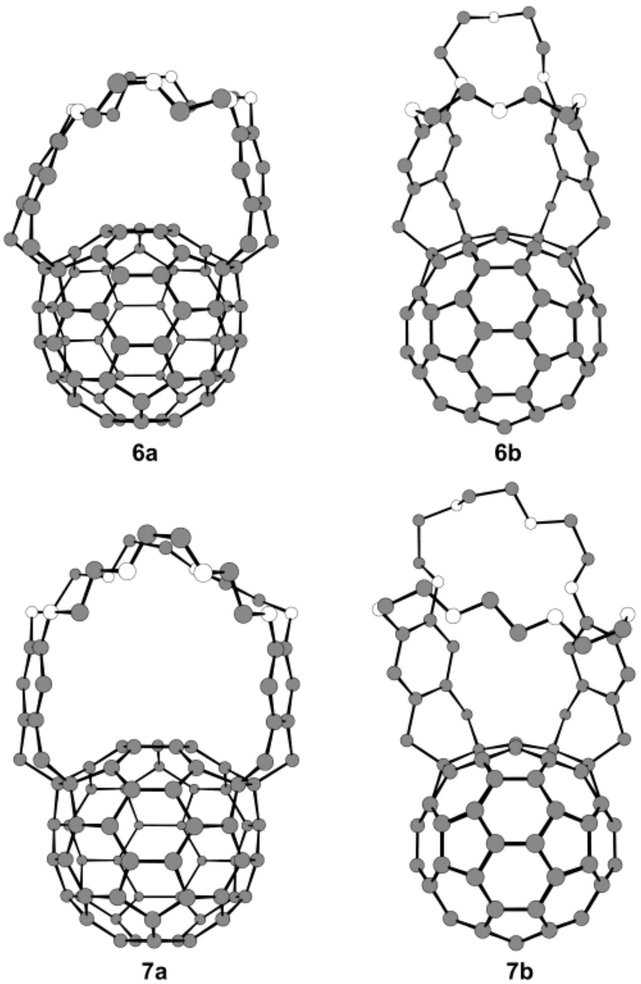


Figure 2. One of the optimized structures of **6a**, **6b**, **7a**, and **7b** by MM2 calculations. White circles denote oxygen atoms.

The mixed solution containing equimolar amounts of these fullerene bisadducts and $MClO_4$ ($M^+ = Li^+$, Na^+, K^+, Rb^+, and Cs^+) in methanol/chloroform (1:1) was subjected to ESI-MS.

The solution of **6a** and each alkali metal ion afforded the peak due to the [**6a** + M]$^+$ ion, implying the complexation with the alkali metal ion in a ratio of 1:1. To compare the complexing ability toward the respective alkali metal ions, the competition experiments with **6a** and all the alkali metal ions listed above were carried out. The peak of [**6a** + K]$^+$ was observed with the highest intensity as shown in Figure 1a, suggesting the highest selectivity of **6a** for K^+ ion. The peaks of [**6a** + Na]$^+$, [**6a** + Rb]$^+$, and [**6a** + Cs]$^+$ are detected with a comparable intensity, while that of the [**6a** + Li]$^+$ ion is extremely weak. On the other hand, **6b** showed only quite weak peaks of [**6b** + M]$^+$ with any alkali metal ions under similar conditions (Figure 1b). The difference in complexing ability between **6a** and **6b** can be readily explained by the difference in the shape of dibenzo-18-crown-6 moiety. According to the MM2 calculations (Figure 2), the dibenzo-18-crown-6 moiety in **6b** suffers from considerable deformation, which is apparently caused by the short distance and relative arrangement between the two addition sites (*cis*-2) that are not situated in parallel. Among the six ether oxygen atoms, one nonphenolic oxygen atom is significantly deviated from the other five that are almost on the same plane. Such an arrangement is unfavorable for complexation with any alkali metal ions. In **6a**, the two nonphenolic oxygen atoms are only slightly deviated from the other four, making the complexation feasible. Since these two oxygen atoms are mobile in contrast with the four phenolic oxygen atoms, the cavity size of the 18-crown-6 moiety is probably induced to fit the size of alkali metal ions. Although it is difficult to estimate the cavity size of **6a** in solution, **6a** is apt to have the most suitable size for the K^+ ion.

