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## A highly efficient generation of $\gamma$ -cyclodextrin-bicapped $C_{60}^{1-}$ in aqueous solution

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### Abstract

The successive treatment of  $\gamma$ -cyclodextrin-bicapped  $C_{60}$  complex (**1**) with  $FeCl_2$  and  $NaOH$  in aqueous solution at ambient temperature produces rapidly its  $C_{60}^{1-}$  complex in quantitative yield. The  $C_{60}^{1-}$  complex formation is quantitative, even in the contact with  $O_2$ , if  $Na_2S_2O_4$  is present. Plausible electron transfer mechanism is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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Generation of  $C_{60}^{n-}$  in aqueous solvent is reported to be difficult because of its kinetic instability (i.e. ready formation of  $O_2^{\bullet-}$  and  $C_{60}$  by dissolved  $O_2$ ).<sup>1,2</sup> Our interest has been focused on the chemical generation of wholly encapsulated  $\gamma$ -cyclodextrin-bicapped  $C_{60}^{n-}$  ( $n = 1 \sim 6$ ), and their characteristic properties and chemical functions. During the course of our investigations on the reduction behavior of  $C_{60}$  in  $\gamma$ -cyclodextrin-bicapped  $C_{60}$  (**1**), (abbreviated as  $C_{60}$ ), we discovered that a facile electron transfer from  $Na_2S_2O_4$  to the  $C_{60}$  in complex **1** in aqueous solution at room temperature under argon, generating the relatively stable  $\gamma$ -cyclodextrin-bicapped  $C_{60}^{n-}$  ( $n = 1$  and 2) (abbreviated as  $C_{60}^{n-}$ ) took place by using an iron(II) chloride-18-crown-6 (1:1) complex as mediator of the electron transfer.<sup>3</sup> Furthermore, we found the selective reduction of **1** with  $NaH$  and  $NaBH_4$  in DMSO leading to the corresponding  $C_{60}^{1-}$  and  $C_{60}^{2-}/\gamma$ -cyclodextrin ( $\gamma$ -CyD) complex, respectively.<sup>4</sup> These reactions are valuable as a generation method for  $C_{60}^{n-}$  ( $n = 1 \sim 2$ ) included in  $\gamma$ -CyDs, but the non-quantitative yield is an inherent drawback. We now report a reaction leading to quantitative formation of the  $C_{60}^{1-}$  in aqueous solution.

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The electron transfer was monitored by VIS/NIR (350–1100 nm) spectrophotometer. A water-soluble sample of  $\gamma$ -CyD-bicapped  $C_{60}$  complex (**1**) was prepared according to our paper.<sup>3,5</sup> The VIS/NIR diagram for the generation of  $C_{60}^{1-}$  is shown in Fig. 1B; the experimental conditions are described in the figure caption. As shown in Fig. 1, 1 h after complex **1** was dissolved in aqueous solution containing iron(II) chloride, a very weak band due to  $C_{60}^{2-}$  (961 nm)<sup>3,6</sup> appeared (time to reach maximum absorption: 1 h, **b**, in Fig. 1A).

