

# Aqueous solubilization of crystalline fullerenes by supramolecular complexation with $\gamma$ -cyclodextrin and sulfocalix[8]arene under mechanochemical high-speed vibration milling

PERKIN

Koichi Komatsu,<sup>\*a</sup> Koichi Fujiwara,<sup>a</sup> Yasujiro Murata<sup>a</sup> and Tibor Braun<sup>b</sup>

<sup>a</sup> Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>b</sup> Department of Inorganic and Analytical Chemistry, L. Eötvös University, PO Box 123, 1143 Budapest, Hungary

Received (in Cambridge, UK) 14th June 1999, Accepted 20th August 1999

The solid-state supramolecular complexation of fullerenes  $C_{60}$  and  $C_{70}$  as well as some derivatives of  $C_{60}$  was attained with  $\gamma$ -cyclodextrin by the use of a mechanochemical high-speed vibration milling technique. Similarly  $C_{60}$  and the fullerene dimer  $C_{120}$  were complexed with sulfocalix[8]arene. The complexes produced were found to be soluble in water, and their solubility was examined by UV-vis spectroscopy.

## Introduction

Solubilization of fullerene  $C_{60}$  in water is of great importance particularly from the viewpoint of possible biological applications of this new carbon material with spherical  $\pi$ -conjugation.<sup>1</sup> So far the complexation by a polyhydroxy compound with a hydrophobic interior such as  $\gamma$ -cyclodextrin<sup>2a-f</sup> has been frequently used for the solubilization of  $C_{60}$  in water. For the same purpose,  $C_{60}$  has also been complexed with a highly polarized polymer such as polyvinylpyrrolidone<sup>3</sup> or encapsulated in a water soluble calixarene.<sup>4</sup> Particularly with  $\gamma$ -cyclodextrin,  $C_{60}$  is supposed to form a 1:2 complex with a bicapped structure.<sup>5</sup>

In contrast to the ordinary complexation conducted in the solution phase, the solid-state mechanochemical technique using ball milling has been discovered to be more effective for the complexation of  $C_{60}$  with  $\gamma$ -cyclodextrin.<sup>6</sup> As a follow up method for activating mechanochemical reactions, we have developed a method which we call "high-speed vibration milling" (HSVM) and utilized it for mechanochemical derivatization of  $C_{60}$  such as selective dimerization of  $C_{60}$ ,<sup>7</sup> nucleophilic addition of an organozinc reagent to  $C_{60}$ ,<sup>8</sup> and the cycloaddition of  $C_{60}$  to condensed aromatic hydrocarbons.<sup>9</sup> Recently we have found that the HSVM technique can be applied to the supramolecular complexation of  $C_{60}$  successfully and more efficiently than classical ball milling. We have also examined the complexation of  $C_{70}$  and various  $C_{60}$  derivatives and here we describe the results obtained.

## Results and discussion

### Complexation of $C_{60}$ with $\gamma$ -cyclodextrin

$C_{60}$  (10 mg) and 4 molar equivalents of  $\gamma$ -cyclodextrin (70 mg) were placed in a stainless steel capsule together with a stainless steel mixing ball and were vigorously mixed by shaking at a rate of 3500 rpm for 10 min by the use of a high-speed vibration mill. The solid mixture was dissolved in 4 cm<sup>3</sup> of water to give a dark brown emulsion, which was filtered by a membrane filter (0.2  $\mu$ m) to give a magenta-colored solution. The UV-visible spectrum of this solution (diluted to  $\frac{1}{3}$ , Fig. 1) exhibited absorptions quite similar to a solution of  $C_{60}$  in cyclohexane. The concentration of the magenta-colored solution was estimated to be  $1.4 \times 10^{-3}$  M by the use of the absorption coefficient  $\epsilon = 5.19 \times 10^4$  determined at  $\lambda_{\max}$  330 nm for the cyclohexane solution. This concentration is to the best of our knowledge the highest solubility of the  $\gamma$ -cyclodextrin- $C_{60}$  complex obtained

