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End-Capping of a Pseudorotaxane via Diels–Alder Reaction for the Construction of C_{60}-Terminated [2]Rotaxanes

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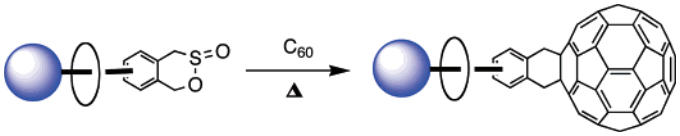
ABSTRACT



The Diels–Alder reaction of various dienophiles such as C_{60} with a pseudorotaxane having a sultine moiety afforded corresponding [2]-rotaxanes in moderate yields. The introduction of a porphyrin moiety on the wheel component considerably enhanced the efficiency of the end-capping reaction with C_{60}.

Buckminsterfullerene (C_{60}) has been given much attention as a potential component for innovative electronic and photonic molecular devices because of its outstanding electro- and photoactivity. Since interlocked compounds such as rotaxanes and catenanes are believed to be superior scaffolds for molecular devices,[1] C_{60}-containing interlocked compounds are of great interest.[2] However, a general method for introducing C_{60} into interlocked compounds is limited, probably due to the poor solubility of C_{60}-containing interlocked compounds and limited variations of C_{60} reactions.

We have demonstrated that the Diels−Alder reaction is an efficient method of introducing C_{60} into rotaxanes.[2c,h] Rotaxanes with a sulfolene moiety as a diene precursor reacted with C_{60} upon heating to afford C_{60}-containing rotaxanes. The method was effective in modifying the wheel component in the rotaxane. However, the application of the method to the end-capping of the pseudorotaxane formed in situ in equilibrium between the axle and the wheel components was quite limited because the decomposition of the sulfolene moiety required very high temperatures. Therefore, we focused our attention on the sultine group that decomposes at rather low temperatures to afford diene and

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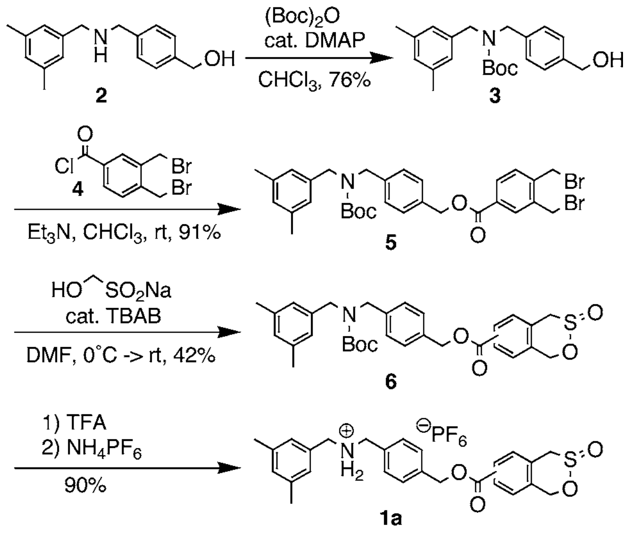
eventually chose the benzosultine group as a precursor of diene that gives a highly reactive *o*-quinodimethane moiety.[3] Here, we report a novel synthetic approach for preparing [2]rotaxanes via Diels−Alder end-capping of a pseudorotaxane having a sultine moiety on the axle terminus. The effectiveness of this method is demonstrated by the introduction of C_{60} into the rotaxanes.

The combination of secondary ammonium salt and crown ether such as dibenzo-24-crown-8 (DB24C8) has been extensively studied as the easily accessible rotaxane system.[4] Axle *sec*-ammonium salt **1a** used in this work was prepared as illustrated in Scheme 1. After protection of amino alcohol **2**[5] with a Boc group, acylation of **3** with **4**[6] afforded ester **5**. The treatment of **5** with sodium hydroxymethanesulfinate in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB) gave *N*-Boc sultine **6**.[3b] The deprotection of **6** with trifluoroacetic acid (TFA) proceeded smoothly. The anion exchange with NH_4PF_6 afforded hexafluorophosphate **1a**.[7] **1a** was obtained as a mixture of the regioisomers of the sultine moiety and was used without separation.

Scheme 1



Stoddart and co-workers reported that the cyclohexyl (Cy) group is larger than the cavity of DB24C8 at room temperature, while at higher temperatures, the Cy group can intrude into the DB24C8 cavity.[8,9] Since the CPK model study showed that the benzosultine moiety was as bulky as the Cy group, we expected it to act as an end-cap for the DB24C8 wheel at ambient temperature. However, the addition of DB24C8 to a suspension of 1.2 equiv of **1a** in chloroform at room-temperature resulted in the dissolution of **1a**. The complexation behavior between **1a** and DB24C8 was demonstrated by ^{1}H NMR study in $CDCl_3/CD_3CN$, as shown in Figure 2. When DB24C8 was added to a solution of **1a**, a new set of signals of the complex **1a·**DB24C8 immediately appeared at room temperature.

