Fullerene-Based Catenanes/Rotaxanes

Preparation of Neutral [60]Fullerene-Based [2]Catenanes and [2]Rotaxanes Bearing an Electron-Deficient Aromatic Diimide Moiety**

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Dedicated to Professor Emeritus Dr. Soichi Misumi on the occasion of his 77th birthday

Since [60]fullerene has become available in macroscopic quantities, its covalent functionalization has been widely developed.[1] In parallel with chemical transformations, supramolecular fullerene chemistry has also been explored.[2] The complexation of [60]fullerene itself by π-electron-rich compounds, such as hydroquinone,[3] BEDT-TTF,[4] ferrocene,[5] porphyrins,[6] and macrocyclic receptors including cyclodextrin,[7] cyclotriveratrylene,[8] calixarenes,[9] and related compounds has been extensively investigated. The progress in covalent functionalization of fullerene has led to further development of supramolecular architectures and molecular assemblies incorporating fullerene.[2,10,11]

In the last decade, a variety of molecules, including rotaxanes and catenanes, have been fabricated through noncovalent bonding interactions.[12] These molecular assemblies have attracted much interest because of their fascinating topological features and potential application in molecular devices. The introduction of [60]fullerene into these systems promises further enhancement of the functionality of such molecular assemblies because of its unique electronic properties, especially as a strong electron acceptor.[13]

However, examples that incorporate [60]fullerene into rotaxanes and catenanes,[14–16] which have been constructed by independent synthetic methodologies, are extremely limited. Diederich, Sauvage, et al. have prepared a [2]rotaxane that possesses two fullerene stoppers at the ends of its threadlike component, which takes advantage of the coordination of Cu^+ ions by 1,10-phenanthroline ligands.[14] In addition Diederich, Stoddart, et al. prepared a [60]fullerene-containing [2]catenane that includes a *trans*-4 bisadduct as a building block, based on the charge-transfer (CT) interaction between the π-electron-deficient cyclobis(paraquat-*p*-phenylene) and the π-electron-rich 1,4-dialkoxybenzene moieties.[15] To the best of our knowledge, this is the only example of a [60]fullerene-based [2]catenane, and there has been no

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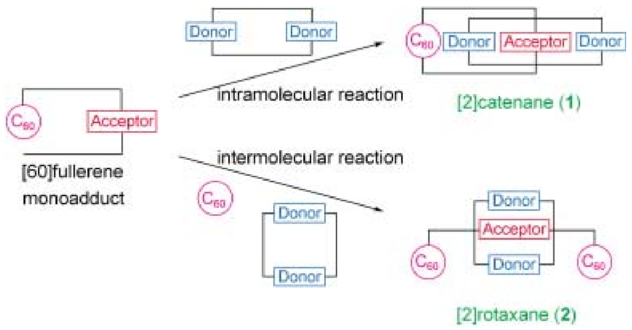
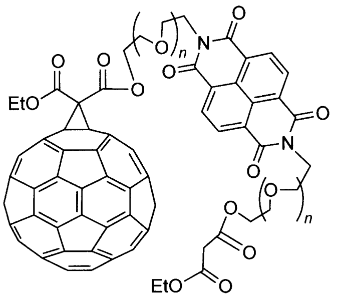
report of [2]catenanes to date, in which the electron-accepting ability of [60]fullerene is directly involved.

In the present study, we have developed new synthetic strategies to form neutral fullerene-based [2]catenanes **1** and [2]rotaxanes **2**, which consist of a fullerene derivative that carries another electron-acceptor moiety and an electron-donating macrocycle, such as a benzocrown ether, as shown in Scheme 1. In the [2]catenanes **1**, a cyclic fullerene bisadduct and a benzocrown ether are interlocked. Since fullerene also serves as an electron acceptor, **1** has an intriguing D-A-D-A (D = donor, A = acceptor) stacking structure. In the [2]rotaxanes **2**, a crown ether encircles the acceptor moiety of a dumbbell-shaped molecule, which carries two [60]fullerene groups that act as stoppers at both termini. Their formation is mainly based on the CT interaction between the components. It is noteworthy that they can be prepared from the identical precursor, namely, an acyclic fullerene monoadduct, which exhibits another electron-accepting moiety; for the [2]catenanes, the monoadduct is transformed into a cyclic bisadduct by appropriate intramolecular reactions in the presence of an electron-donating macrocycle, while for the [2]rotaxanes, the monoadduct reacts with another [60]fullerene molecule.