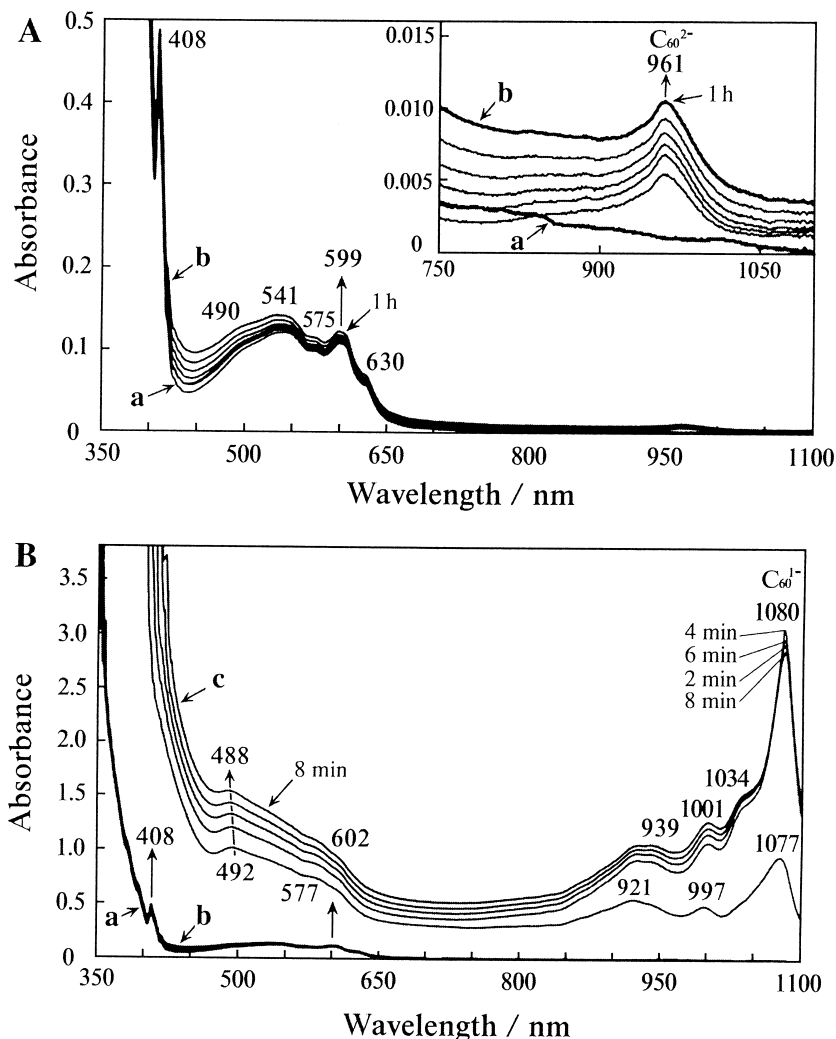
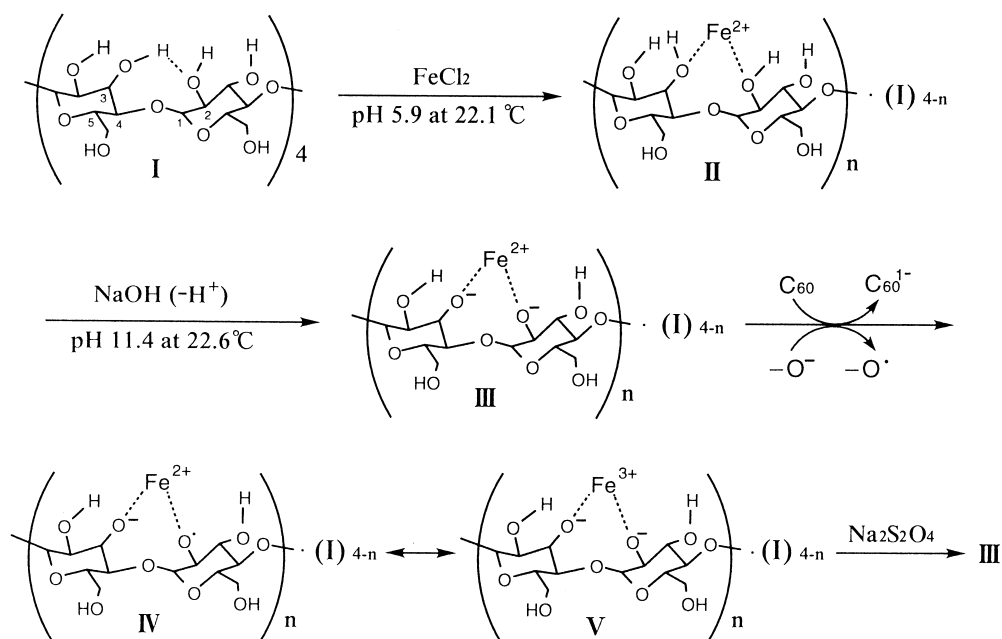