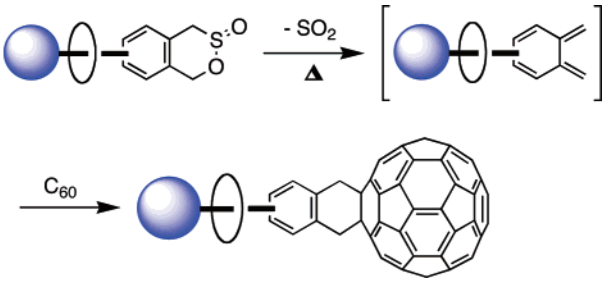


Figure 1. Strategy toward the synthesis of C_{60}-end-capped [2]-rotaxane.

Benzylic ammonium α-methylene proton signals of the mixture were observed as complex multiplets at lower fields than those of **1a**, indicating the formation of pseudorotaxane.[10] The benzosultine group behaved as a less bulky group than the Cy group probably because of the flexible nature of the S═O bond.

The pseudorotaxane structure was fixed by Diels−Alder reaction with excess dimethyl fumarate in $CHCl_3$ at 80 °C in a sealed tube. The corresponding [2]rotaxane **7a** was obtained in 29% yield. Thus, a highly reactive *o*-quinodimethane intermediate was actually produced at 80 °C, at which temperature the sulfolene group is thermally stable. To estimate the effect of temperature, the stability constant (K_a) of complex **1a·**DB24C8 was determined in $CDCl_3$ by ^{1}H NMR study.[11] The apparent K_a was 189 ± 14 L mol^{-1} at 23 °C when [**1a**] = 0.167 mol L^{-1}. From the extrapolation of the VT-NMR experiments, K_a at 80 °C was calculated as 38 ± 2 L mol^{-1}, suggesting that ca. 75% of **1a** formed the complex with DB24C8. The results indicate that the efficiency of the Diels−Alder reaction of pseudorotaxane **1a·**DB24C8 was merely ca. 40%, presumably because of the steric bulkiness of the DB24C8 wheel of the pseudorotaxane.

Several rotaxanes were prepared by this method. [2]-Rotaxane **7b** was obtained in 28% yield when **1b** was used

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(7) **Spectroscopic Data for 1a.** Off-white solid. Mp: 93−97 °C. ^{1}H NMR (270 MHz, CD_3CN): δ 7.92−7.83 (m, 2H), 7.46−7.37 (m, 4H), 7.32−7.28 (m, 1H), 6.99−6.97 (m, 3H), 5.29 (s, 2H), 5.16 (d, 1H, J = 14.0 Hz), 4.94 (d, 1H, J = 14.0 Hz), 4.34−4.26 (m, 1H), 4.11 (s, 2H), 4.05 (s, 2H), 3.59 (d, 2H, J = 15.8 Hz), 2.21 (s, 6H) ppm. FAB-MS (matrix; mNBA): $m/z = 450.0$ $[M - PF_6]^+$, 386.2 $[M - PF_6 - SO_2]^+$. Anal. Calcd for $C_{26}H_{28}F_6N_1O_4P_1S_1$: C, 52.44; H, 4.74; N, 2.35; S, 5.38. Found: C, 52.66; H, 4.82; N, 2.27; S, 5.19.

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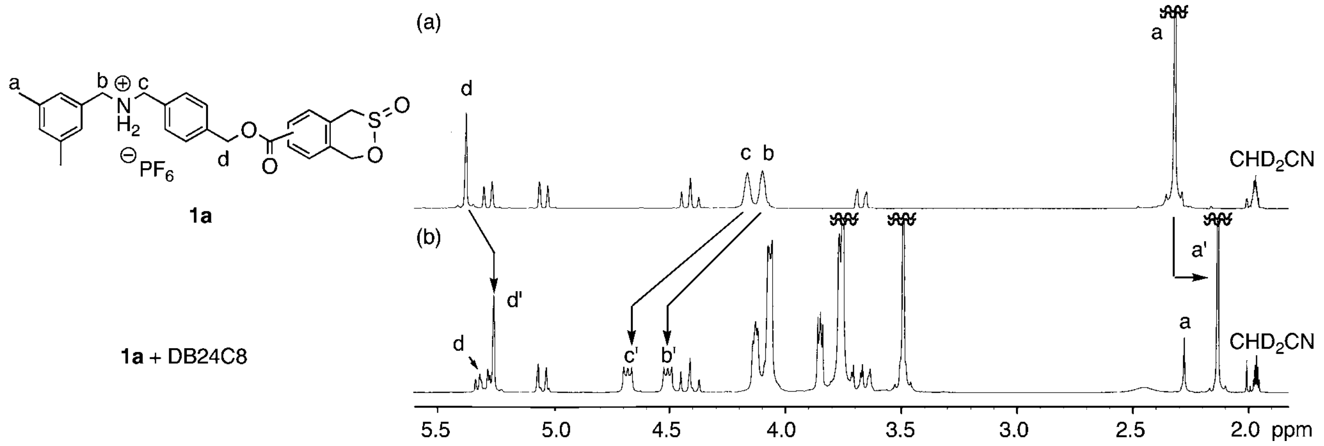