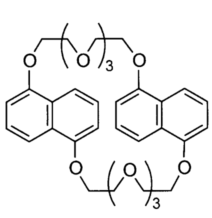


Scheme 1. Synthetic strategies toward fullerene-based [2]catenanes or [2]rotaxanes.

To realize the strategies highlighted in Scheme 1, we designed monoadducts **3a** and **3b**, which incorporate a naphthalenetetracarboxylic diimide moiety as an acceptor, a malonate ester as a reactive site for [60]fullerene, and oligooxyethylene linkages to connect them. Since such a diimide has been suitably employed as a component of catenanes by Sanders et al.,[17] **3a** and **3b** are suitable to perform as the key building blocks outlined in Scheme 1. In practice, we have succeeded in the preparation of both [2]rotaxanes and [2]catenanes.



monoadduct
3a: $n = 2$
3b: $n = 3$



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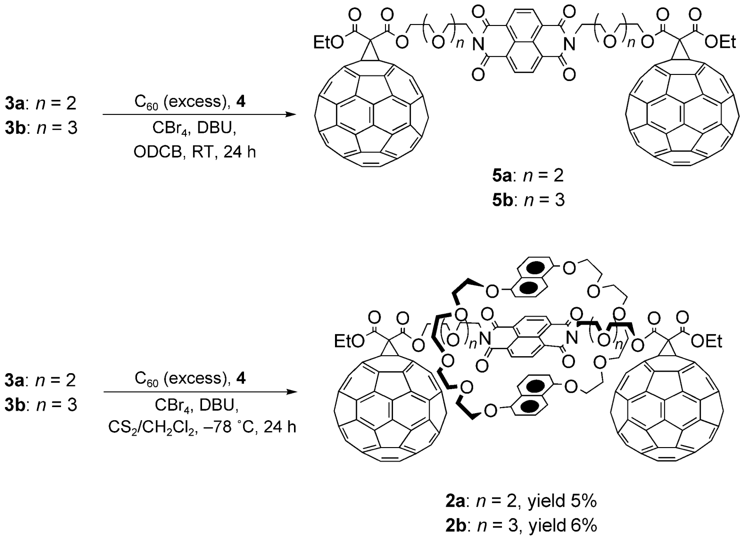
Monoadducts **3a** and **3b** were prepared using the Bingel reaction[18,19] by treating the corresponding naphthalenetetracarboxylic-diimide-containing bis(ethyl malonate) moiety with [60]fullerene in the presence of CBr_4 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature. Both **3a** and **3b** were isolated by column chromatography followed by GPC, if necessary, and readily characterized by APCI mass spectrometry and ^1H NMR spectroscopy.

To prepare the fullerene-based [2]rotaxanes **2**, the Bingel reaction of **3a** or **3b** with an excess of [60]fullerene was first carried out in the presence of 1,5-dinaphtho-[38]crown-10 ether (**4**) in *o*-dichlorobenzene (ODCB) at room temperature. Although the dumbbell-shaped [60]fullerene dimers **5a** and **5b** were produced without incorporating **4**, the desired [2]rotaxane **2** was not detected (Scheme 2). Thus, the Bingel reactions were carried out in CS_2/CH_2Cl_2 at −78 °C, where the formation of a pseudorotaxane was expected to be more preferable from the viewpoint of entropy. In a remarkable contrast with the reactions at room temperature, the desired [2]rotaxanes **2a** and **2b** were successfully produced and isolated by column chromatography and GPC.



Scheme 2. Synthesis of fullerene-based [2]rotaxanes **2**.

