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Studies on Novel Cyclodextrans: Inclusion of C_{60} and C_{70}

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Abstract. Cycloisomalto-heptaose (CI-7) and cycloisomalto-octaose (CI-8) are two novel cyclodextrans. Treatment with C_{60} or C_{70} by kneading leads to the formation of four distinct water-soluble inclusion complexes: CI-7/C_{60} (2 : 1), CI-8/C_{60} (2 : 1), CI-7/C_{70} (2 : 1) and CI-8/C_{70} (2 : 1). Their formation and structures have been examined by UV-vis spectroscopy, X-ray powder diffraction and fluorescence spectral studies. The reaction is a reversible process.

Key words: C_{60}, C_{70}, cyclodextrans, cycloisomalto-heptaose, cycloisomalto-octaose, water-soluble inclusion complex.

1. Introduction

The C_{60} and C_{60} molecules are two important members of the fullerene family. Their availability in a high degree of purity has prompted many studies on their structures, properties and reactions [1, 2]. However the solubility of fullerenes, poor in most organic solvents, and negligible in water, has been one of the greatest impediments to studying their reactions and possible biological functions.

To make C_{60} and C_{60} soluble in water, the cyclodextrins (CDs) are quite promising agents. C_{60} looks like a soccer ball while C_{70} looks like a rugby ball and their diameters, calculated for the carbon cage itself, are 7.1 Å and 6.82 Å, respectively [3, 4] (Figure 1). Cyclodextrins consist of six (α-CD), seven (β-CD) or eight (γ-CD) sugar molecules joined together in a ring by α-1,4-glucosidic bonds [5, 6]. With a hydrophobic cavity inside the molecule, it may act as a host for organic molecules. Among α-, β- and γ-CD, only γ-CD can include C_{60} and two distinct water-soluble inclusion complexes (γ-CD/C_{60} (1 : 1) and γ-CD/C_{60} (2 : 1)) have been obtained [7, 8].

Cycloisomalto-heptaose (CI-7) and cycloisomalto-octaose (CI-8) are two novel cyclodextrans consisting of seven and eight D-glucose moieties bound by α-1,6 linkages, respectively [9] (Figure 2). Comparison with CD using CPK models, shows that CI-7 (or CI-8) also has a hydrophobic cavity inside the molecule, but its cavity is larger than that of β-CD (or γ-CD) and the molecule is flatter. Judging from

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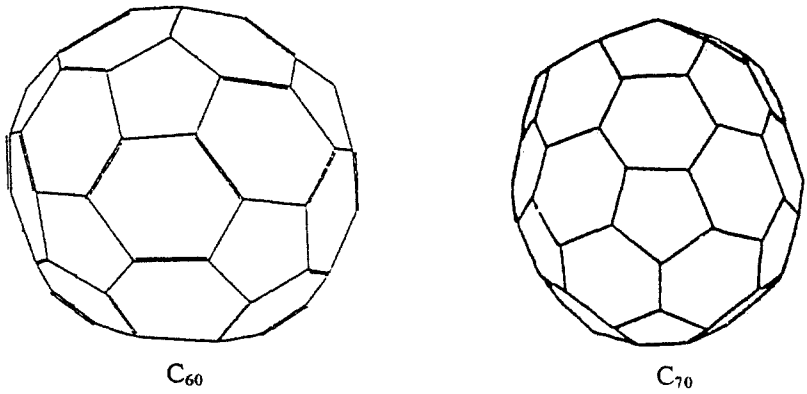

Figure 1. Sketch of the structures of C_{60} and C_{70}.

