Available online at www.sciencedirect.com

Tetrahedron Letters 45 (2004) 2071–2073

Tetrahedron Letters

Solvent-free self-assembly of C_{60} and cucurbit[7]uril using high-speed vibration milling

Friederike Constabel and Kurt E. Geckeler*

Laboratory of Applied Macromolecular Chemistry, Department of Materials Science and Engineering, Kwangju Institute of Science and Technology, 1 Oryong-dong, Buk-gu, Kwangju 500-712, South Korea

Received 16 December 2003; revised 10 January 2004; accepted 16 January 2004

This paper is dedicated to Prof. Schue on the occasion of his 65th birthday anniversary

Abstract—The synthesis of a cucurbit[7]uril-[60]fullerene supramolecular complex using a simple, green, and efficient pathway is reported for the first time. In the complex, which was found to be of the 1:2 type, the compounds interact weekly with each other. Since the complexation can be achieved by a solid–solid reaction without solvent both the waste and contact with harmful solvents can be reduced to a minimum. A significant increase of reaction rate and yield compared to the heterogeneous complexation was observed.

Cucurbituril (CB_n), a synthetic macrocycle, can interact with easily polarizable molecules, polar compounds, or ions through ion–dipole interactions and hydrogen bonding.[1,2] Its hydrophobic hollow core, which is accessible through two identical carbonyl-fringed portals, makes this compound very attractive as a synthetic receptor and building block for supramolecular chemistry.[2] Since CB_n is only poorly soluble in common organic solvents, the complexation usually takes place in strongly acidic, aqueous solutions containing alkaline metal salts, or as two-phase reactions between the solid cucurbituril and the dissolved or gaseous guest molecules.[1,3]

Fullerenes have been the focus of interest in many research groups as they have many unique properties and can be used in a wide range of applications.[4,5]

Since fullerenes show a poor solubility in most common solvents, many efforts have been made to modify these molecules in green pathways under solvent-free conditions.[6] One access to modified fullerenes through covalent and noncovalent binding describes a mechanochemical technique, in which the solid reactants are ball-milled under high speed.[6,7] Also studies for the γ-cyclodextrin (CD)-C_{60} complex by mechanochemical synthesis have been reported.[7]

Here, we report the synthesis of the first supramolecular complex **3** between cucurbit[7]uril (CB_7) **1** and [60]fullerene (C_{60}) **2** through noncovalent binding.[8] Since another goal was to find a synthetic pathway, which should be as efficient as possible, we performed the synthesis as solid–liquid reaction between the solid guest molecule C_{60} and an alkaline aqueous solution of CB_7 as well as under high-speed vibration (HSVM) conditions of the solid compounds (Scheme 1).[9,10] The stoichiometry of the complex was found to be 1:2 according to thermogravimetric analysis. The reaction conditions and yields are shown in Table 1.

It can be seen that the rate increased significantly by synthesizing **3** under HSVM conditions compared to the solid–liquid synthesis (Table 1, entry 2–4 vs 1). After 4 h of milling the yields were similar to those, which could be obtained after 4 days when the complexation was performed as solid–liquid reaction. Yields close to 80% could be achieved. Furthermore, contact with harmful solvents and waste was reduced to a minimum.

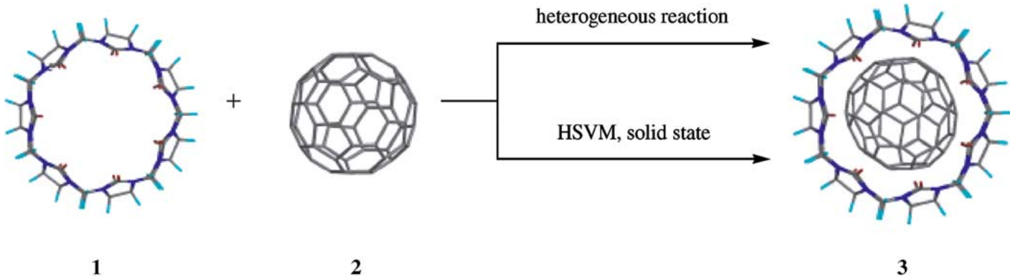
In all cases (entries 1–4) and independent of the molar ratio of CB_7 to C_{60} (entries 1–4) a dark-brown solid was formed, which was not soluble in common organic solvents, lyes, and acid solutions. The product was

---

Keywords: C_{60}; Cucurbit[7]uril; Solvent free; High-speed vibration milling; Solid-state reaction; [60]fullerene.