Compounds **2a** and **2b** were characterized by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry. As shown in Figure 1, the MALDI-TOF mass spectrum of **2a** clearly indicates the molecular ion peak ($m/z = 2830$). A fragmentation peak at $m/z = 1474$ is also observed, which results from the loss of [60]fullerene and **4** from **2a** by cleavage of the cyclopropane ring (retro-Bingel reaction). In the ^1H NMR spectrum of **2a** (Figure 2a), the malonate methylene protons ($\delta = 3.35$ ppm) of **3a** are missing, and the methyl protons of two ethoxycarbonyl groups are observed as a single triplet ($\delta = 1.50$ ppm). These observations indicate that the reaction between **3a** and [60]fullerene had proceeded, since the

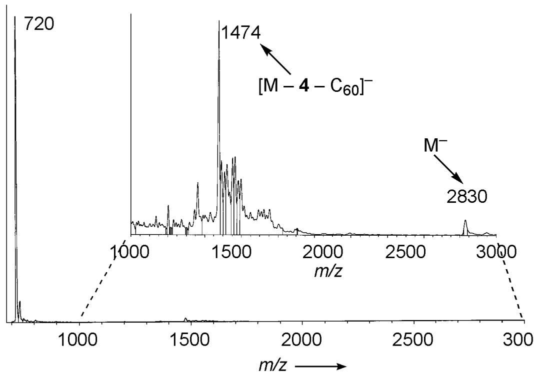


Figure 1. MALDI-TOF mass spectrum of [2]rotaxane **2a**; mode: negative; matrix: dithranol.

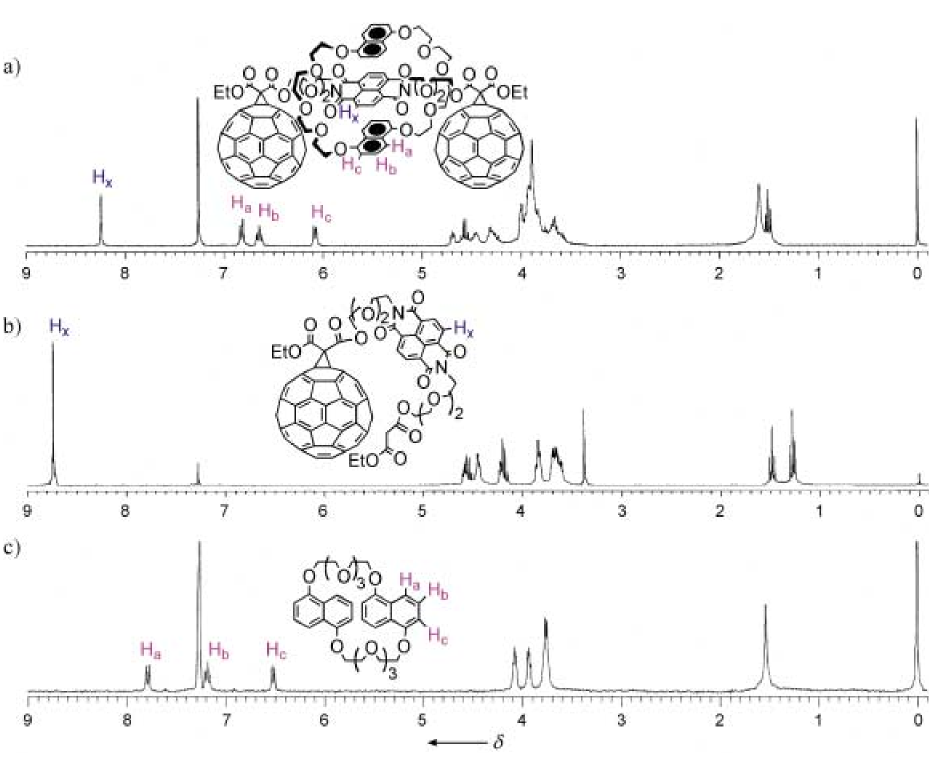
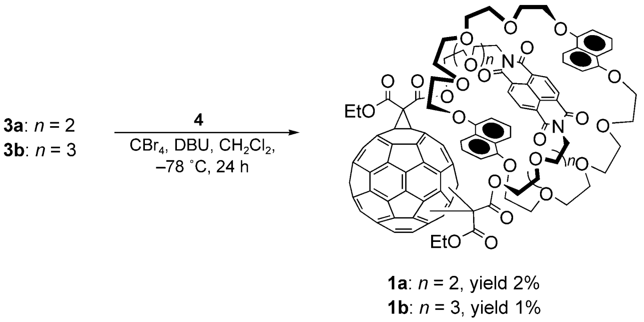


Figure 2. ^{1}H NMR spectra of a) **2a**, b) **3a**, and c) **4** in $CDCl_3$ at room temperature (300 MHz).