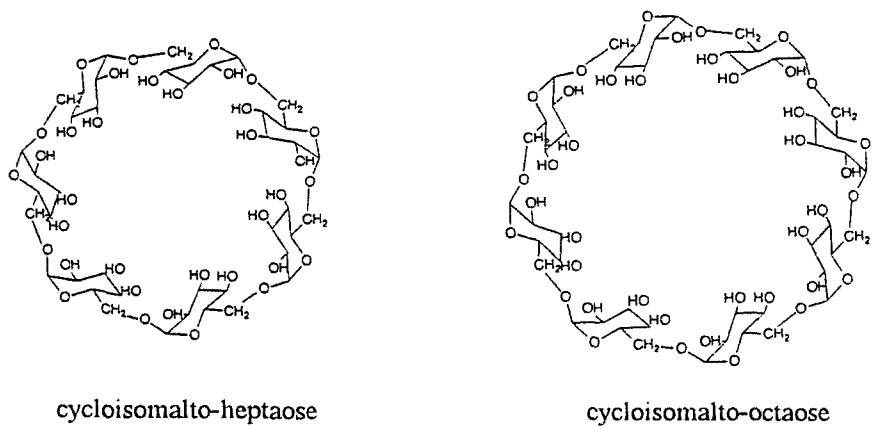

Figure 2. Chemical structures of cycloisomalto-heptaose (CI-7) and cycloisomalto-octaose (CI-8).

the cavity size of cyclodextrans, and the size of soccer ball C_{60} (7.1 Å diameter) and rugby ball C_{60} (6.82 Å diameter at the equator, 8 Å between the poles), we deduced that both CI-7 and CI-8 can accommodate either C_{60} or C_{70}, and the bicapped structure of the complex should be the more stable (Figure 3).

Considering the specific characteristics of C_{60} or C_{60} as a guest of cyclodextrans, we treated them with C_{60} or C_{60} by the kneading method and obtained, for the first time, four distinct solid inclusion complexes. In this paper, we describe the high-yield production of the complexes, and proof for determination of the formation and their structures.

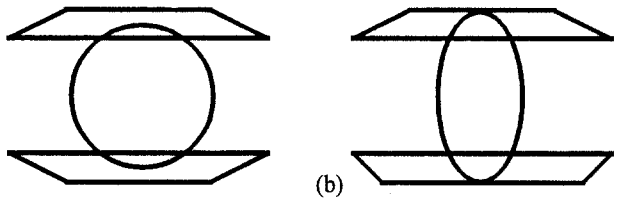

Figure 3. Possible structures of cyclodextran/fullerene 2 : 1 complexes in aqueous solution. (a) Cyclodextran/C_{60} 2 : 1 complex, (b) cyclodextran/C_{70} 2 : 1 complex.

2. Experimental

2.1. Materials

Cycloisomalto-heptaose and cycloisomalto-octaose were produced by Tetsuya Oguma. C_{60} and C_{70} are products of the Department of Chemistry, Peking University, and the purity is 99.0% or higher. Distilled water was used throughout the study.

2.2. Preparation of the Inclusion Complexes

CI-7/C_{60} (2 : 1): 8.8 mg (1.2×10^{-5} mol) C_{60} and 28.0 mg (2.4×10^{-5} mol) CI-7 were homogenized and kneaded for 2 h with dropwise addition of water (about 2 mL). The product was vacuum-dried at 117 °C for 3 h. Yield: 34.2 mg. C_{60} content: 24.1%.

CI-8/C_{60} (2 : 1): 11.5 mg (1.6×10^{-5} mol) C_{60} and 41.6 mg (3.2×10^{-5} mol) CI-8 were homogenized and kneaded for 2 h with dropwise addition of water (about 2.5 mL). The product was vacuum-dried at 117 °C for 3 h. Yield: 50.6 mg. C_{60} content: 21.7%.

CI-7/C_{70} (2 : 1): 4.1 mg (4.9×10^{-6} mol) C_{70} and 11.2 mg (9.8×10^{-6} mol) CI-7 were homogenized and kneaded for 2 h with dropwise addition of water (about 1 mL). The product was vacuum-dried at 117 °C for 3 h. Yield: 13.8 mg. C_{70} content: 27.0%.

CI-8/C_{70} (2 : 1): 4.0 mg (4.8×10^{-6} mol) C_{70} and 12.4 mg (9.5×10^{-6} mol) CI-8 were homogenized and kneaded for 2 h with dropwise addition of water (about 1 mL). The product was vacuum-dried at 117 °C for 3 h. Yield: 14.4 mg. C_{70} content: 24.5%.

2.3. Physical Measurements

UV-vis spectra were recorded on a HP-8452A UV spectrometer.

X-ray powder patterns were obtained with a Rigaku-D/max-Rb diffractometer with a monochromator of Ni utilizing CuK_α radiation with 40 kV and 30 mA at a scan rate of 8°/min.

Fluorescence spectra were recorded on a OMA spectrofluorometer, and all samples were excited at 532 nm.