The competition experiments with **7a** and **7b** were also performed under conditions similar to those in **6a** and **6b**. As Figure 3a shows, **7a** affords all the peaks of [**7a** + M]$^+$ without sufficient selectivity, though the peak of [**7a** + Cs]$^+$ is the most intense. These results are apparently due to the larger cavity size of the crown ether moiety in **7a** than in **6a**. The enhancement of cavity size permitted the complexation with larger metal ions such as Cs^+, while the resultant increased flexibility of cavity brought about the lowering of selectivity. *cis*-2 Bisadduct **7b** also exhibits all the peaks, and the intensity of [**7b** + K]$^+$ is the highest (Figure 3b). This observation is considerably different from that for **6b**. The remarkable increase in the complexation ability of **7b** relative to **6b** is caused by the increased number of ether oxygen atoms. In the optimized structure of **7b** by MM2 calculations, two nonphenolic oxygen atoms are much apart from the cavity plane consisting of the other oxygen atoms, since the two phenolic oxygen atoms are located close to each other. Although this situation is similar to that in **6b**, **7b** has six ether oxygen atoms that can contribute to the complexation with metal ions. The size and geometry of cavity formed by these oxygen atoms must be suitable for capturing the K^+ ion.

The selectivity of **6a** and **7b** toward the K^+ over the Na^+ ion was further investigated with an ion-selective electrode. The selectivity coefficients ($K_{Na,K}^{pot}$), which correspond to the ability of the ion-selective electrode to distinguish between Na^+ and

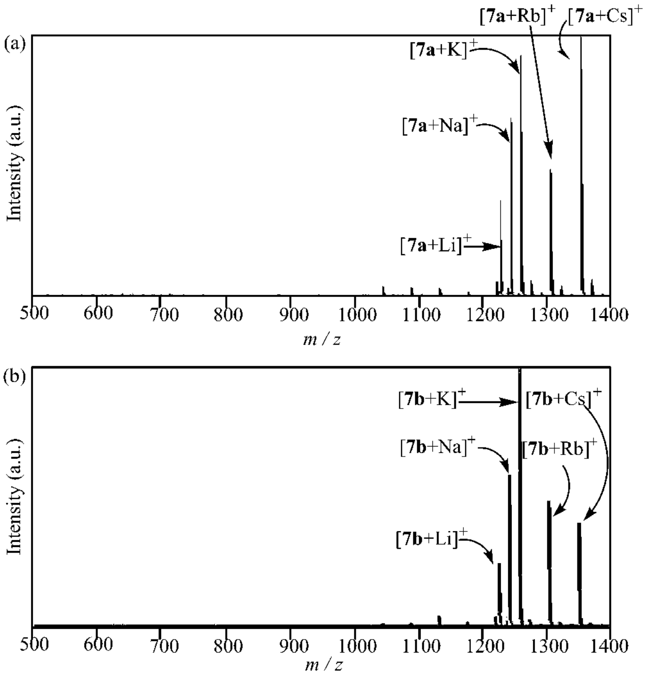


Figure 3. ESI-mass spectra of (a) **7a** and (b) **7b** in the presence of alkali metal ions. Solvent: $CHCl_3$/MeOH (1:1 (v/v)). Concentration: $[\mathbf{6}] = [Li^+] = [Na^+] = [K^+] = [Rb^+] = [Cs^+] = 0.1$ mM.