methyl protons in **3a** were observed as two sets of non-equivalent triplets. No aromatic proton peaks resulting from pristine **3a** and **4** were detected in **2a** (cf. Figure 2b, and c). Instead, only one set of high-field-shifted aromatic peaks of **3a** and **4** were observed. This high-field shift is ascribed to the shielding effect of the opposite aromatic groups, apparently indicating that **4** encircles the diimide moiety of **3a**, since no high-field shift was observed for the mixed solution containing dimer **5a** and **4**. The stoichiometry of **3a** and **4** was found to be 1:1 based on the integral ratio. Therefore, the data undoubtedly demonstrates that **2a** is a [2]rotaxane composed of **3a**, **4**, and [60]fullerene. [2]Rotaxane **2b** bearing longer linkages showed spectroscopic features similar to those of **2a**.

For the preparation of fullerene-based [2]catenanes **1**, the intramolecular Bingel reactions of the monoadducts **3** were examined in the presence of crown ether **4**. First, **3a** or **3b** was allowed to react with CBr_4 and DBU in the presence of **4** in CH_2Cl_2 at room temperature. However, only bisadducts that did not incorporate **4** were obtained as a regioisomeric mixture. In contrast, the reaction at −78 °C successfully afforded the desired [2]catenanes **1a** and **1b**, similar to the [2]rotaxane formation at this temperature (Scheme 3).

Compounds **1a** and **1b** were isolated and characterized in a similar fashion to **2a** and **2b**. In the MALDI-TOF mass spectrum of **1a**, the molecular-ion peak of catenane **1a** ($m/z = 2110$) was observed (Figure 3). The fragmentation peak ($m/z = 1474$) arising from the loss of **4** from cleavage of the cyclopropane ring is also detected. The relative intensity of the molecular-ion peak is much higher than that for the rotaxanes **2a** and **2b**, which suggests that **1a** has much higher stability. This is reasonably explained as follows: **1a** contains a [60]fullerene bisadduct as a building block, in which a fullerene moiety and a diimide moiety are connected through two cyclopropane rings, whereas **2a** and **2b** are both composed of two monoadduct residues possessing a single cyclopropane ring. Furthermore, the D-A-D-A stacking structure enhances the stability of **1a**. In the ^{1}H NMR spectrum of **1a**, no aromatic signals from free **3a** and **4** are detected, and the malonate methylene protons of **3a** are also missing (Figure 4). Only a set of high-field-shifted aromatic peaks of **3a** and **4** are observed. Therefore, **1a** must be a [2]catenane composed of **3a** and **4**. Compared to the ^{1}H NMR spectrum of **2a**, the signals of **1a** are subjected to considerable broadening. This suggests that the two components are tightly interlocked so that the mobility of crown ether **4** is considerably limited. [2]Catenane **1b**



Scheme 3. Synthesis of fullerene-based [2]catenanes **1**.

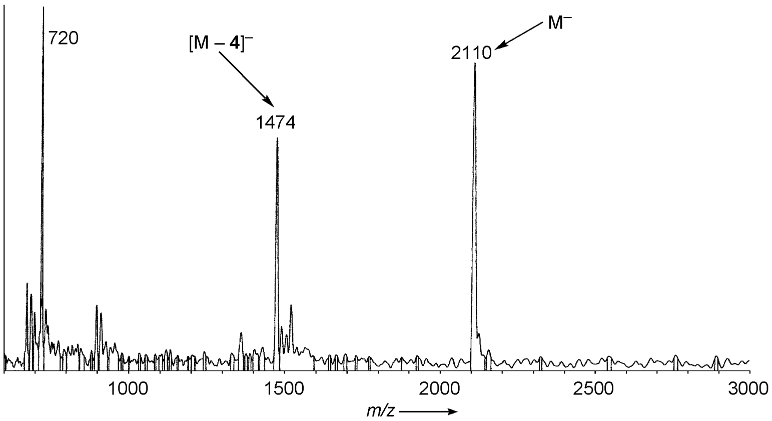


Figure 3. MALDI-TOF mass spectrum of [2]catenane **1a**; mode: negative; matrix: dithranol.