3. Results and Discussion

3.1. UV-VIS SPECTRA

Since C_{60} and C_{70} have strong absorption features in the ultraviolet region [3, 10], the aqueous solution containing C_{60} or C_{70} can also be detected by UV-vis spectroscopy [7]. Initially homogenized molar equivalents of cyclodextran and C_{60} (or C_{70}) were kneaded for 2 h (sample 1). Then 2 equiv. of cyclodextran and 1 equiv. of C_{60} (or C_{70}) were treated as above giving sample 2. In the first case, the solution was very turbid and much C_{60} (or C_{70}) was precipitated from the aqueous solution of the product. In the second case, the product was completely dissolved in water (the color of the cyclodextran/C_{60} aqueous solution is yellow and that of the cyclodextran/C_{70} aqueous solution is dark purplish red) without any C_{60} (or C_{70}) precipitate.

Comparison of their UV-vis spectra, showed that the spectrum of sample 1 is the same as that of sample 2. Furthermore, when 3, 4 or more equiv. of cyclodextran were treated with 1 equiv. of C_{60} (or C_{70}) by kneading, their UV-vis spectra were the same. Because of the large cavity and the flat stereo structure of the cyclodextran molecules, a bicapped structure is likely to be the more stable form for the cyclodextran/C_{60} (or C_{70}) inclusion complex, i.e. cyclodextran/C_{60} (2 : 1) (or cyclodextran/C_{70} (2 : 1)) should be the 2 : 1 complex (Figure 3).

The UV-vis spectra of CI-7/C_{60} (2 : 1), CI-8/C_{60} (2 : 1), CI-7/C_{70} (2 : 1) and CI-8/C_{70} (2 : 1), shown in Figures 4 and 5, indicated the formation of the complexes. The maximum absorption wavelengths are listed in Table I. One can observe that the spectrum of cyclodextran/C_{60} (2 : 1) (or cyclodextran/C_{70} (2 : 1)) is red-shifted compared to that of the cyclohexane solution of C_{60} (or C_{70}). It is due to the intermolecular interaction between the cavity of the cyclodextrans and the π-systems of the fullerenes [8]. The polarity of the hydrophobic cavity of the cyclodextrans is analogous to that of cyclohexane and non-polar compared with water. It is thought that the increasing surface available for contact with water is responsible for the systematic red-shift of the UV-vis spectra, from pure C_{60} (or C_{70}) in cyclohexane to aqueous cyclodextran/C_{60} (or cyclodextran/C_{70}) solution.

3.2. SOLUBILITIES

The solubilities of CI-7/C_{60} (2 : 1), CI-8/C_{60} (2 : 1), CI-7/C_{70} (2 : 1) and CI-8/C_{70} (2 : 1), were measured at 25 °C by spectrophotometric analysis in aqueous solution with determination at 268 nm, 268 nm, 268 nm and 278 nm, respectively. The results are listed in Table II.

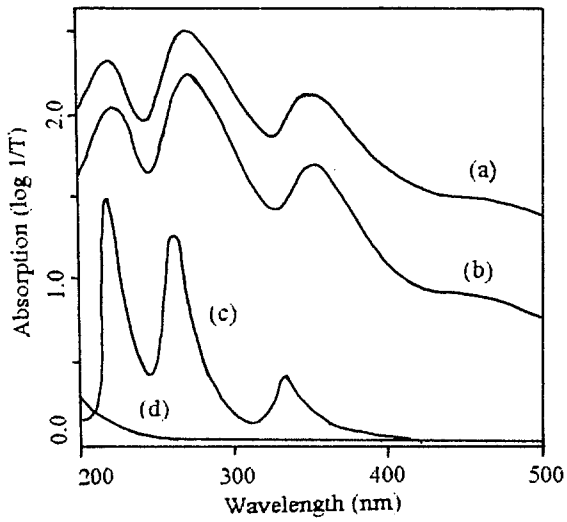

Figure 4. UV-vis spectra of (a) CI-8/C_{60} (2 : 1) aq. solution (4.2×10^{-5} mol · dm^{-3}), (b) CI-7/C_{60} (2 : 1) aq. solution (4.0×10^{-5} mol · dm^{-3}), (c) C_{60} cyclohexane solution, (d) cyclodextran aq. solution.