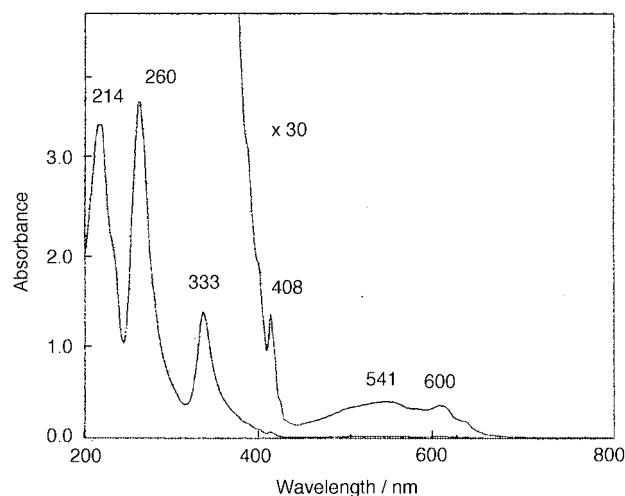


Fig. 1 The UV-vis spectrum of  $C_{60}$ - $\gamma$ -cyclodextrin in water. The original saturated solution was diluted to  $\frac{1}{3}$ .

in water so far. It is much higher than the values previously reported for the solubility of  $C_{60}$  in water obtained by refluxing an aqueous solution of  $\gamma$ -cyclodextrin and  $C_{60}$  ( $8 \times 10^{-5}$  M)<sup>2a</sup> or by the classical ball-milling method ( $1.5 \times 10^{-4}$  M).<sup>6</sup> It should also be noted that when using the present HSVM method, the complexation can be attained after only 10 min as compared to refluxing in aqueous solution for more than 24 hours<sup>2a</sup> or classical ball-milling for about 20 hours.<sup>7</sup> This milling time of 10 min is considered to be an optimum since a shorter time (5 min) or a longer time (20 min) was found to cause the dissolution of  $C_{60}$  in water in lower concentrations, *i.e.*  $4.5 \times 10^{-4}$  M (5 min milling) or  $7.5 \times 10^{-4}$  M (20 min milling).<sup>†</sup>

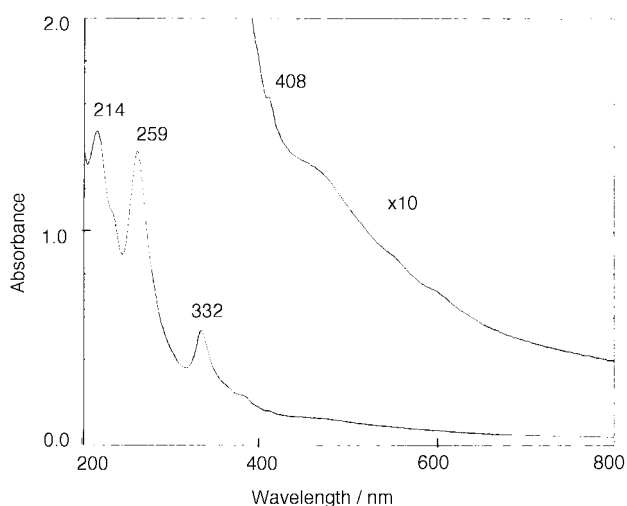
After letting the aqueous solution stand for 2 weeks, purple crystalline plates separated. The solid-state <sup>13</sup>C NMR spectrum of this crystal exhibited signals which are in good agreement with the reported data for the  $C_{60}$ - $\gamma$ -cyclodextrin complex in D<sub>2</sub>O (Table 1). The purple plates of a  $C_{60}$ - $\gamma$ -cyclodextrin complex have already been isolated by Yoshida *et al.* and have

<sup>†</sup> The lowering of the concentration upon elongated milling time would be due to destruction of the formed complexes resulting in the occurrence of an insoluble aggregation of  $C_{60}$  particles.