Figure 2. Partial ^{1}H NMR spectra ($CDCl_3/CD_3CN$ (2/1)) of (a) axle **1a** and (b) a 1.0:1.2 mixture of **1a** and DB24C8. Assignment of peaks as "prime" denotes the protons in the pseudorotaxane.

as an axle. The reaction of **1a** with dimethyl acetylenedicarboxylate in the presence of DB24C8 afforded [2]rotaxane **7c** in 28% yield. These results show that the Diels–Alder reaction of pseudorotaxane having an *o*-quinodimethane moiety constitutes one of the general methods that can be used to prepare various [2]rotaxanes, although the yield is not very high.

The Diels–Alder end-capping protocol was applied to the preparation of C_{60}-containing [2]rotaxane. 1,2-Dichlorobenzene (ODCB) was used as a solvent in which C_{60} was rather soluble. The reaction of **1a** with 1.5 equiv of C_{60} in the presence of 2.0 equiv of DB24C8 at 80 °C was carried out in ODCB to give the corresponding C_{60}-containing [2]rotaxane **7d**[12] in 33% yield (Scheme 2).

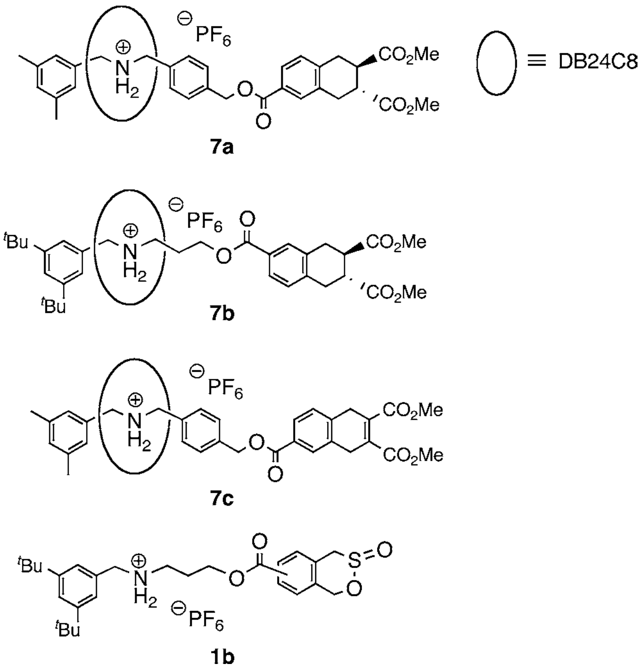
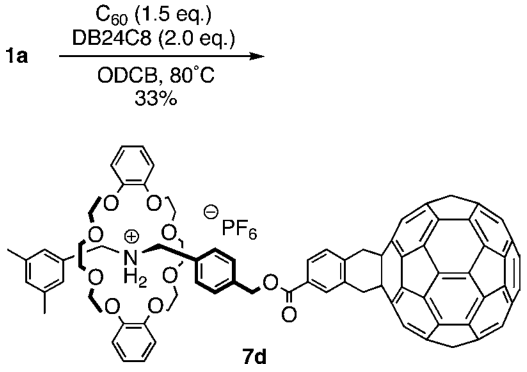


Figure 3. [2]Rotaxanes **7a–c** and axle **1b**.