Figure 1. The VIS/NIR spectra of  $\gamma$ -cyclodextrin-bicapped  $C_{60}$  complex (**1**)-iron(II) chloride–NaOH system in aqueous solution at room temperature, leading to the quantitative generation of  $C_{60}^{1-}$  (measured by a Beckman DU 640 spectrophotometer). (A) The inset illustrates the enlargement of the absorbance between 750 and 1100 nm. **a**: Complex **1** in the presence of  $\gamma$ -cyclodextrin in aqueous solution [3 mL, concentration of complex **1**: 1.0 mg/mL (ca. 0.15  $\mu$ mol, length of the cell: 1 cm, pH 6.4, 25.4°C]. **b**: One hour after complex **1** (3.0 mg, ca. 0.45  $\mu$ mol) was dissolved in aqueous solution containing iron(II) chloride [3 mL, concentration of iron(II) chloride: 0.2 mg/mL (1.6  $\mu$ mol), pH 5.9, 22.1°C] (interval time = 10 min). (B) **c**: After adding aq. NaOH (2.5 M, 10  $\mu$ L) to the aqueous solution **b** in contact with air (pH 11.4, 22.6°C, interval time = 2 min)

By adding aq. NaOH to the solution **b**, the solution turned a pale reddish-brown and each absorbance of the characteristic bands for  $C_{60}^{1-}$  (1080, 1034sh, 1001, 939, and 921 nm)<sup>2,7-11</sup> (time to reach maximum absorption = 4 min, **c** in Fig. 1B) and its related bands (602sh and 488 nm) (time to reach maximum absorption = 8 min) was increased. From Fig. 1, it is demonstrated that formation of  $\gamma$ -CyD-bicapped  $C_{60}^{1-}$  is quantitative.<sup>12</sup> Although the characteristic NIR absorption bands for the generated  $C_{60}^{1-}$  gradually decreased in contact with air, quantitative generation of the  $C_{60}^{1-}$  species was completely restored by adding  $Na_2S_2O_4$  to the solution.<sup>12,13</sup> Thus, we have established the quantitative generation of  $C_{60}^{1-}$  in water in its  $\gamma$ -cyclodextrin bicapped form even in the presence of molecular oxygen. From the experimental data, the molar absorption coefficient ( $\epsilon$ ) of  $\gamma$ -CyD-bicapped  $C_{60}^{1-}$  was determined to be 8600 at  $\lambda_{max}$  1080 nm.

Experiments under the same conditions as above, using other transition metal chlorides [i.e. iron(III) chloride, copper(I) chloride, copper(II) chloride, ruthenium(III) chloride, or rhodium(III) chloride] in place of iron(II) chloride in the presence and absence of  $Na_2S_2O_4$  showed no generation of  $\gamma$ -CyD-bicapped  $C_{60}^{n-}$  ( $n = 1$  and  $2$ ).

The highly efficient (100%) generation of  $C_{60}^{1-}$  in the wholly encapsulated complex might be explained by the following sequential processes (Scheme 1): (1) formation of the complex **II** (spectra **b** in Fig. 1) by coordination of hydroxy oxygens at the belt region<sup>5</sup> of **I** to the  $Fe^{2+}$  ion; (2) formation of complex **III** having a strong electron donor system ( $-O^{\cdot-} \cdots Fe^{2+} \cdots O^{\cdot-}$ ) by deprotonation of complex **II** with NaOH; (3) formation of complex **IV** by highly efficient intramolecular electron transfer from  $O^{\cdot-}$  to  $C_{60}$  in the complex **III** (spectra **c** in Fig. 1B), and (4) regeneration of complex **III** from complex **IV** (or complex **V**) by  $Na_2S_2O_4$ .



Scheme 1. A plausible electron transfer mechanism for the formation of  $\gamma$ -cyclodextrin-bicapped  $C_{60}^{1-}$  in the **I**- $FeCl_2$ -NaOH (and  $Na_2S_2O_4$ ) system in aqueous solution:  $C_{60}$  and  $\gamma$ -CyD of the upper side in **I**~**V** are omitted. The value of  $n$  is considered to be 1

This very simple and highly efficient generation method of  $C_{60}^{1-}$  from  $C_{60}$  in water in the  $\gamma$ -CyD-bicapped form is expected to be valuable for developing new reactions which proceed via electron transfer.

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13.  $Na_2S_2O_4$  (1.0 mg, 5.7  $\mu$ mol) dissolved in water (50  $\mu$ L) was added to **c** (Fig. 1B) in contact with air.