**Table 1** The solid-state  $^{13}\text{C}$  NMR data (ppm) for  $\text{C}_{60}$ ,  $\gamma$ -cyclodextrin ( $\gamma$ -CyD) and the  $\text{C}_{60}$ - $\gamma$ -CyD complex

	$\text{C}_{60}$	C-1	C-2,3,5	C-4	C-6
$\text{C}_{60}$	143.56	—	—	—	—
$\gamma$ -CyD	—	101.68	73.80	82.64	61.08
$\text{C}_{60}$ - $\gamma$ -CyD	143.45	104.89	73.51	82.25	60.30
$\text{C}_{60}$ - $\gamma$ -CyD (in $\text{D}_2\text{O}$ ) <sup>a</sup>	144.05	104.59	73.55 (C-2) 74.21 (C-3) 73.64 (C-5)	83.38	61.45

<sup>a</sup> Ref. 5a.



**Fig. 2** The UV-vis spectrum of the water solution of carbon raw soot mechanochemically treated with  $\gamma$ -cyclodextrin.

been shown to have a 1:2 composition based on  $^{13}\text{C}$  NMR and elemental analyses.<sup>5a</sup> The crystals obtained in the present work were also shown to have a 1:2 composition of  $\text{C}_{60}$  and  $\gamma$ -cyclodextrin from the results of thermogravimetry and elemental analyses.

Next, carbon raw soot containing ca. 8% of  $\text{C}_{60}$  (Vacuum Metallurgical Co., 10 mg) was treated as shown above with  $\gamma$ -cyclodextrin (150 mg) by the HSVM technique for 10 min. After addition of water ( $4.5 \text{ cm}^3$ ) and filtration, a faintly sepia-colored solution was obtained. From the UV-vis spectrum (Fig. 2) it is apparent that  $\text{C}_{60}$  and a very small amount of  $\text{C}_{70}$  were extracted into the aqueous phase. The concentration of  $\text{C}_{60}$  was calculated to be  $1 \times 10^{-5} \text{ M}$  using  $\epsilon = 5.19 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  332 nm, tentatively assuming that the amount of  $\text{C}_{70}$  is negligible.

### Complexation of $\text{C}_{70}$ with $\gamma$ -cyclodextrin

Wennerström *et al.* reported that boiling  $\text{C}_{70}$  in a concentrated aqueous  $\gamma$ -cyclodextrin solution (0.8 M) for several hours can give an aqueous solution of the  $\text{C}_{70}$ -complex albeit at low  $\text{C}_{70}$  concentration (ca.  $5 \times 10^{-5} \text{ M}$ ).<sup>10</sup> In contrast, when  $\text{C}_{70}$  (5 mg) was mechanochemically treated with 8 molar equivalents of  $\gamma$ -cyclodextrin (61 mg) under HSVM conditions for 10 min and the mixture treated with water, a red-brown solution was obtained which exhibited a UV-vis spectrum (diluted to  $\frac{1}{5}$ , Fig. 3) quite similar to that of  $\text{C}_{70}$  in cyclohexane. The  $\text{C}_{70}$  concentration of the original aqueous solution was calculated to be  $7 \times 10^{-4} \text{ M}$  using  $\epsilon = 3.80 \times 10^4$  at  $\lambda_{\text{max}}$  381 nm, again showing the high efficiency of the solid-solids complexation using the present HSVM technique.

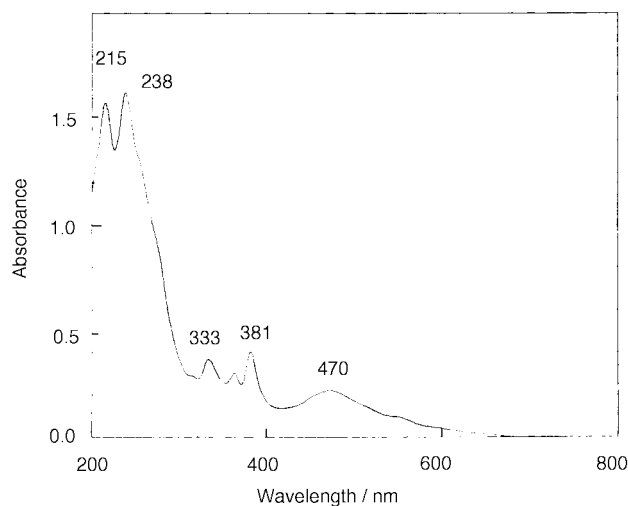
### Complexation of $\text{C}_{60}$ derivatives with $\gamma$ -cyclodextrin