* Corresponding author. Tel.: +82-62-970-2316; fax: +82-62-970-2338; e-mail: keg@kjist.ac.kr

0040-4039/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2004.01.071



Scheme 1. Synthesis of the cucurbit[7]uril-[60]fullerene complex performed as heterogeneous as well as solid state reaction (tube models). Color code: oxygen: red, nitrogen: dark blue, carbon: grey, hydrogen: light blue.

Table 1. Synthesis of the cucurbit[7]uril-[60]fullerene (CB_7-C_{60}) complex performed as heterogeneous as well as solid state reaction[10]

Entry	Preparation method	pH	Molar ratio CB_7/C_{60}	Temperature (°C)	Time (h)	Yield (%)
1	Heterogeneous	12	2/1	23	96	55
2	Solid state	Neutral	2/1	>30[a]	4	55
3	Solid state	Neutral	1/1	>30[a]	4	77
4	Solid state	Neutral	1/2	>30[a]	4	29

[a] Measurements of the temperature were performed inside the cups after 2 h of grinding.

analyzed by XRD, FT-IR spectroscopy, and thermogravimetric analysis (TGA).[11]

The X-ray diffractogram pattern (Fig. 1) shows that the synthesized product exhibits neither the typical 2θ values of CB_7 nor those of C_{60} at $2\theta = 11.0°$, 17.5°, and 21.7°.[12] In accordance with previous observations for C_{60} inclusion complexes a total suppression of the crystalline structure of the initial compounds takes place.[13,14] Consequently, a single-crystal X-ray diffraction structure could not be recorded.

The FT-IR spectra of **3** showed the typical band for C_{60} at 527 cm^{-1} in addition to the bands for CB_7. While the characteristic carbonyl band of CB_7 at 1728 cm^{-1} was slightly shifted to 1732 cm^{-1} due to complexation, the typical C_{60} band remained constant. The slight shift of the carbonyl band of CB_7 indicates weak interactions, probably van der Waals forces, between the host and the guests.[15]

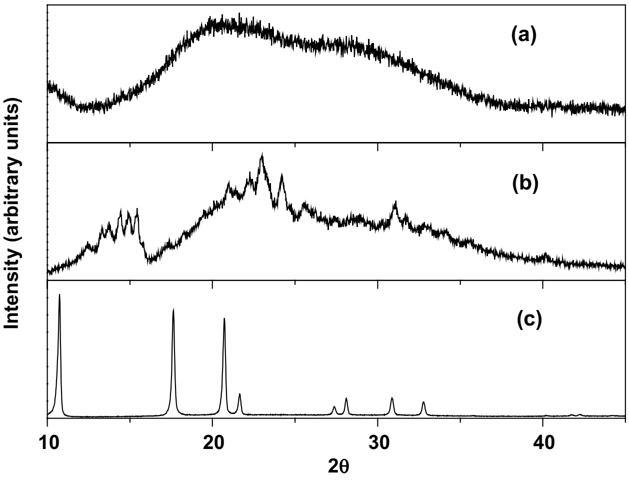


Figure 1. X-ray diffractograms of (a) the cucurbit[7]uril-[60]fullerene complex, (b) cucurbit[7]uril, and (c) [60]fullerene.

In order to specify the stoichiometry of **3**, we performed thermogravimetric analysis of the product as well as from the initial compounds, CB_7, and C_{60}. The complex showed two decomposition temperatures: one at 390 °C and the other one at 550 °C, assigned to the decomposition of CB_7 and the decomposition of C_{60}, respectively.

The total mass loss at 410 °C was 40.1%. Up to this temperature only CB_7 decomposes, whereas C_{60} remains stable. The theoretical calculated mass content of CB_7 for a 1:2, 1:1, or 2:1 complex would be 44.7%, 61.8%, and 76.4%, respectively. Thus, the observed mass loss of 40.1% clearly indicates that the ratio of CB_7 to C_{60} in the complex is 1:2. From the elemental analysis of the vacuum-dried sample we have calculated that on the average 26 molecules of water are attached to one monomeric unit of the complex so that the composition of the complex was found to be $[C_{42}H_{42}N_{28}O_{14}\cdot 2C_{60}]\cdot 26H_2O$.[16]

As deduced from model images (not shown), each fullerene sphere is intercalated partially into the cavity of the host through the opposite portals.

In conclusion, we report the first synthesis of a supramolecular complex between CB_7 and C_{60} by an efficient procedure. The analytical data show that the complex is of the 1:2 type in which the compounds interact weakly with each other. It is reported that the formation of a γ-CD-C_{60} complex is completed after 20 h of milling. Interestingly, we obtained compound **3** in high yields after 4 h of ball milling. Since only the purification step of the complex requires the use of solvents, the complex could be obtained in high yield and the reaction time was shortened considerably compared to the solid–

liquid synthesis this pathway becomes attractive for both environmental and economical points of view.