K^+ ions, were determined for the electrodes containing **6a**, **7b**, and dibenzo-18-crown-6 as a reference by the separate solution method.[15]

The $K_{Na,K}^{pot}$ values are calculated from eq 5,

$$K_{Na,K}^{pot} = (E_K - E_{Na})(Z_{Na}F)/2.303RT + (1 - Z_{Na}/Z_K) \log a_{Na} \quad (5)$$

where E is the obtained electromotive force (emf), Z is the charge on cations, F is the Faraday constant, R is the gas constant, T is the temperature, and a_{Na} is the activity of the Na^+ ion. Since Z_{Na} and Z_K are 1, eq 5 is simplified into eq 6.

$$K_{Na,K}^{pot} = (E_K - E_{Na})F/2.303RT \quad (6)$$

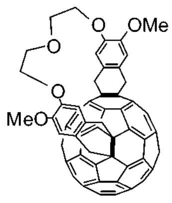
Thus, if E_{Na} and E_K are given at the same a values, the $K_{Na,K}^{pot}$ value can be obtained. By utilizing the E_{Na} and E_K values for the 0.1 M cation solutions (i.e. $a_{Na} = a_K = 0.1$), the $K_{Na,K}^{pot}$ values for **6a** and **7b** were determined as 42 and 49, respectively. Intriguingly, these values are much higher than that (=13) of dibenzo-18-crown-6 electrode, indicating the higher selectivity of **6a** and **7b** toward K^+. Such high selectivity suggests that the fullerene skeleton forces the ring size and/or geometry of crown ether moiety to be suited for the complexation with K^+ ion.

2. Electrochemical Properties. The electrochemical properties of **6a** were investigated by cyclic voltammetry (CV) in benzonitrile at room temperature. Since **6a** was found to form the K^+ complex, CV was performed in the presence of 1 equiv of [2.2.2]cryptand that is able to bind the K^+ ion. Two quasireversible waves were observed, assignable to the reduction of the C_{60} moiety, and the $E_{1/2}$ values are listed in Table 2. To analyze the effect of bisaddition patterns on the electrochemical properties, we have also determined the redox potentials of bisadducts **9a** (*e*) and **9b** (*cis*-2) obtained from **2**.[11] Their substituents, two dialkoxybenzene moieties, are regarded as comparable to those of **6a**. Both **9a** and **9b** afforded two reversible waves, whose potentials $E_{1/2}$ are quite similar to each other, as shown in Table 2. Table 2 also lists the $E_{1/2}$ values of [60]fullerene and monoadduct **10** measured under the same conditions for comparison. The $E_{1/2}$ values are obviously negative-shifted in the order of [60]fullerene, monoadduct **10**, and bisadducts (**6a**, **9a**, and **9b**) corresponding to the decrease of electron affinity. However, there is only a slight difference among the three bisadducts, suggesting that the electron affinity is not appreciably influenced by addition sites, at least for *cis*-2, *e*, and *trans*-4 isomers. Diederich et al. also reported that *trans*-1, -2, and -3 biscyclopropanated adducts afford $E_{1/2}$ values similar to one another.[9c]

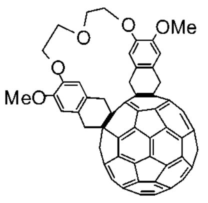
Table 2. Half-Wave Potentials of [60]Fullerene and Its Derivatives[a]

compd	E1	E2
C_{60}	−0.93	−1.35
10	−1.06	−1.47
6a[b]	−1.22	−1.66
9a	−1.22	−1.63
9b	−1.20	−1.59

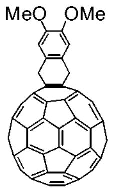
[a] V vs Fc/Fc^+. [b] Measured in the presence of 1 equiv of [2.2.2]cryptand.