Since biphenyl<sup>11</sup> and *n*-alkyl chains<sup>12</sup> are known to be complexed by cyclodextrin molecules, it was speculated that  $\text{C}_{60}$  derivatives possessing these functional groups might have some

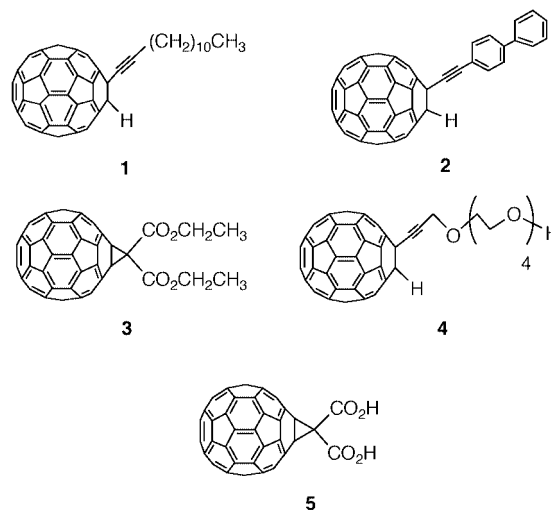
**Table 2** Aqueous solubilization of fullerene derivatives by complexation with  $\gamma$ -cyclodextrin ( $\gamma$ -CyD) by use of the HSVM technique

Derivative	Weight/ mg	$\gamma$ -CyD weight/mg	Added $\text{H}_2\text{O}/$ $\text{cm}^3$	Concentration/ M
<b>1</b>	5.1	63.5	4.0	$3.0 \times 10^{-6a}$
<b>2</b>	5.0	59.3	4.0	$5.4 \times 10^{-6b}$
<b>3</b>	5.2	59.5	4.0	$2.2 \times 10^{-5c}$
<b>4</b>	5.6	49.8	3.0	$8.3 \times 10^{-5d}$
<b>5</b>	5.8	63.5	4.0	$1.2 \times 10^{-3e}$

<sup>a</sup> Determined using  $\epsilon = 3.52 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 323 nm. <sup>b</sup> Determined using  $\epsilon = 1.11 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 259 nm. <sup>c</sup> Determined using  $\epsilon = 4.12 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 329 nm. <sup>d</sup> Determined using  $\epsilon = 3.98 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 327 nm. <sup>e</sup> Determined using  $\epsilon = 2.65 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 331 nm.

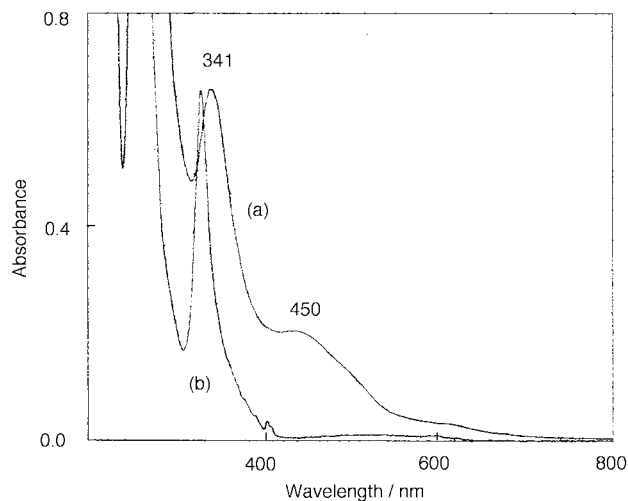


**Fig. 3** The UV-vis spectrum of  $\text{C}_{70}$ - $\gamma$ -cyclodextrin in water. The original saturated solution was diluted to  $\frac{1}{5}$ .



specific interaction with  $\gamma$ -cyclodextrin. Thus, the  $\text{C}_{60}$  derivatives **1** and **2** were freshly synthesized, and their ability for complexation was examined together with that of the known derivatives **3**, **4** and **5**.