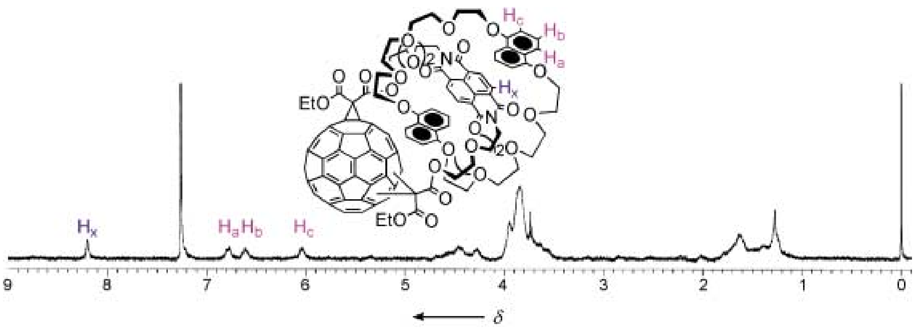


Figure 4. ^{1}H NMR spectra of [2]catenane **1a** in $CDCl_3$ at room temperature (300 MHz).

bearing longer linkages exhibited spectroscopic features similar to those of **1a**.

In summary, the intramolecular Bingel reactions of monoadducts **3a** and **3b** in the presence of **4** at −78 °C successfully afforded novel neutral [2]catenanes **1a** and **1b** with a D-A-D-A stacking structure, while the intermolecular Bingel reactions of **3a** and **3b** with [60]fullerene gave [2]rotaxanes **2a** and **2b**. The lowering of reaction temperature is critical for the formation of the [2]catenanes and [2]rotaxanes. The former is the first example of a [2]catenane in which the electron-accepting ability of [60]fullerene is explicitly involved in the catenane formation and in which [60]fullerene is a part of the cyclic components. It is noteworthy that both interlocked compounds were obtained from the same precursors. An investigation of the electrochemical, electronic, and photophysical properties of the obtained [2]catenanes and [2]rotaxanes is now in progress.

Experimental Section

2a: A solution of **3a** (219.4 mg, 0.149 mmol), **4** (565.4 mg, 0.889 mmol), and CBr_4 (493 mg, 1.49 mmol) in CH_2Cl_2 (20 mL) was added to a solution of C_{60} (1.07 g, 1.49 mmol) in CS_2 (20 mL), and the mixture was cooled down to −78 °C. Subsequently, DBU (226 mg, 1.49 mmol) was added, and then the mixture was stirred at −78 °C for 24 h under a nitrogen atmosphere. Purification of the obtained mixture by column chromatography (SiO_2, toluene/MeOH (1:1)) and GPC ($CHCl_3$) gave 21.0 mg of [2]rotaxane **2a** as a brown solid (yield 5 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.50$ (t, $J = 7.2$ Hz, 6H), 3.56–4.49 (m, 56H), 4.57 (q, $J = 7.1$ Hz, 4H), 4.69 (t, $J = 4.8$ Hz, 4H), 6.08 (d, $J = 7.5$ Hz, 4H), 6.65 (t, $J = 8.0$ Hz, 4H), 6.82 (d, $J = 8.3$ Hz, 4H), 8.24 ppm (s, 4H). MALDI-TOF-MS: m/z 2830 [M^-], 1474 ([M-**4**-C_{60}]$^-$).

1a: DBU (308.4 mg, 2.03 mmol) was added to a solution of **3a** (598.9 mg, 0.406 mmol), **4** (388.0 mg, 0.610 mmol), and CBr_4 (673.5 mg, 2.03 mmol) in CH_2Cl_2 (40 mL) at −78 °C, and the mixture was stirred for 24 h at the same temperature under a nitrogen atmosphere. Purification of the obtained mixture by column chromatography (SiO_2, toluene/MeOH (1:1)) and GPC ($CHCl_3$) gave 9.37 mg of [2]catenane **1a** as a brown solid (yield 2 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta =$ 3.45–4.69 (m, 60H), 6.03 (br, 4H), 6.61 (br, 4H), 6.77 (br, 4H), 8.20 ppm (s, 4H). MALDI-TOF-MS: m/z 2110 [M^-], 1474 ([M-**4**]$^-$).

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Keywords: catenanes · donor–acceptor systems · fullerenes · rotaxanes · supramolecular chemistry

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