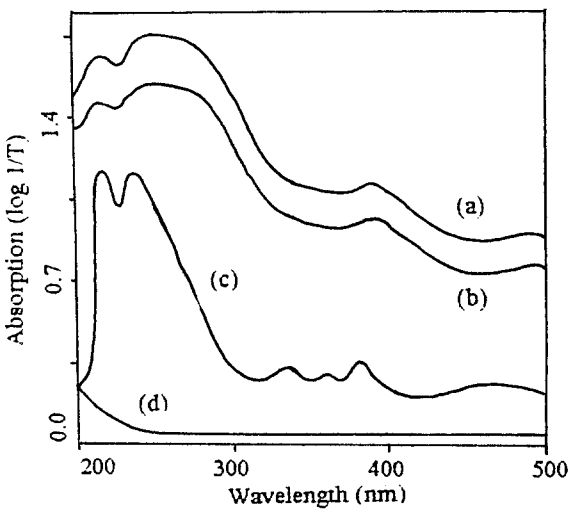

Figure 5. UV-vis spectra of (a) CI-8/C_{70} (2 : 1) aq. solution (3.4×10^{-5} mol · dm^{-3}), (b) CI-7/C_{70} (2 : 1) aq. solution (3.2×10^{-5} mol · dm^{-3}), (c) C_{70} cyclohexane solution, (d) cyclodextran aq. solution.

3.3. X-Ray Diffraction

The X-ray powder patterns for the individual components, the CI-7/C_{60} complex (2 : 1), and a physical mixture (molar ratio 2 : 1) are presented in Figure 6. A comparison of the CI-7/C_{60} (2 : 1) pattern with that of the physical mixture, which

Table I. UV data of the samples

C_{60}	λ_{max} (nm)				
cyclohexane solution	CI-7/C_{60} (2 : 1) aq. solution	CI-8/C_{60} (2 : 1) aq. solution	C_{70} cyclohexane solution	CI-7/C_{70} (2 : 1) aq. solution	CI-8/C_{70} (2 : 1) aq. solution
216	220	222	216	216	216
258	270	272	238	248	256
330	350	352	380	390	390
			470	496	498

Table II. Solubilities of the samples in water

Sample	Solubility of the complex (mg/100 mL)	Highest concentration of C_{60} or C_{70} in aq. solution (mol · dm^{-3})
CI-7/C_{60} (2 : 1)	40	1.4×10^{-4}
CI-8/C_{60} (2 : 1)	21	6.2×10^{-5}
CI-7/C_{70} (2 : 1)	11	3.5×10^{-5}
CI-8/C_{70} (2 : 1)	40	3.8×10^{-5}

can be interpreted as an approximate superposition of the components, shows that the pattern of CI-7/C_{60} (2 : 1) does not correspond to those of the pure components. These observations prove that the solid product is a new crystalline phase associated with the formation of an inclusion complex. The differences in the X-ray diffraction patterns between CI-8/C_{60} (2 : 1) and the physical mixture of CI-8 and C_{60} at 2 : 1 molar ratio (shown in Figure 7) also provides proof for inclusion of C_{60}.

3.4. Fluorescence Spectra

Using laser excitation (15 ns pulse, 532 nm), the fluorescence emission spectra of C_{60} and C_{70} in cyclohexane, CI-7 and CI-8, and their complexes with C_{60} or C_{70} in water were obtained (Figure 8). The fluorescence of C_{60} in cyclohexane (1.3×10^{-5} mol · dm^{-3}) at room temperature consists of a large band in the 720 nm region (the strong peak at about 630 nm is due to the cyclohexane) [11]. In the fluorescence spectrum of the cyclodextran/C_{60} aqueous solution with a C_{60} concentration of 1.3×10^{-5} mol · dm^{-3}, the fluorescence band of the C_{60} nearly disappeared indicating that the complex has a strong quenching effect on the fluorescence of the C_{60} (the strong peak at about 650 nm is due to the Raman scattering of the water at the intense laser excitation). The fluorescence of C_{70} in cyclohexane (1.3×10^{-5} mol · dm^{-3}) has a peak at 652 nm and a large band in the 680 nm region [11], which are also quenched by the cyclodextrans in the cyclodextran/C_{70} complexes.