A series of mixtures of 5 mg each of compounds **1**–**5** and the  $\sim 7$ – $8$  molar equivalents of  $\gamma$ -cyclodextrin were subjected to an HSVM treatment for 10 min. After addition of water and filtration, the filtrates were examined by UV-vis spectroscopy. From the UV absorbance of the characteristic absorption band of each compound, the concentration was estimated to give the values shown in Table 2. While compound **5** having polar substituents dissolved with relatively high concentration, the solubility of the rest of the compounds **1**–**4** was found to be rather

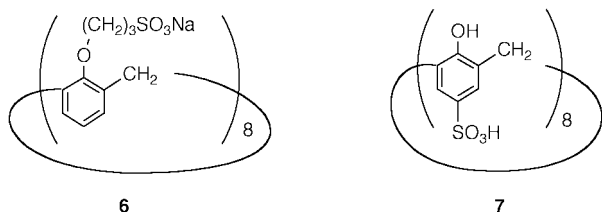


**Fig. 4** The UV-vis spectra of (a)  $C_{60}$ -calixarene **7** in water and (b)  $C_{60}$  in cyclohexane.

low. Although compound **5** is known to dissolve in alkaline water of pH > 9,<sup>13</sup> the pH value of the aqueous solution containing **5** and  $\gamma$ -cyclodextrin was found to be 3.5. The order of the solubility seems to be in accordance with the polarity of the functional groups. It is proposed that the presence of functional groups prevented the formation of the 1:2 bicapped complex and that complexation could actually only take place at one side of the  $C_{60}$  cage far from the functional groups.

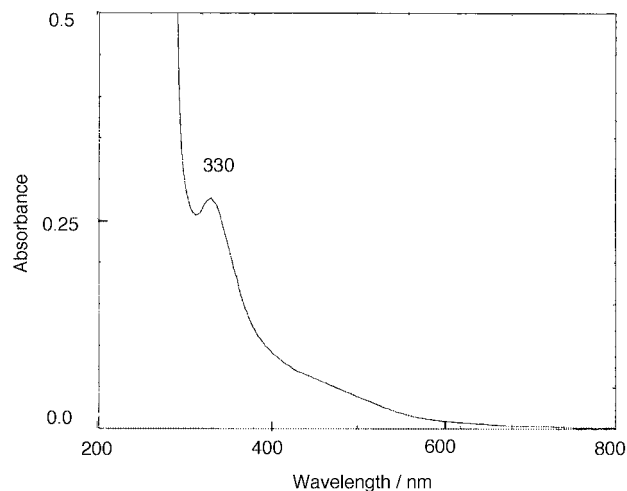
#### Supramolecular complexation of $C_{60}$ and $C_{120}$ with sulfocalix[8]arene

Although the complexation of  $C_{60}$  with calixarenes has been extensively studied,<sup>14</sup> there has been only one report on the aqueous solubilization of  $C_{60}$ , that is, by the complexation with a large excess (14 molar) of calixarene **6**.<sup>4</sup> In the present study,



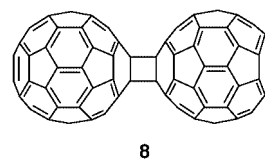
the complexation ability of sulfocalixarene **7** was examined using the HSVM technique. Thus, equimolar amounts of  $C_{60}$  and **7** (11 and 20 mg each) were subjected to the HSVM treatment for 10 min as described above and then dissolved in water. The resulting aqueous solution was yellow in color and exhibited the UV-vis spectrum shown in Fig. 4. In this spectrum, the maximum absorption undergoes a slight bathochromic shift as compared to a spectrum of  $C_{60}$  in cyclohexane, and a broad absorption at  $\lambda_{\max}$  450 nm is observed, which can be assigned to the charge-transfer absorption originating from the interaction between the calixarene  $\pi$ -system and  $C_{60}$ .<sup>4</sup> The concentration of  $C_{60}$  was calculated to be  $1.3 \times 10^{-4}$  M using  $\epsilon = 5.19 \times 10^4$  at  $\lambda_{\max}$  341 nm.

