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A highly selective generation of γ-cyclodextrin-bicapped C_{60}^{n-} (n: 1 and 2) in DMSO[†]

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Abstract

Highly selective generation of the supramolecular C_{60}^{1-} and C_{60}^{2-} species from γ-cyclodextrin-bicapped C_{60} in DMSO has been achieved for the first time even in the presence of oxygen by using a large excess of NaH and excess $NaBH_4$, respectively.

Keywords: cyclodextrins; complexes; electron transfer; fullerenes.

As part of our basic studies for the discovery of novel reactions in which supramolecular C_{60} complexes participate, we reported the first successful generation of a C_{60}^{n-} (n: 1 and 2) species in water from γ-cyclodextrin-bicapped C_{60} (**1**) and $Na_2S_2O_4$ in the presence of an 18-crown-6–$FeCl_2$ (1:1) complex as a mediator for the electron-transfer.[1] In the light of the importance of aprotic dipolar solvents in organic synthesis, we have investigated the generation of C_{60}^{n-} (n: 1 or 2) from **1** and metal hydrides in DMSO as a typical aprotic dipolar solvent. To our knowledge, there have been some papers dealing with chemical generation of C_{60}^{n-} in DMSO[2] for C_{60} itself, but there have been none so far for wholly encapsulated supramolecular C_{60} complexes like **1**.

We report here the first highly selective generation of 'C_{60}^{1-}' and 'C_{60}^{2-}' species from **1** in DMSO. In this investigation we used $\mathbf{1}\cdot 24H_2O$[3,4] which is considered to exist as **1** (anhydrous form) in DMSO–NaH and DMSO–$NaBH_4$ because of the strong dehydration ability of those systems.[5] The AM1 structure of **1** using MOZYME (semiempirical molecular orbital program designed by Stewart for study of large molecular systems) is shown in Fig. 1.

Confirmation of generation of the C_{60}^{n-} species was made by examining the characteristic NIR bands for C_{60}^{n-} using a Beckman DU 640 spectrophotometer.

Highly selective generation of γ-cyclodextrin-bicapped C_{60}^{1-} in DMSO: Although sodium hydride (60% dispersion in mineral oil) is insoluble in DMSO, it becomes soluble upon heating or standing for

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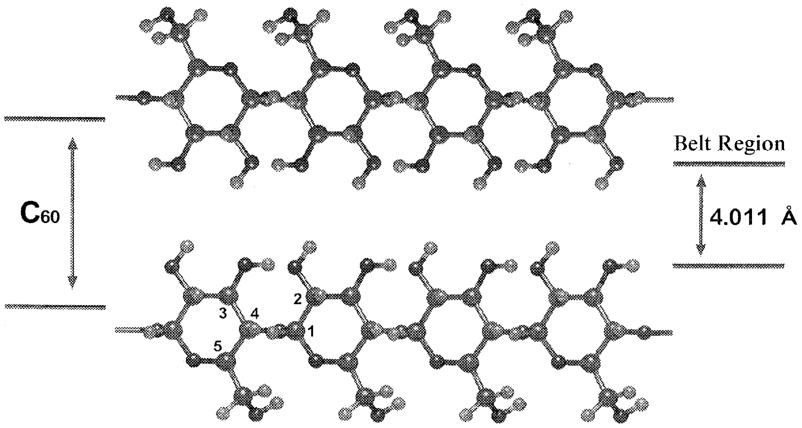


Fig. 1. Side view of a part of **1** obtained by MOZYME calculation

some time because of the formation of dimsylsodium.[5] In view of the fact that supramolecular complex **1**·24H_2O is sparingly soluble in DMSO even in the presence of several equivalents of dimsylsodium, a large excess (more than 185 equiv.) of NaH (dimsylanion) is necessary to prepare the transparent solution, in which, as mentioned before,[5] **1**·24H_2O is considered to exist as its anhydrous form as shown in Fig. 1. Complex formation between **1** and **2** (probably at the belt region) seems to be a reason for dissolution of **1** in DMSO. Thus, by using 185~740 equiv. of NaH (or dimsylsodium), highly selective generation of γ-cyclodextrin-bicapped C_{60}^{1-} (λ_{max}: 1076 nm)[1,6] was achieved even in the presence of oxygen as exemplified in Fig. 2. After reaching the maximum absorptions, the characteristic bands were slowly decreased because of dissolved oxygen. A linear relationship with a positive slope was found between absorbance at 1076 nm and the apparent dimsylanion concentration.