9a (*e*)



9b (*cis*-2)



10

The CV of **6a** was also carried out in the presence of 10 equiv of KPF_6, to examine the effect of the K^+ ion. Addition of KPF_6 made the voltammogram quite irreversible with the potentials unchanged. The origin of this irreversibility is not clear, but it is probable that the K^+ ion interacts with the anion radical species generated during the redox process. Addition of excess [2.2.2]cryptand reproduced the original voltammogram observed in the absence of KPF_6, which indicates that the K^+ binding process with **6a** was reversible.

3. Fluorescence Spectra. We have reported the fluorescence spectra of three bisadduct regioisomers, *cis*-2, *cis*-3, and *e*, prepared from **1**; the *cis*-3 isomer (**11**) afforded a relatively distinct emission with a maximum at 745 nm, whereas *cis*-2 and *e* only gave quite weak and poorly resolved emission.[1d] These features were found to be dependent on addition patterns, almost independent of the substituents on the benzene rings. Thus, among the bisadducts obtained in the present study, the fluorescence spectrum of *trans*-4 isomer **6a** was measured in both cyclohexane and benzonitrile upon 400-nm excitation at room temperature (Figure 4). At this excitation wavelength, the C_{60} moiety of **6a** can be exclusively excited, to give the locally excited singlet state of the C_{60} moiety. In cyclohexane, **6a** affords a relatively well-defined emission, which appears to be the mirror image of the longest absorption band with an extremely small Stokes shift. These behaviors are similar to

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(15) Guilbault, G. G.; Durst, R. A.; Frant, M. S.; Freiser, H.; Hansen, E. H.; Light, T. S.; Pungor, E.; Rechnits, G.; Rice, N. M.; Rohm, T. J.; Simon, W.; Thomas, J. D. R. *Pure Appl. Chem.* **1976**, *48*, 129.

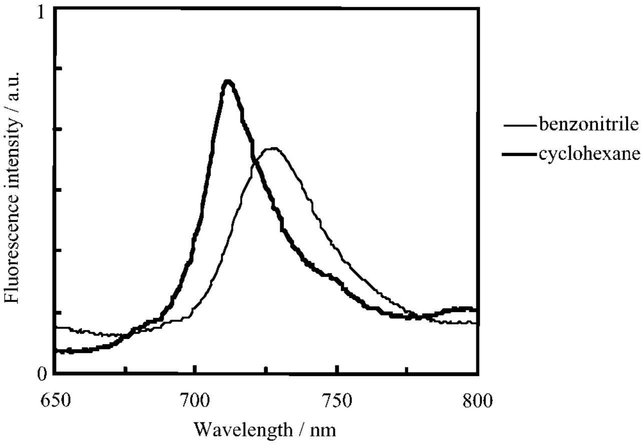
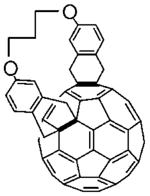


Figure 4. Fluorescence spectra of **6a** in cyclohexane and benzonitrile upon 400-nm excitation at room temperature.

those of **11**. The fluorescence intensity of **6a** is also comparable to that of **11**, although the precise quantum yield has not been determined. However, the maximum position in the fluorescence of **6a** (711 nm) is blue-shifted (ca. 30 nm) relative to that of **11**, corresponding to the shift in the $S_1 \leftarrow S_0$ band of the absorption spectrum.



11 (*cis*-3)

To investigate the solvent effect, the fluorescence spectrum of **6a** was measured in benzonitrile. Although the shape of the spectrum is rather broadened and slightly red-shifted, the intensity is almost unchanged relative to that in cyclohexane. It has been reported that the fluorescence of [60]fullerene derivative with an *N*,*N*-dimethylaniline moiety was quenched in a polar solvent by the intramolecular electron transfer.[16] Apparently, such an electron transfer is not involved in **6a**, since the fluorescence is hardly quenched in benzonitrile. This result is ascribed to the lack of electron-donating ability of the dialkoxybenzene moieties in **6a**.