Previously we synthesized the fullerene dimer,  $C_{120}$  (**8**), by a solid-state mechanochemical reaction.<sup>7</sup> This compound is hardly soluble in most common organic solvents; the solubility in *o*-dichlorobenzene (ODCB), a solvent often employed in fullerene chemistry, is only  $8 \times 10^{-5}$  M. It was anticipated that the supramolecular complexation of both ends of this molecule with calixarene might help dissolving it, even in water. As described above, **8** and an equimolar amount of sulfocalixarene **7** (7 and 12 mg each) were mechanochemically treated by the HSVM technique for 10 min and then dissolved in water. The



**Fig. 5** The UV-vis spectrum of  $C_{120}$ -sulfocalixarene **7** in water.

aqueous solution thus obtained was a pale yellow color and exhibited the UV-vis spectrum shown in Fig. 5. Using  $\epsilon = 1.74 \times 10^5$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  at  $\lambda_{\max}$  330 nm, the concentration was calculated to be  $1.6 \times 10^{-4}$  M, which is twice as high as the solubility of **8** in ODCB.



Thus, by using solid-solid reaction conditions, the present mechanochemical HSVM technique was shown to be highly effective for the supramolecular complexation of fullerenes and their derivatives with host molecules such as  $\gamma$ -cyclodextrin and sulfocalix[8]arene **7**. This has resulted in efficient aqueous solubilization of these exotic carbon materials, which could open up the way to applications mainly in the biomedical sciences.

## Experimental

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian Mercury-300 spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2100PC spectrometer. APCI mass spectra were obtained on a Finnigan TSQ7000 spectrometer.

### Materials

$C_{60}$  and  $C_{70}$  were commercial materials purchased from Term Co. and used as received.  $\gamma$ -Cyclodextrin and sulfocalix[8]arene (**7**) were commercial materials purchased from Wako and Acros Organics Co., respectively. 1,2-Methano-1,2-dihydro[60]fullerene-61,61-dicarboxylic acid (**5**),<sup>13</sup> diethyl 1,2-methano-1,2-dihydro[60]fullerene-61,61-dicarboxylate (**3**)<sup>15</sup> and 1-(15-hydroxy-4,7,10,13-tetraoxapentadec-1-yn-1-yl)-1,2-dihydro[60]fullerene (**4**)<sup>16</sup> were prepared as described in the literature.

### 1-(Tridec-1-ynyl)-1,2-dihydro[60]fullerene (**1**)

A solution of tridec-1-ynyllithium was prepared by adding 0.39  $\text{cm}^3$  (0.52 mmol) of 1.33 M *n*-BuLi to a stirred solution of tridec-1-yne (94.4 mg, 0.52 mmol) in 2.3  $\text{cm}^3$  of THF at 0 °C and stirred for 20 min. To a vigorously stirred suspension of finely dispersed  $C_{60}$  (99.2 mg, 0.138 mmol) in 40  $\text{cm}^3$  of THF, obtained by sonication, 1.7  $\text{cm}^3$  (0.32 mmol) of a 0.19 M THF

solution of tridec-1-ynyllithium was added over 15 min dropwise by the use of a syringe. After stirring for 15 min, trifluoroacetic acid (0.2 ml, 2.4 mmol) was added to the resulting dark green solution to give a dark brown suspension, which was then evaporated under vacuum. The residual solid was extracted with toluene-CS<sub>2</sub> (6:1) and separated by recycle gel permeation chromatography eluted with toluene. The second fraction resulted in some unreacted C<sub>60</sub> (16.0 mg, 16.2%) being isolated. From the first fraction **1** (40.3 mg, 32.4%) was isolated as a dark brown solid: <sup>1</sup>H NMR (300 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>) δ 6.96 (s, 1H, C<sub>60</sub>-H), 2.62 (t, 2H), 1.83 (m, 2H), 1.63 (m, 2H), 1.45–1.28 (br, 14H), 0.88 (t, 3H); <sup>13</sup>C NMR (75 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>) δ 151.99, 151.61, 147.44, 147.17, 146.54, 146.21 (2C), 146.05 (2C), 145.66, 145.50, 145.41, 145.30, 145.24, 145.19, 144.53, 144.39, 143.05, 142.42, 142.40, 141.96, 141.89, 141.84, 141.78, 141.52, 141.44, 140.19, 140.12, 135.99, 134.72, 84.63, 83.55, 62.03, 54.61, 32.05, 29.84, 29.82, 29.76, 29.54, 29.41, 29.30, 28.88, 22.93, 19.48, 14.27; UV-vis (cyclohexane) λ<sub>max</sub>/nm 212 (log (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 5.08), 255 (5.02), 327 (4.55), 431 (3.78), 701 (2.88); MS (-APCI) *m/z* 900 (M), 901 (M + 1).