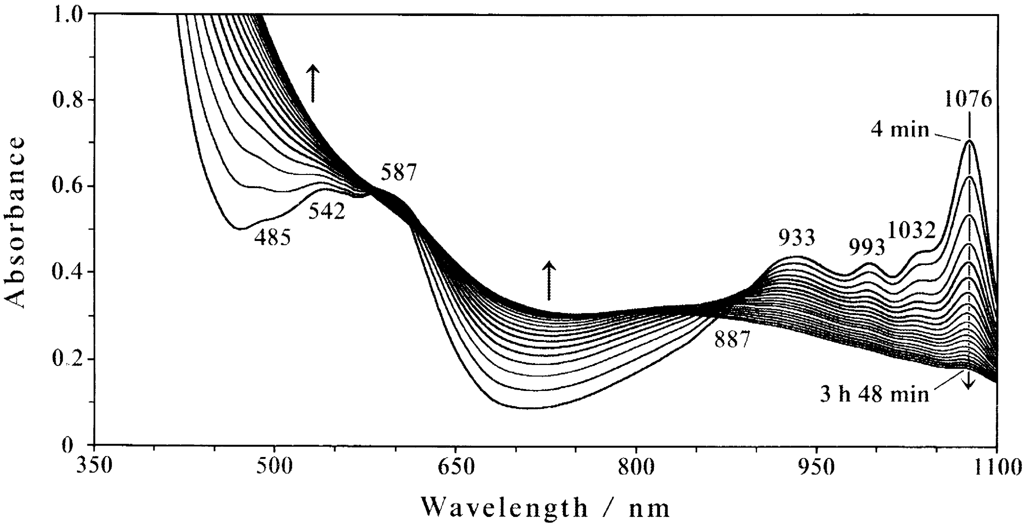
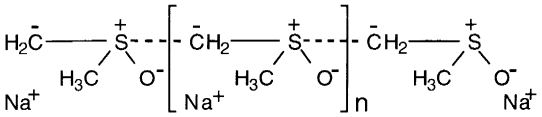


Fig. 2. VIS/NIR spectra showing a highly selective generation of γ-cyclodextrin-bicapped C_{60}^{1-} from **1** and large excess of NaH (or dimsylanion) in DMSO at 25°C in contact with air. Experimental conditions: NaH (60% dispersion in mineral oil), (17 mg, 0.42 mmol, 525 equiv.) was dissolved in DMSO (1 mL) through standing for some time, which was added to the suspension of **1** (3.0 mg, 0.8 μmol) in DMSO (1 mL). The mixture was shaken until it became transparent, and passed through a membrane filter. This solution was immediately used for the measurement. Time reaching the maximum absorbance=4 min. The same result was obtained using dimsylsodium prepared according to Corey's procedure[5]

Dimsylsodium is known to make a molecular aggregate by its self-association,[5] and we observed the viscosity enhancement of the solution of dimsylsodium in DMSO with increase of its concentration from 50 mM to 400 mM. It can, therefore, be presumed that: (1) a linear molecular aggregate, **2** is formed, and its terminal carbanion serves as a base center for deprotonation of a hydroxy group at the belt region of **1** (see Fig. 1); and (2) electron transfer from the resulting -O^- to C_{60} in **1** generates '$C_{60}{}^{1-}$'.



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Increase in the chain length (viscosity) of **2** due to increase in dimsylanion concentration seems to facilitate the generation of '$C_{60}{}^{1-}$' because of increasing interaction between **1** (belt region) and **2**. However, in dimsylanion concentration higher than 400 mM (in the case of **2** with longer chain), the spectra due to '$C_{60}{}^{1-}$' disappeared momentarily, presumably because of the instantaneous back electron transfer from $\mathbf{1}^-$ to $\mathbf{2}^+$. Under these circumstances, generation of '$C_{60}{}^{1-}$' due to the direct attack of monomeric dimsylanion to wholly encapsulated supramolecular complex, **1** seems to be unlikely.

Highly selective generation of γ-cyclodextrin-bicapped $C_{60}{}^{2-}$ *in DMSO*: Although both $\mathbf{1}\cdot 24H_2O$ (and also **1**) and $NaBH_4$ were sparingly soluble in DMSO,[7] a transparent solution was obtained by mixing both components in DMSO, suggesting the formation of a DMSO-soluble group in **1** by the reaction with $NaBH_4$.

The time-dependent VIS/NIR spectra of the transparent solution (**1**-$NaBH_4$–DMSO system) immediately after preparation is shown in Fig. 3. The detailed procedures are described in the figure caption. As shown in Fig. 3, by using excess $NaBH_4$, the highly selective generation of γ-cyclodextrin-bicapped $C_{60}{}^{2-}$ (λ_{max}: 950 nm)[1,6] was achieved even in the presence of oxygen. After reaching the maximum absorption, the characteristic bands (950, 834 nm) were slowly decreased on approach to the absorption spectra of **1**, because of dissolved oxygen.