The fluorescence spectra of **6a** were also measured in the presence of KPF_6, since the complexation with K^+ was recognized in the ESI-MS. The addition of a large excess of the K^+ ion, however, had no effect on the fluorescence intensity or wavelength. This observation suggests that the crown ether moiety is located not so close to the fullerene surface as to affect the electronic properties of fullerene moiety in the excited state. Thus, it seems difficult to apply these bisadducts as fluorescent sensors for the K^+ ion.

Summary

In the reaction of [60]fullerene with **3**−**5** containing a dibenzocrown ether moiety, the regioselectivity was remarkably dependent on the ring size. Precursor **3** with the smallest 18-crown-6 ring produced *trans*-4 bisadduct **6a** as the major product with a relatively high regioselectivity. From **4** with a medium-sized ring, *trans*-4 bisadduct **7a** was obtained as the major product, though the selectivity was lower than that in **3** and a small amount of *e* isomer **7c** was also obtained. On the contrary, **5** with the largest ring exclusively gave *e* bisadduct **8**, similar to **1c** with a single oligomethylene linkage. The relative arrangement of two *o*-quinodimethane species was most effectively regulated in the case of **3**. The complexation behavior of these bisadducts with alkali metal ions was different; the size and geometry of the cavity formed by the crown ether ring depended on the addition pattern and the number of ether oxygen atoms. Intriguingly, **6a** and **7b** displayed remarkably high selectivity toward the K^+ ion; their selectivity coefficients ($K^{\mathrm{pot}}_{\mathrm{Na,K}}$) toward K^+ over Na^+ ion, determined with an ion-selective electrode, were higher than that of dibenzo-18-crown-6 itself. This high K^+-selectivity suggests the potential application of these bisadducts in biological systems.

Experimental Section

General. NMR spectra were recorded on a JEOL α-500 FT NMR spectrometer with tetramethylsilane as an internal standard. FAB-mass spectra were taken on a JEOL JMS-HX100A mass spectrometer. APCI-mass spectra were taken on a Shimadzu QP8000 mass spectrometer. ESI-mass spectra were taken on a Perkin-Elmer Sciex API-100 mass spectrometer. Absorption spectra were recorded on a Hitachi U3210 spectrophotometer. Fluorescence spectra was measured on an Hitachi-4010 spectrofluorimeter. The MM2 calculation was performed by CS Chem 3D Pro Ver 5.0 (Cambridge Soft Corporation). Toluene was distilled over sodium after prolonged heating. Other materials and reagents were commercially available and used without further purification.

Electrochemical measurements. Cyclic voltammetry (CV) was performed on a Hokuto HAB-151 potentiostat/galvanostat with a function generator. The working electrode was a platinum disk and the counter electrode a platinum wire. The reference electrode was an Ag/0.01 M $AgNO_3$ electrode filled with 0.1 M n-Bu_4NPF_6 in benzonitrile (BN). Measurements were run at room temperature on a 0.2 mM solution of the sample in BN containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte, after the solution was deaerated by bubbling argon gas. Voltammograms were recorded on a Graphtec WX-1100 X−Y recorder at a sweep rate of 200 mV s^{-1}. All the potentials were referenced to the Fc/Fc^+ redox couple observed at +0.07 V vs Ag/$AgNO_3$.

General Procedure For Determination of Selectivity Coefficients by the Ion Selective Electrode. The ion sensitive membrane of the poly(vinyl chloride) matrix was prepared as follows: **6a** (0.9 mg), *o*-nitrophenyl octyl ether (63 mg), poly(vinyl chloride) (25 mg), and potassium tetrakis(*p*-chlorophenyl)borate (0.6 mg) were dissolved in THF (1 mL). The solution was injected to fill the final 4 mm of the tip of a glass pipet (0.74 mm i.d.). A transparent membrane was obtained by evaporation of the solvent at room temperature. The electrode was conditioned with soaking in 0.3 M KCl solution during 15 h before use. The reference electrode was an Ag·AgCl electrode with agar bridge containing 50 mM NaCl. The electrode cell for emf measurement is as follows: Ag·AgCl/4 M KCl/PVC membrane/sample solution/0.05 M NaCl agar bridge/4 M KCl/AgCl·Ag. Emf was measured at 25 ± 0.5 °C with a digital mV meter. The $K^{\mathrm{pot}}_{\mathrm{i,j}}$ (i, primary ion; j, interfering ion) values were calculated from response potential in a 0.1 M cation chloride solution by the separate solution method.