### 1-(Biphenyl-4-ylethynyl)-1,2-dihydro[60]fullerene (2)

A solution of (biphenyl-4-ylethynyl)lithium was prepared by adding 0.54 cm<sup>3</sup> (0.864 mmol) of 1.60 M *n*-BuLi to a stirred solution of 4-ethynylbiphenyl (152 mg, 0.857 mmol) in 3 cm<sup>3</sup> of THF at 0 °C and stirring for 20 min. To the vigorously stirred suspension of finely dispersed C<sub>60</sub> (205 mg, 0.285 mmol) in THF, obtained by sonication, 2.4 cm<sup>3</sup> (0.36 mmol) of a 0.15 M THF solution of (biphenyl-4-ylethynyl)lithium was added over 20 min dropwise by the use of a syringe. After stirring for 20 min, trifluoroacetic acid (0.2 cm<sup>3</sup>, 2.4 mmol) was added to the resulting dark green solution to give a dark brown suspension, which was then evaporated under vacuum. The residual solid was extracted with CS<sub>2</sub> and the extract was separated by flash chromatography on silica gel eluted with hexane-CS<sub>2</sub> (4:1). The first fraction resulted in some unreacted C<sub>60</sub> (20.5 mg, 10.0%). From the second fraction, **2** (106 mg, 41.2%) was isolated as a dark brown solid: <sup>1</sup>H NMR (300 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>) δ 7.87 (d, 2H), 7.71 (d, 2H), 7.67 (d, 2H), 7.50 (t, 2H), 7.41 (d, 1H), 7.17 (s, 1H, C<sub>60</sub>-H); <sup>13</sup>C NMR (75 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>) δ 151.47, 151.27, 147.55, 147.27, 146.60, 146.33, 146.17, 145.76, 145.62, 145.42, 145.38, 145.29, 144.64, 144.46, 143.15, 142.54, 142.06, 141.99, 141.95, 141.83, 141.65, 141.61, 141.56, 140.63, 136.05, 135.14, 140.33, 140.28, 132.53, 128.86, 127.75, 127.15, 127.00, 121.22, 92.85, 83.55, 61.78, 55.15; UV-vis (cyclohexane) λ<sub>max</sub>/nm 210 (log (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 5.24), 258 (5.04), 324sh (4.57), 432 (3.54), 700 (2.71); MS (-APCI) *m/z* 898 (M), 899 (M + 1).

### High-speed vibration mill

Throughout the present study, we used an in-house built mill which consisted of a capsule and a milling ball made of stainless steel (Fe-Cr-Ni with a composition of 74:18:8 by weight). The capsule containing the milling ball was fixed in a vibrating machine so that the capsule could be shaken along its long axis horizontally at a rate of 3500 cycles min<sup>-1</sup>.<sup>7b</sup>

### Complexation using high-speed vibration milling

As a general procedure, solid crystalline fullerenes or their derivatives and the host compound (γ-cyclodextrin or sulfolix[8]arene (**7**)) were weighed into a stainless-steel capsule together with a mixing ball. The materials were thoroughly mixed by high-speed vibration milling (HSVM) technique for 10 min. The mixture was washed into 3–4 cm<sup>3</sup> of distilled water, and filtered through a membrane filter (0.2 μm) to give a clear solution, which was subjected to the UV-vis spectral measurement (after appropriate dilution).

### Thermogravimetric analysis and elemental analysis

The C<sub>60</sub>-γ-cyclodextrin complex (2.2 mg) was subjected to thermogravimetric analysis.<sup>2f</sup> The sample was heated from 30 to 330 °C at rates of 2 °C min<sup>-1</sup> for 30–200 °C and 0.5 °C min<sup>-1</sup> for 200–330 °C under a nitrogen atmosphere. While the weight loss amounted to 83% for γ-cyclodextrin and 0% for C<sub>60</sub>, weight loss of 65% was observed for the C<sub>60</sub>-γ-cyclodextrin complex. This value corresponds to a 1:2 ratio for the composition of C<sub>60</sub> and γ-cyclodextrin. The result of the elemental analysis was as follows. Found: C, 54.00; H, 5.36%. Calcd. for C<sub>60</sub>·2(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>8</sub>·8H<sub>2</sub>O: C, 54.17; H, 5.13%.