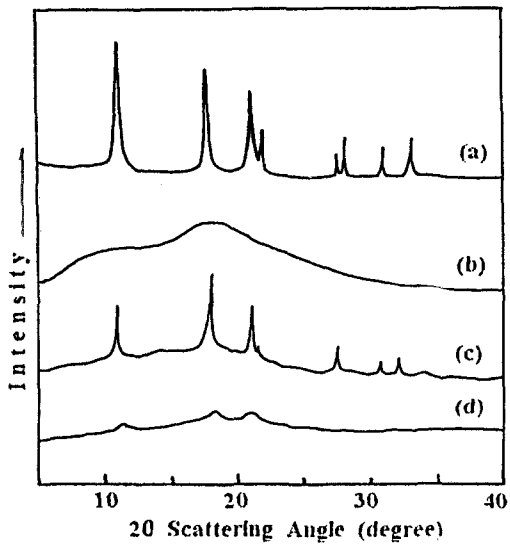

Figure 6. X-ray diffraction patterns. (a) C_{60}, (b) CI-7, (c) physical mixture of CI-7 and C_{60}, (d) CI-7/C_{60} (2 : 1).

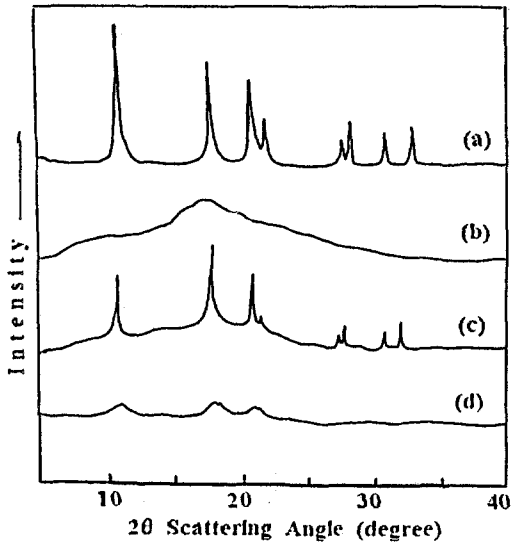

Figure 7. X-ray diffraction patterns. (a) C_{60}, (b) CI-8, (c) physical mixture of CI-8 and C_{60}, (d) CI-8/C_{60} (2 : 1).

3.5. The Reversible Process

Both CI-7/C_{60} (2 : 1) and CI-8/C_{60} (2 : 1) can be dissolved in water to give yellowish, transparent solutions. At room temperature, they are so stable in water that they show no change in the UV-vis spectrum after several days. However, they decomposed under reflux, and Figures 9 and 10 show the process of the decomposition of CI-7/C_{60} (2 : 1) and CI-8/C_{60} (2 : 1) in aqueous solution.