Preparation of Tetrakis(bromomethyl)dibenzo-18-crown-6 ether (3). To a mixture of paraformaldehyde (0.41 g, 13.6 mmol) and dibenzo-18-crown-6 ether (0.50 g, 1.38 mmol) dissolved in AcOH (250 mL) were added sodium bromide (1.0 g, 9.7 mmol) and H_2SO_4 (4 mL). After being stirred for a week at room temperature under a nitrogen

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

atmosphere, the reaction mixture was poured into ice water and extracted with benzene. The benzene extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure to give 0.80 g (79% yield) of **3** as yellowish powder, which was subjected to the next reaction without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.81 (4H, s), 4.59 (8H, s), 4.17 (8H, t, $J = 4.4$ Hz), 3.99 (8H, t, $J = 4.4$ Hz). HRMS (FAB) calcd for $C_{24}H_{28}Br_4O_6$ (M^+) 727.8619, found 727.8604.

Preparation of Tetrakis(bromomethyl)dibenzo-24-crown-8 ether (4). To a mixture of paraformaldehyde (0.65 g, 21.7 mmol) and dibenzo-24-crown-8 ether (0.45 g, 1.0 mmol) dissolved in AcOH (200 mL) were added sodium bromide (2.3 g, 22.3 mmol) and H_2SO_4 (4 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for a week. The white precipitate formed during the period was separated from the solution by filtration, washed with water, and dried under vacuum to give 0.6 g (72% yield) of **4** as yellowish powder, which was subjected to the next reaction without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.83 (4H, s), 4.59 (8H, s), 4.15 (8H, t, $J = 4.3$ Hz), 3.90 (8H, t, $J = 4.3$ Hz), 3.80 (8H, s). Anal. Calcd for $C_{28}H_{36}Br_4O_8$: C, 41.00; H, 4.42. Found: C, 41.30; H, 4.37.

Preparation of Tetrakis(bromomethyl)dibenzo-30-crown-10 ether (5). To a mixture of paraformaldehyde (0.38 g, 12.6 mmol) and dibenzo-30-crown-10 ether (0.45 g, 0.84 mmol) dissolved in AcOH (150 mL) were added sodium bromide (1.3 g, 12.6 mmol) and H_2SO_4 (0.65 mL). After being stirred for 20 days at room temperature under a nitrogen atmosphere, the reaction mixture was poured into ice water and extracted with benzene. The benzene extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure to give 0.56 g (73% yield) of **5** as yellowish powder, which was subjected to the next reaction without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.84 (4H, s), 4.59 (8H, s), 4.15 (8H, t, $J = 4.6$ Hz), 3.87 (8H, t, $J = 4.6$ Hz), 3.75 (8H, t, $J = 4.7$ Hz), 3.67 (8H, t, $J = 4.6$ Hz). Anal. Calcd for $C_{32}H_{44}Br_4O_8$: C, 42.31; H, 4.88. Found: C, 42.10; H, 4.96.

