Supplementary Information

Pseudorotaxane structure of a fullerene derivative–cyclodextrin 1:2 complex

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Experimental Section

General procedures. Compounds **1** and **2** were synthesized according to previously reported methods {(a) A. Polese, S. Mondini, A. Bianco, C. Toniolo, G. Scorrano, D. M. Guldi, M. Maggini, *J. Am. Chem. Soc.* **1999**, *121*, 3446-3452. (b) M. Maggini, A. Karlsson, L. Pasimeni, G. Scorrano, M. Prato, L. Valli, *Tetrahedron Lett.* **1994**, *35,* 2985-2988.}.

Measurements. UV-vis spectra were obtained using an UV-2550 spectrophotometer (Shimadzu Co., Kyoto, Japan). The hydrodynamic diameters of the **2**•γ-CDx and **3**•γ-CDx complexes were measured on an instrument for electrophoretic light scattering with a laser Doppler system (Zetasizer Nano ZS, Malvern Instruments Ltd., Malvern, UK). ^{1}H NMR spectra were recorded on a JNM ECA-600 spectrometer (JEOL Ltd., Tokyo, Japan), using 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt as an internal standard. The MALDI-TOF MS was measured with an autoflex II instrument (Bruker Daltonics, Bremen, Germany) with 2,5-dihydroxyacetophenone (Wako Pure Chemical Industries, Tokyo, Japan) as the matrix.

Synthesis of 3. A solution of *N*-H fulleropyrrolidine **1** (40.0 mg, 0.049 mmol) and succinic anhydride (49.0 mg, 0.49 mmol) in toluene (50 ml) was heated at the reflux temperature for 6 h. After the reaction mixture was cooled to room temperature, the precipitate was recovered by filtration and washed by toluene several times. Title compound was obtained in 71% (30.1 mg, 0.035 mmol) as a brown solid. Physical data: FTIR (KBr) ν_{max}/cm^{-1} 527, 553, 576, 768, 804, 1091, 1130, 1191, 1209, 1270, 1308, 1341, 1425, 1658, 1708, 2840, 2914, 3469; ^{1}H NMR (600 MHz; DMSO-d_6; 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt) δ_H 2.69 (2H, t, J = 6.6 Hz, CH_2COO), 3.06 (2H, t, J = 6.6 Hz, CH_2CON), 5.45 (2H, s, CH_2N), 5.59 (2H, s, CH_2N); HRMS (ESI, DMSO, pos. mode) calcd for $[C_{66}H_9NO_3 + Na]^+$ 886.0480, found: 886.0480.

Preparation of the 2•γ-CDx and 3•γ-CDx complexes. A mixture of **2** (2.80 mg, 3.47 mmol) or **3** (3.00 mg, 3.47 mmol) with γ-CDx (18.03 mg, 13.90 mmol) was placed in an agate capsule together with two agate mixing balls and mixed vigorously at 1800 rpm for 20 min using a high-speed vibration mill (MM200, Retsch Co. Ltd., Haan, Germany). The mixture was then dissolved in D_2O or 0.9% w/v NaCl solution (1.5 mL) to produce a brown emulsion, and centrifuged to remove non-disperse **2** or **3**.

Crystallisation of the 3•γ-CDx complex. A 0.9% w/v NaCl solution of the **3**•γ-CDx complex (1.5 mL) was prepared by the above procedure. After leave the solution to stand for one or two days, brown crystals formed.

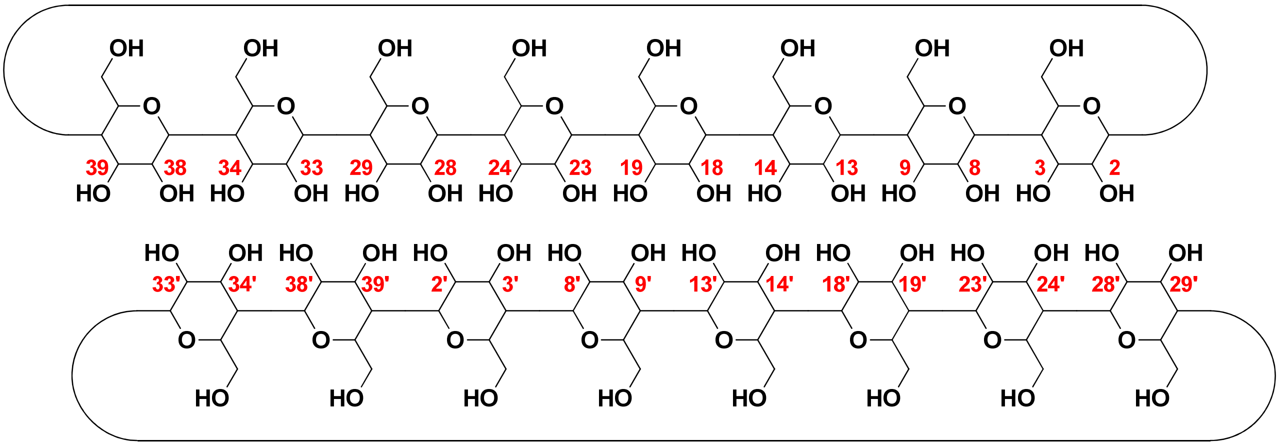
Crystallographic study. X-ray diffraction data for the **3**•γ-CDx complex were collected with a Rigaku VariMax RAPID RA-Micro7HFM using MoKα radiation at 123 K. A total of 63008 reflections were collected for the complex and 8378 of the reflections were unique. All calculations were performed using the Crystal Structure crystallographic software package except for refinement, which was performed using SHELXL-97. Disordered solvents (H_2O) were taken into account using the Platon SQUEEZE program.