Scheme 2



The structure of **7d** was fully characterized by FAB-MS, NMR, and IR spectra as well as by elemental analyses. When 4.0 equiv of DB24C8 was used, the yield of **7d** decreased to 17%. Thus, excess DB24C8 enhanced the polarity of the system to decrease the K_a of the complex.[13] It is noteworthy that **7d** is very soluble in ordinary organic solvents such as

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(12) **Typical Procedure.** A mixture of **1a** (54 mg, 0.09 mmol), DB24C8 (81 mg, 0.18 mmol), and C_{60} (97 mg, 0.14 mmol) in dry ODCB (1.0 mL) under an argon atmosphere in the dark was slowly heated to 80 °C and stirred at 80 °C for 12 h. The reaction mixture was directly chromatographed (SiO_2, eluent: toluene to $CHCl_3$/methanol (90/10)) to collect a dark brown band (118 mg), a part of which (107 mg) was further purified by preparative GPC (eluent: $CHCl_3$) to give **7d** as a dark brown solid (46 mg, 33%). Mp: 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 323 K): δ 8.37 (s, 1H), 8.27 (d, 1H, $J = 6.3$ Hz), 7.79 (d, 1H, $J = 7.8$ Hz), 7.56 (br, 2H), 7.37–7.35 (m, 4H), 6.88–6.76 (m, 11H), 5.35 (s, 2H), 4.82–4.48 (m, 8H), 4.12–4.09 (m, 8H), 3.82–3.71 (m, 8H), 3.51–3.46 (m, 8H), 2.13 (s, 6H) ppm. IR (NaCl): 2922, 1716, 1504, 1455, 1253, 1210, 1180, 1123, 1102, 1056, 953, 842, 749, 557, 526 cm^{-1}. FAB-MS (matrix: mNBA): $m/z = 1554.5$ $[M - PF_6]^+$. Anal. Calcd for $C_{110}H_{60}F_6N_1O_{10}P_1\cdot(CHCl_3)_{0.5}$: C, 75.39; H, 3.46; N, 0.80. Found: C, 75.06; H, 3.56; N, 0.87.

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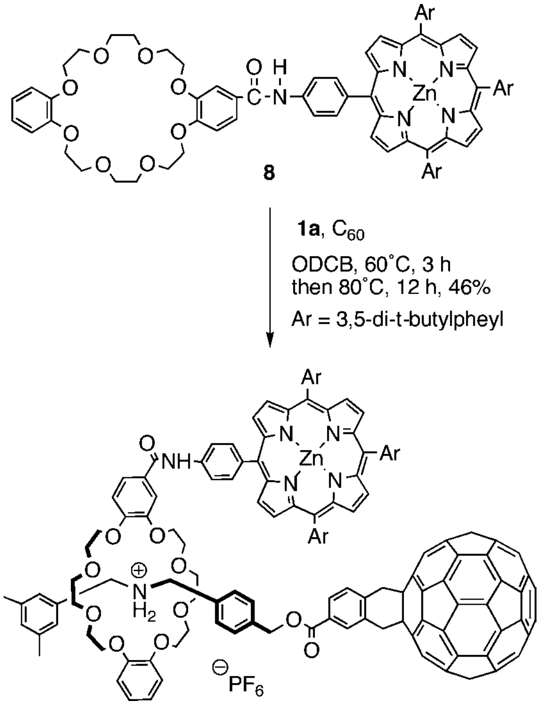
acetone, acetonitrile, chloroform, and THF, whereas most C_{60}-derivatives are insoluble in these solvents.

If the wheel component can attract the dienophile, the rotaxane yield may increase by the cooperative effect between the components. Since various C_{60} receptors have been prepared using porphyrin as a C_{60}-attractive group,[14] a novel crown ether **8** having zinc porphyrinate (ZnP) moiety was prepared. The pseudorotaxane prepared from **1a** and **8** was reacted with 2.0 equiv of C_{60} in ODCB. The corresponding [2]rotaxane **9** was obtained in 46% yield (Scheme 3). The apparent K_a of **1a** and **8** determined as described above was 37 ± 3 L mol^{-1} in $CDCl_3$ at 80 °C ([**1a**] = 90 mM). Since pseudorotaxane **1a·8** is as stable as **la**·DB24C8, the clear increase in the yield of **9** can be explained by the attractive interaction between C_{60} and the ZnP moiety that accelerated the Diels−Alder reaction to enhance the efficiency of the end-cap.

In summary, we have demonstrated that the benzosultine group is a useful functional group for the end-capping of pseudorotaxane with a highly reactive *o*-quinodimethane generated at lower temperatures (80 °C) at the axle end. The Diels−Alder reaction of various dienophiles such as C_{60} with pseudorotaxane afforded corresponding [2]rotaxanes in moderate yields. The introduction of a porphyrin moiety on the wheel considerably enhanced the efficiency of the end-capping reaction with C_{60}.

Scheme 3



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Supporting Information Available: Spectroscopic data for compounds **7a**−**c** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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