Pergamon

Tetrahedron Letters 42 (2001) 6727–6729

TETRAHEDRON
LETTERS

Synthesis of fullerene–cyclodextrin conjugates

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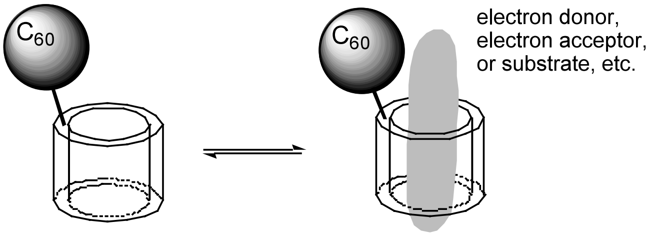
Received 3 July 2001; revised 26 July 2001; accepted 27 July 2001

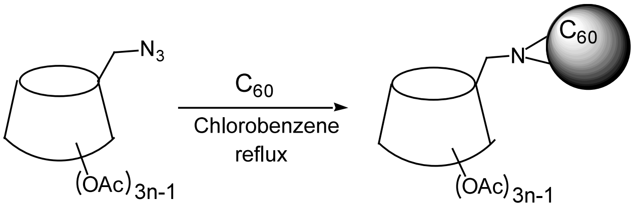
Abstract—[60] Fullerene derivatives bearing α-, β- and γ-cyclodextrin units as hydrophobic binding sites have been synthesized by the reaction of C_{60} and peracetylated cyclodextrin 6-azides in chlorobenzene. The C_{60}–β-cyclodextrin conjugate demonstrated efficient quenching effect on the bound photo-luminescent guest rhodamine B. © 2001 Elsevier Science Ltd. All rights reserved.

The unique physical and chemical properties of C_{60} have received significant interest and lots of fullerene derivatives have been prepared by introducing electron donors or acceptors in order to investigate their redox behaviors.[1] Among the various fullerene derivatives, the C_{60}–photo-luminescent polymer systems exhibit charge transfer in the excited state in a picosecond time scale and, as one of the most outstanding application of fullerenes, have been used to prepare improved photovoltaic cells with higher efficiency.[2] C_{60}–porphyrin conjugates efficiently generate singlet oxygen and are of interest in photodynamic therapy.[3] Recent attention has been directed to water-soluble fullerenes because of their potential biomedical applications[4] and strategies such as multi-hydroxylation, polymer embedding and encapsulation with cyclodextrins etc. have been developed to make fullerenes more water-soluble. On the other hand, molecular recognition plays an important role in many molecular devices or chemical processes. Incorporating the molecular recognition property into fullerenes may provide a new approach to improve their functions (Scheme 1). For example, trapping a proper electron donor or acceptor into a covalently linked recognition site may mediate the electronic state of C_{60}, while a substrate bound in that site may be promoted to react and then release that site to make the fullerene an enzyme-like catalyst. Cyclodextrins (CDs), a series of cyclic oligosaccharides having hydrophobic cavity and being water-soluble, are suitable to exercise the molecular recognition. Gekckeler et al. reported the first synthesis of fullerene–β-CD conjugates by the reaction of C_{60} with CD amines.[4b] In this paper, we describe the synthesis of C_{60}–CD conjugates via 1,3-dipolar cycloaddition of CD azides to C_{60} and the preliminary results on the quenching effect of these conjugates on the bound fluorescent guest.



Scheme 1.

As a general procedure for the synthesis, peracetyl α-, β-, or γ-cyclodextrin azide[5] (0.15 mmol) was dissolved in 10 ml C_6H_5Cl and added to a solution of 45 ml C_6H_5Cl containing 0.1 mmol C_{60}. After deareated with a nitrogen stream, the reaction solution was refluxed in the dark until the increase of product ceased (monitored by TLC). The reaction mixture was then subjected to column chromatography on silica gel. The column was first eluted with toluene to recover the unreacted C_{60}, and then with toluene–methanol (29:1, v/v) to afford the C_{60}–CD conjugates (Scheme 2).[6]



1	n = 6: α-CD	**4**
2	n = 7: β-CD	**5**
3	n = 8: γ-CD	**6**

Scheme 2.

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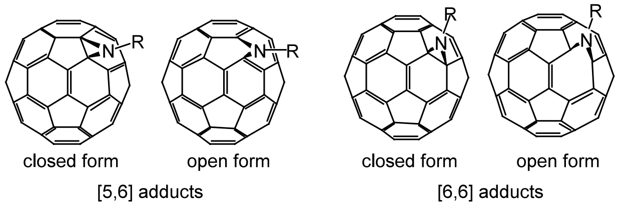
PII: S0040-4039(01)01375-2



Scheme 3.