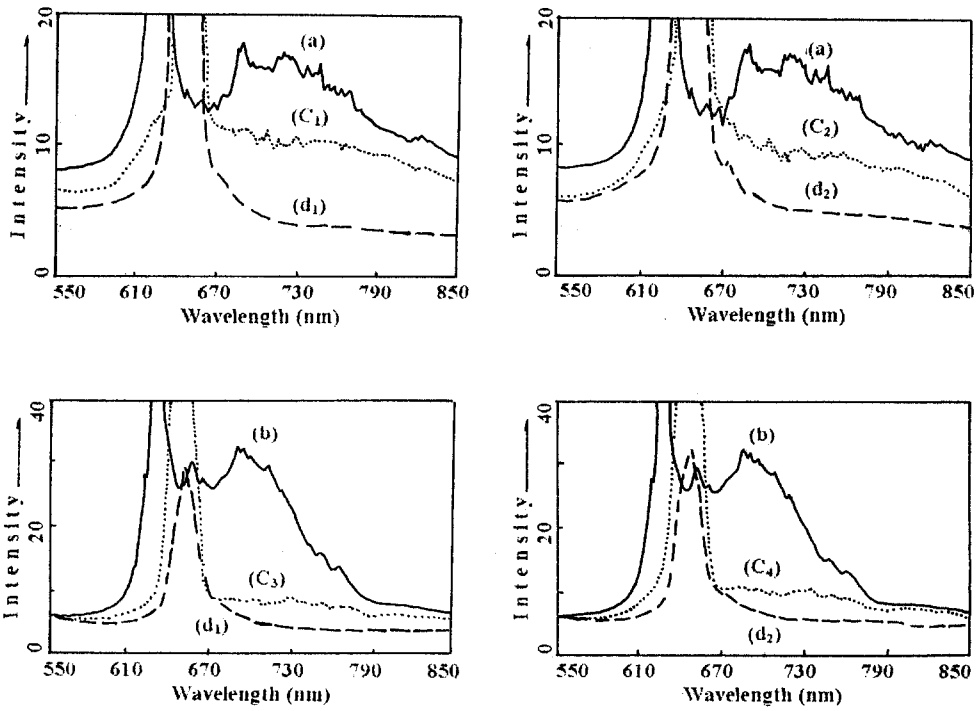

Figure 8. Fluorescence emission spectra of (a) C_{70} in cyclohexane, (b) C_{70} in cyclohexane, (C_1) CI-7/C_{60} (2 : 1) aq. solution, (C_2) CI-8/C_{60} (2 : 1) aq. solution, (C_3) CI-7/C_{70} (2 : 1) aq. solution, (C_4) CI-8/C_{70} (2 : 1) aq. solution, (d_1) CI-7 aq. solution, and (d_2) CI-8 aq. solution. The concentration of d_1 or d_2 is 2.6×10^{-5} mol · dm^{-3} and others are 1.3×10^{-5} mol · dm^{-3}.

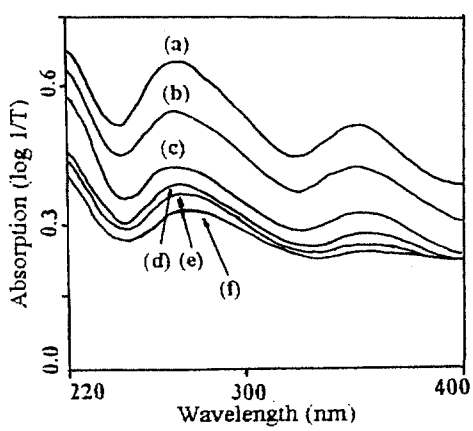

Figure 9. UV-vis spectrum of CI-7/C_{60} (2 : 1) aq. solution under reflux after (a) 0 h, (b) 40 min, (c) 1.5 h, (d) 2 h, (e) 3 h, (f) 4 h.

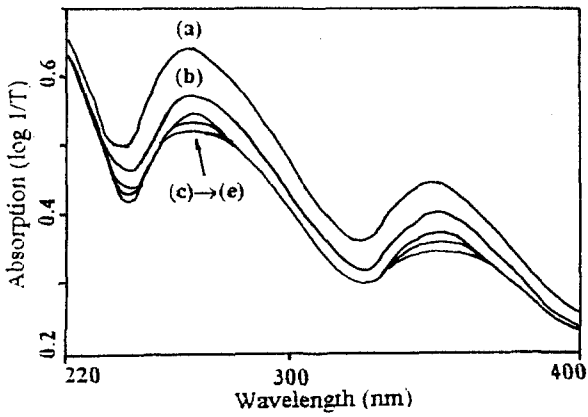

Figure 10. UV-vis spectrum of CI-8/C_{60} (2 : 1) aq. solution under reflux after (a) 0 h, (b) 40 min, (c) 1.5 h, (d) 2 h, (e) 3 h.

Reversible process of the reaction:

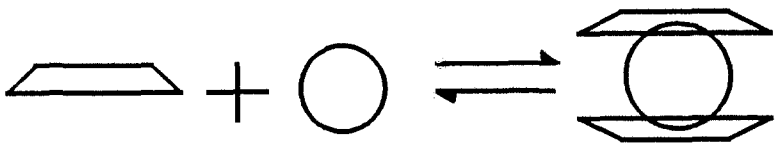

Figure 11.

C_{60} treated with excess of cyclodextran in water under reflux, also gives the cyclodextran/C_{60} complex (the UV-vis spectrum is shown in Figure 4). The reversible process of the complex can be described as in Figure 11. (The cyclodextran/C_{70} complex, behaves in a similar fashion.)

4. Conclusion

Four different cyclodextran C_{60} or C_{70} inclusion complexes have been formed under proper experimental conditions. As relatively pure aqueous solutions of the complexes are available, the various physical and chemical properties of C_{60} and C_{70} in water can now be measured and speculations concerning their potential biological functions in water can be assayed.

Acknowledgments

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