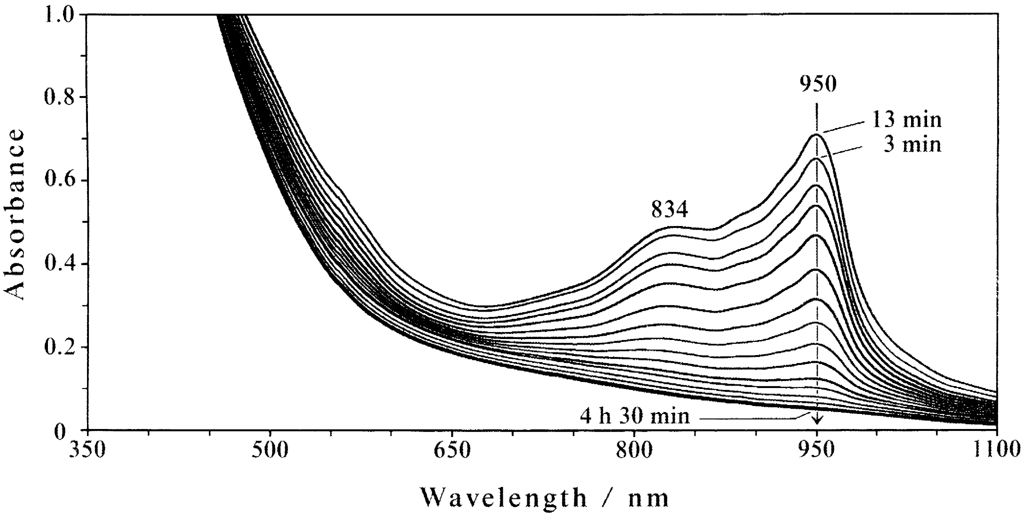
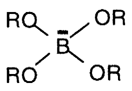


Fig. 3. VIS/NIR spectra showing a highly selective generation of γ-cyclodextrin-bicapped $C_{60}{}^{2-}$ from **1** and $NaBH_4$ (33 equiv.) in DMSO at 25°C in contact with air. Experimental conditions: suspension of $NaBH_4$ (1.0 mg, 26.3 μmol) in DMSO (1 mL) was added to the suspension of **1** (3.0 mg, 0.8 μmol) in DMSO (1 mL). The mixture was shaken until it became transparent, and passed through a membrane filter. This solution was immediately used for measurement. Time reaching the maximum absorbance=13 min

We observed that a sodium salt of **3** (R: CH_3, R-R: CH_2CH_2) and **4**[8] did not generate '$C_{60}{}^{2-}$'. It is, therefore, inferred that: (1) the essential functional group responsible for highly selective generation of '$C_{60}{}^{2-}$' should be **5** whose reactive hydrogen atoms serve as the base for deprotonation of two hydroxy groups at the belt region of **1** (see Fig. 1); and (2) electron transfer from the resulting two -O^- to C_{60} in **1** generates '$C_{60}{}^{2-}$'. Formation of ' $C_{60}{}^{2-}$' due to the direct attack of $NaBH_4$ on the C_{60} molecular surface in the hydrophobic cavity of **1** is unlikely, because $NaBH_4$ does not enter γ-cyclodextrin as the cavity model of **1**.



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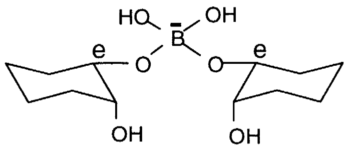

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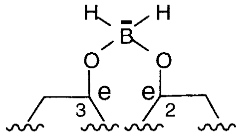

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Since the '$C_{60}{}^{1-}$' and'$C_{60}{}^{2-}$' species generated here are fairly stable even in the presence of oxygen, they could be conveniently used as a catalyst having electron-donating nature in various synthetic reactions.[9]

Acknowledgements

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4. We used a deposit produced by refluxing the biphasic mixture of C_{60} toluene solution and γ-cyclodextrin aqueous solution.[3] Thermal and elemental analyses indicated that this deposit was composed of **1** and $24H_2O$. Details will be published elsewhere.
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6. Lawson, D. R.; Foss, C. A.; Elliott, C. M.; Martin, C. R.; Parkinson, B. *J. Electrochem. Soc.* **1992**, *139*, L68–L71.
7. We observed that $NaBH_4$ was difficult to produce dimsylsodium.
8. Reactions of $NaBH_4$ as well as $RB(OH)_2$ (R: H, Ph etc.) with various alcohols including carbohydrates are well known.[10,11] Thus, reaction of *cis*-1,2-cyclohexanediol with $NaBH_4$ in DMSO (which includes a slight amount of water) occurred selectively at the equatorial OH to provide **4** as the Na salt. ^{1}H NMR (DMSO-d_6): CH_2 at δ 1.08(2H), 1.19(2H), 1.39(4H), 1.42(2H), 1.50(2H), 1.60(4H); CH at 3.52(4H); axial OH at 4.06(2H); B-OH at 7.06(2H). This indicates that the BH_2 group of the 2:1 adduct is reactive toward water included in DMSO.
9. We observed extremely interesting catalytic functions of γ-cyclodextrin-bicapped C_{60} under mild conditions which will be reported in due course.
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