### Acknowledgements

This work was supported by Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan. T. B. thanks the OTKA foundation for support by way of grants 025860 and 023043.

### References

- For a review, see T. Da Ros and M. Prato, *Chem. Commun.*, 1999, 663.
- (a) T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. Wennerström, *J. Chem. Soc., Chem. Commun.*, 1992, 604; (b) W. Kutner, P. Boulas and K. M. Kadish, *J. Electrochem. Soc.*, 1992, **139**, 243C; (c) M. Sundahl, T. Andersson, K. Nilsson, O. Wennerström and G. Westman, *Synth. Met.*, 1993, **55–57**, 3252; (d) T. Andersson, G. Westman, O. Wennerström and M. Sundahl, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1097; (e) P. Boulas, W. Kutner, M. T. Jones and K. M. Kadish, *J. Phys. Chem.*, 1994, **98**, 1282; (f) K. I. Priyadarsini, H. Mohan and J. P. Mittal, *Fullerene Sci. Technol.*, 1995, **3**, 479. (For a complete bibliographic list, see also T. Braun, *Fullerene Sci. Technol.*, 1997, **5**, 615.)
- Y. Nakajima-Yamakoshi, T. Yamagi, K. Fukuhara, S. Sueyoshi and N. Miyata, *J. Chem. Soc., Chem. Commun.*, 1994, 517.
- R. M. Williams and J. W. Verhoeven, *Rec. Trav. Chim. Pays-Bas*, 1992, **111**, 531.
- (a) Z. Yoshida, H. Takekuma, S. Takekuma and Y. Matsubara, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1597; (b) A. Buvári-Barcza, L. Barcza and T. Braun, *Supramol. Chem.*, 1994, **4**, 131; (c) A. Buvári-Barcza, L. Barcza, T. Braun, I. Konkoly-Thege, K. Ludanyi and K. Vekey, *Fullerene Sci. Technol.*, 1997, **5**, 311; (d) T. Braun, *Fullerene Sci. Technol.*, 1997, **5**, 615.
- T. Braun, A. Buvári-Barcza, L. Barcza, I. Konkoly-Thege, M. Fodor and B. Migali, *Solid State Ionics*, 1994, **74**, 47.
- (a) G.-W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583; (b) K. Komatsu, G.-W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, K. Yamamoto and M. Saunders, *J. Org. Chem.*, 1998, **63**, 9358.
- G.-W. Wang, Y. Murata, K. Komatsu and T. S. M. Wan, *Chem. Commun.*, 1996, 2059.
- Y. Murata, N. Kato, K. Fujiwara and K. Komatsu, *J. Org. Chem.*, 1999, **64**, 3483.
- T. Andersson, M. Sundahl, G. Westman and O. Wennerström, *Tetrahedron Lett.*, 1994, **35**, 7103.
- T. V. S. Rao and D. S. Lawrence, *J. Am. Chem. Soc.*, 1990, **112**, 3614.
- (a) A. Harada, J. Li and M. Kamachi, *Chem. Commun.*, 1997, 1413; (b) A. Harada, J. Li and M. Kamachi, *Nature*, 1992, **356**, 325.
- I. Lamparth and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1994, 1727.
- For typical examples, see the following: (a) J. L. Atwood, G. A. Koutsantonis and C. Raston, *Nature*, 1994, **368**, 229; (b) T. Suzuki, K. Nakashima and S. Shinkai, *Chem. Lett.*, 1994, 699; (c) R. M. Williams, J. M. Zwier and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, **116**, 6965; (d) T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259; (e) L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1997, 1439; (f) T. Haino, M. Yanase and Y. Fukazawa, *Tetrahedron Lett.*, 1997, **38**, 3739.
- C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
- K. Fujiwara, Y. Murata, T. S. M. Wan and K. Komatsu, *Tetrahedron*, 1998, **54**, 2049.