Preparation of Bisadducts 6a and 6b. To [60]fullerene (89 mg, 0.124 mmol) dissolved in toluene (300 mL) by sonication were added potassium iodide (0.512 g, 2.48 mmol), 18-crown-6 ether (1.314 g, 4.97 mmol), and precursor **3** (100 mg, 0.137 mmol). The mixture was refluxed under a nitrogen atmosphere for 60 h, cooled to room temperature, washed with 5% KCl aqueous solution (500 mL), 3% $NaHSO_3$ aqueous solution (500 mL), and water (500 mL), and dried over sodium sulfate. After insoluble materials were removed by filtration, the solvent was removed under reduced pressure. Purification of the residue by GPC gave mainly two bisadducts **6a** (major) and **6b** (minor) (total 90 mg, 64% yield), which were successfully separated by PTLC (silica gel, chloroform/ethyl acetate = 4/1).

Spectroscopic data of **6a** and **6b** are as follows.

6a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.01 (2H, s), 6.75 (2H, s), 4.5−4.6, (6H, m), 4.28 (4H, m), 4.15 (2H, m), 3.97 (2H, d, $J = 12.5$ Hz), 3.79 (2H, d, $J = 13.2$ Hz), 3.73 (2H, m), 3.54 (2H, m), 3.18 (4H, m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.57, 155.24, 153.21, 151.06, 149.35, 148.83, 148.57, 146.30, 146.22, 145.98, 145.69, 145.56, 144.85, 144.61, 143.14, 142.87, 142.02, 141.93, 141.64, 141.12, 140.76, 138.86, 136.75, 136.46, 135.38, 131.44, 129.95, 129.23, 122.05, 115.29, 69.10, 68.83, 68.59, 67.40, 66.15, 65.74, 44.35, 43.37. FAB MS m/z 1132 (M^+).

6b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (2H, s), 6.98 (2H, s), 4.70 (4H, m), 4.51 (2H, m), 4.33 (2H, m), 4.31 (2H, d, $J = 14.4$ Hz), 4.1 (2H, m), 4.09 (2H, d, $J = 14.4$ Hz), 3.99 (2H, d, $J = 13.2$ Hz), 3.95 (2H, m), 3.62 (2H, d, $J = 13.2$ Hz), 3.37 (2H, m), 2.69 (2H, m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.03, 158.20, 151.07, 149.71, 149.37, 149.11, 147.76, 147.25, 147.07, 146.92, 146.71, 146.51, 145.96, 145.95, 145.88, 145.74, 145.31, 145.14, 144.89, 144.62, 144.46, 144.27, 144.24, 143.42, 142.56, 141.86, 141.42, 136.60, 134.51, 133.57, 133.06, 132.93, 129.14, 122.19, 116.45, 71.95, 70.46, 70.45, 68.72, 64.03, 63.65, 43.09, 43.05. FAB MS m/z 1132 (M^+).

Preparation of Bisadducts 7a, 7b, and 7c. To [60]fullerene (79.8 mg, 0.11 mmol) dissolved in toluene (300 mL) by sonication were added potassium iodide (0.405 g, 2.44 mmol), 18-crown-6 ether (1.29 g 4.88 mmol), and precursor **4** (100 mg, 0.12 mmol). The mixture was refluxed under a nitrogen atmosphere for 60 h, cooled to room temperature, washed with 5% KCl aqueous solution (500 mL), 3% $NaHSO_3$ aqueous solution (500 mL), and water (500 mL), and dried over sodium sulfate. After insoluble materials were removed by filtration, the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, chloroform/ethyl acetate) gave three bisadducts **7a**, **7b**, and **7c** (**7a**:**7b**:**7c** = 23:10:2, total 47 mg, 35% yield).

Spectroscopic data of **7a**, **7b**, and **7c** are as follows.