Acknowledgement

This work was supported by the Ministry of Education within the scope of the 'Brain Korea 21' project.

References and notes

1. Mock, W. L.; Shih, N.-Y. *J. Org. Chem.* **1986**, *51*, 4440–4446.
2. Haouaj, M. E.; Ko, Y. H.; Luhmer, M.; Kim, K.; Bartik, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2104–2107.
3. Buschmann, H.-J.; Jonas, C.; Schollmayer, E. *European Water Pollution Control* **1996**, *6*, 21–24.
4. Guhr, K. I.; Greaves, M. D.; Rotello, V. M. *J. Am. Chem. Soc.* **1994**, *116*, 5997–5998.
5. *Advanced Macromolecular and Supramolecular Materials and Processes*; Geckeler, K. E., Ed.; Kluwer Academic/Plenum: New York, 2003; pp 29–40, 55–63, 291–307.
6. Wang, G.-W.; Zhang, T.-H.; Li, Y.-J.; Lu, P.; Zhan, H.; Liu, Y.-C.; Murata, Y.; Komatsu, K. *Tetrahedron Lett.* **2003**, *44*, 4407–4409.
7. Braun, T.; Buvari-Barcza, A.; Barcza, L.; Konkoly-Thege, I.; Fodor, M.; Migali, B. *Solid State Ionics* **1994**, *74*, 47–51.
8. Geckeler, K. E.; Constabel, F. Korean Patent Application no. 200311583, submitted on 26.11.2002.
9. A capsule (stainless steel; inner diameter: 18 mm) containing the compounds and a milling ball (stainless steel; diameter: 12 mm) was fixed in a vibration machine (Mixer Mill, type MM 200, Retsch, Germany) and the capsule was shaken horizontally (20 cycles/s) at rt.
10. Typical procedure is as follows. (a) solid–liquid reaction: CB7 (16 mg; 14 μmol) was dissolved in water (18 mL) by adding 1 M NaOH until a pH = 12 was reached. After filtering solid C_{60} (5 mg; 7 μmol) was added and the mixture was stirred at rt. Within 24 h of stirring a brown solid started to precipitate indicating the formation of a complex. After three more days of stirring excess of C_{60} was removed by adding toluene, freezing the aqueous phase and decanting the organic phase. The aqueous phase was allowed to reach the room temperature, centrifuged, and carefully decanted. The solid was washed out by water up to neutral pH. Finally the residual water was evaporated and the dark-brown product was dried in vacuo (5.1 mg; 55% yield). (b) solid–solid reaction: The mixture of solid C_{60} and solid CB7 in different molar ratios was grinded on a mixer mill. The brown solid was flushed out by warm water followed by adding 1 or 2 M NaOH up to pH = 12 and toluene to dissolve both the excess of CB7 and C_{60}. The aqueous phase was frozen and the upper organic phase decanted. Subsequent performance was carried out as described above.
11. XRD measurements were carried out with copper radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA. TGA were conducted in flowing nitrogen at a heating rate of 10 °C/min. FT-IR measurements were recorded from KBr pellets.
12. Scanloss, J. C.; Ebert, L. B. *J. Phys. Chem.* **1993**, *97*, 7138–7140.
13. Murthy, C. N.; Geckeler, K. E. *Chem. Commun.* **2001**, 1194–1195.
14. Priyadarsini, K. I.; Mohan, H.; Tyagi, A. K.; Mittal, J. P. *J. Phys. Chem.* **1994**, *98*, 4756–4759.
15. FT-IR (KBr) **1:** ν 3446 (b), 1728 (s), 1478 (s), 1425 (m), 1383 (m), 1324 (m), 1235 (s), 1189 (m), 1154 (m), 1048 (m), 968 (s), 806 (s), 758 (m), 675 (m); **2:** ν 1428 (m), 1181 (m), 575 (s), 526 (s); **3:** 3417 (b), 1732 (s), 1474 (s), 1423 (m), 1380 (m), 1324 (m), 1233 (m), 1188 (m), 1154 (w), 966 (m), 804 (s), 759 (w), 674 (w), 527 (m).
16. Elemental analysis, calculated: C, 63.22; N, 12.77; H, 3.07; O, 20.84. Found: C, 59,00; N, 13.76; H, 1.12; O, 26.12.