The FAB-MS spectra demonstrated molecular ion peaks at *m*/*z* 2405 for **4**, *m*/*z* 2693 for **5** and *m*/*z* 2981 for **6**, indicating that all three C_{60}–CD conjugates are of a monoimino-fullerene type.[7] The imino addends may be attached either to the [6,6] junctions or to the [5,6] junctions of C_{60}, generating 'closed' or 'open' [5,6] and [6,6] adducts (Scheme 3). The NMR spectra of **4**–**6** supported the open form of the [5,6] adducts.

All conjugates **4**, **5** and **6** showed the chemical shift pattern of CDs in both ^1H and ^{13}C NMR spectra. The C_{60} section demonstrated a set of signals in the range of δ 135–150 ppm in ^{13}C NMR spectra but showed no signals beyond this range, which rules out the possibility of closed form structures since the newly generated saturated carbons in the closed form structures should resonate at a much higher field than normal unsaturated carbons of C_{60}. Moreover, the C_s symmetry of [5,6] adducts divides the 60 carbons into 32 different kinds, while the C_{2v} symmetry of [6,6] adducts reduces this number to 17. Although all signals are not well resolved, the number of peaks within δ 135–150 ppm obviously exceeded 17 in the ^{13}C NMR spectra of each C_{60}–CD conjugate. These facts suggest that all the C_{60}–CD conjugates take the open form of the [5,6] adducts. This assignment is consistent with literature documents that the closed [6,6] and open [5,6] adducts have been observed in the reactions of C_{60}, while the closed [5,6] and open [6,6] adducts are extremely scarce.[8]

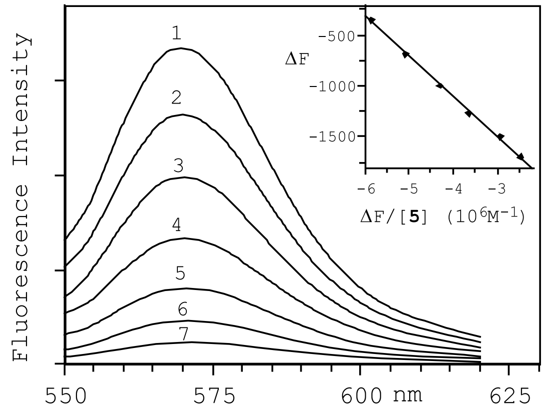
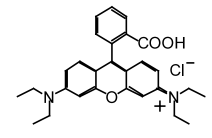


Figure 1. Fluorescence spectra of 1.0×10^{-6} M rhodamine B in 80% aqueous acetonitrile solution (1) and in the presence of 6.0×10^{-5} M (2), 1.3×10^{-4} M (3), 2.3×10^{-4} M (4), 3.5×10^{-4} M (5), 4.9×10^{-4} M (6) and 6.3×10^{-4} M (7) C_{60}–β-CD **5**. The inset represents the Scatchard plot of the fluorescence titration data, indicating the formation of a 1:1 inclusion complex with an associate constant of 2800 M^{-1}.

Rhodamine B



The UV–vis spectra of **4**–**6** in chloroform showed two absorption bands with maxima at ~260 nm (log ε= 4.78, 4.89 and 5.10, respectively) and ~332 nm (log ε= 4.16 4.36 and 4.49, respectively), very similar to that of C_{60} itself. This implies that the basic structure of C_{60} is retained in the conjugates. The fluorescence quenching property of the C_{60}–CD conjugates has been preliminarily examined by taking rhodamine B as the guest. As shown in Fig. 1, rhodamine B emits strongly around 570 nm in 80% aq. CH_3CN solution. Upon addition of the C_{60}–β-CD **5**, the intensity of this emission decreases rapidly and more than 90% of fluorescence is finally quenched. Treatment of the titration data with the Scatchard method gives an association constant of 2800 M^{-1} for the 1:1 binding of the guest and C_{60}–β-CD. Further investigation on this fluorescence quenching property is in progress.

Acknowledgements

We thank Japan Maize Products Co. Ltd. for a generous gift of CDs. D-Q.Y. thanks the NSFC for projects 29632004 and 29772023 and the State Education Ministry of China for project 380.

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