7a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.07 (2H, s), 6.94 (2H, s), 4.52 (2H, d, $J = 13.5$ Hz), 4.42 (4H, m), 4.27 (4H, m), 4.11 (2H, m), 4.07 (2H, d, $J = 13.1$ Hz), 3.83−3.91 (6H, m), 3.72 (2H, m), 3.58−3.65 (4H, m), 3.53 (2H, m), 3.17 (2H, m), 3.09 (2H, m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.96, 154.86, 153.06, 151.73, 151.47, 149.72, 149.54, 149.50, 148.55, 148.23, 148.17, 146.74, 146.57, 146.44, 146.31, 146.23, 145.83, 144.82, 143.66, 142.76, 142.68, 142.20, 141.92, 141.42, 141.03, 141.00, 138.82, 137.58, 135.97, 135.25, 132.94, 130.49, 129.93, 118.47, 114.06, 70.46, 70.11, 69.99, 69.45, 69.10, 68.72, 65.38, 65.22, 29.69. APCI MS m/z 1220 (M^-).

7b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (2H, s), 7.05 (2H, s), 4.62 (2H, m), 4.56 (2H, m), 4.55 (2H, d, $J = 14.0$ Hz), 4.45 (2H, m), 4.22 (2H, m), 4.09 (4H, m), 3.98 (2H, d, $J = 14.6$ Hz), 3.97 (2H, d, $J = 13.7$ Hz), 3.91 (4H, m), 3.72 (2H, d, $J = 13.7$ Hz), 3.68 (2H, m), 3.50 (2H, m), 3.14 (2H, m), 2.93 (2H, m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.58, 159.0, 151.11, 149.72, 149.06, 148.09, 147.71, 147.40, 147.31, 147.28, 146.92, 146.46, 145.73, 145.34, 145.14, 144.97, 144.61, 144.52, 144.33, 143.75, 142.66, 141.77, 141.36, 137.92, 133.41, 132.82, 131.77, 130.75, 121.89, 120.99, 117.35, 71.00, 70.97, 70.95, 70.65, 70.34, 70.20, 63.49, 62.87, 44.16, 42.83. APCI MS m/z 1220 (M^-).

7c; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (1H, s), 7.15 (1H, s), 7.04 (1H, s), 6.91 (1H, s), 4.81 (1H, m), 4.54 (4H, m), 4.47 (1H, d, $J = 12.5$ Hz), 4.40 (1H, m), 4.22 (1H, d, $J = 14.9$ Hz), 4.13 (1H, m), 3.99−4.09 (4H, m), 3.82−3.90 (8H, m), 3.76 (1H, m), 3.65 (2H, m), 3.38 (2H, m), 3.29 (1H, d, $J = 14.6$ Hz), 3.21 (1H, m), 3.07 (2H, m), 2.88 (1H, m), 2.53 (1H, m). APCI MS m/z 1220 (M^-).

Preparation of Bisadduct 8. To [60]fullerene (72.0 mg, 0.10 mmol) dissolved in toluene (300 mL) by sonication were added potassium iodide (0.341 g, 2.05 mmol), 18-crown-6 ether (1.10 g 4.17 mmol), and precursor **5** (91 mg, 0.10 mmol). The mixture was refluxed under a nitrogen atmosphere for 40 h, cooled to room temperature, washed with 5% KCl aqueous solution (500 mL), 3% $NaHSO_3$ aqueous solution (500 mL), and water (500 mL), and dried over sodium sulfate. After insoluble materials were removed by filtration, the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, chloroform/ethyl acetate) gave bisadduct **8** (9 mg, 7% yield).

^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.22 (1H, bs), 7.12 (1H, s), 7.11 (1H, s), 6.99 (1H, bs), 4.60−4.40 (6H, m), 4.40−4.10 (5H, m), 3.99−3.92 (4H, m), 3.90−3.78 (15H, m), 3.52−3.49 (2H, m), 3.31−3.20 (3H, m), 3.10−3.01 (3H, m), 2.93−2.77 (2H, m). APCI MS m/z 1308 (M^-).

Acknowledgment. This work was financially supported by the Japan Society for the Promotion of Science.

Supporting Information Available: GPC chromatogram of **6a**,**b** and ^{1}H NMR spectra of **6a**,**b**, **7a−c**, and **8** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0257063