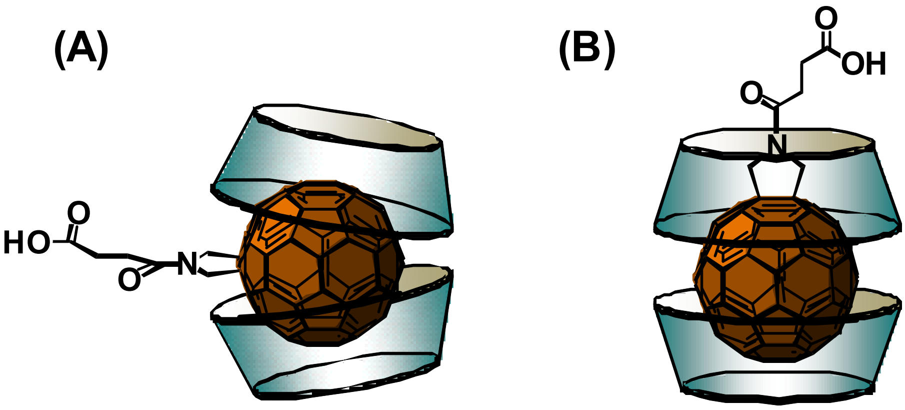
Physical data of the 3•γ-CDx complex. The preparation of the **3**•γ-CDx complex is described in Experimental Section. Physical data: ^{1}H NMR (600 MHz, D_2O) δ_H 2.74 (2H, t, *J* = 6.9 Hz, CH_2COO), 3.06 (2H, t, *J* = 6.9 Hz, CH_2CON), 3.50-3.63 (40 H, m, H-2, H-2’, H-4, H-5’ and H-6a’ of γ-CDx), 3.69-3.77 (8H, m, H-4’ of γ-CDx), 3.80-3.86 (8H, m, H-5 of γ-CDx), 3.95-4.09 (40H, m, H-3, H-3’, H-6a’, H-6b and H-6b of γ-CDx), 4.98 (8H, d, *J* = 3.6 Hz, H-1’ of γ-CDx), 5.03 (8H, d, *J* = 3.6 Hz, H-1 of γ-CDx), 5.33 (2H, s, CH_2N), 5.39 (1H, d, *J* = 12.6 Hz, CH_2N), 5.45 (1H, d, *J* = 12.6 Hz, CH_2N); MS (MALDI-TOF MS, 2,5-dihydroxyacetophenone, neg. mode) *m/z* (M^-) {[1:2 **3**•γ-CDx complex]$^-$}: 3456.9.

Table S1. Intermolecular distances between two oxygen atoms

Atoms[a]	Distance / Å	Atoms[a]	Distance / Å
O24-O 3’	2.808 (6)	O 2-O24’	3.234 (6)
O23-O 8’	2.985 (5)	O 3-O23’	3.294 (6)
O19-O 9’	2.851 (5)	O 8-O19’	3.376 (8)
O18-O13’	2.938 (5)	O 9-O18’	3.355 (8)
O14-O14’	2.791 (5)	O13-O14’	3.440 (1)
O 2-O28’	2.877 (6)	O28-O39’	3.279 (5)
O39-O29’	2.787 (6)	O29-O38’	3.358 (6)
O38-O33’	2.932 (9)	O33-O34’	3.463 (8)
O34-O34’	2.766 (9)	O24-O 2’	3.234 (6)
O 3-O24’	2.808 (6)	O23-O 3’	3.294 (6)
O 8-O23’	2.985 (5)	O19-O 8’	3.376 (8)
O 9-O19’	2.851 (5)	O18-O 9’	3.355 (8)
O13-O18’	2.938 (5)	O14-O13’	3.440 (1)
O28-O 2’	2.877 (6)	O39-O28’	3.279 (5)
O29-O39’	2.787 (6)	O38-O29’	3.358 (6)
O33-O38’	2.932 (9)	O34-O33’	3.463 (8)

[a] A single dash denotes the oxygen of another γ-CDx.





Scheme S1. Two possible structures for the **3**•γ-CDx complex.

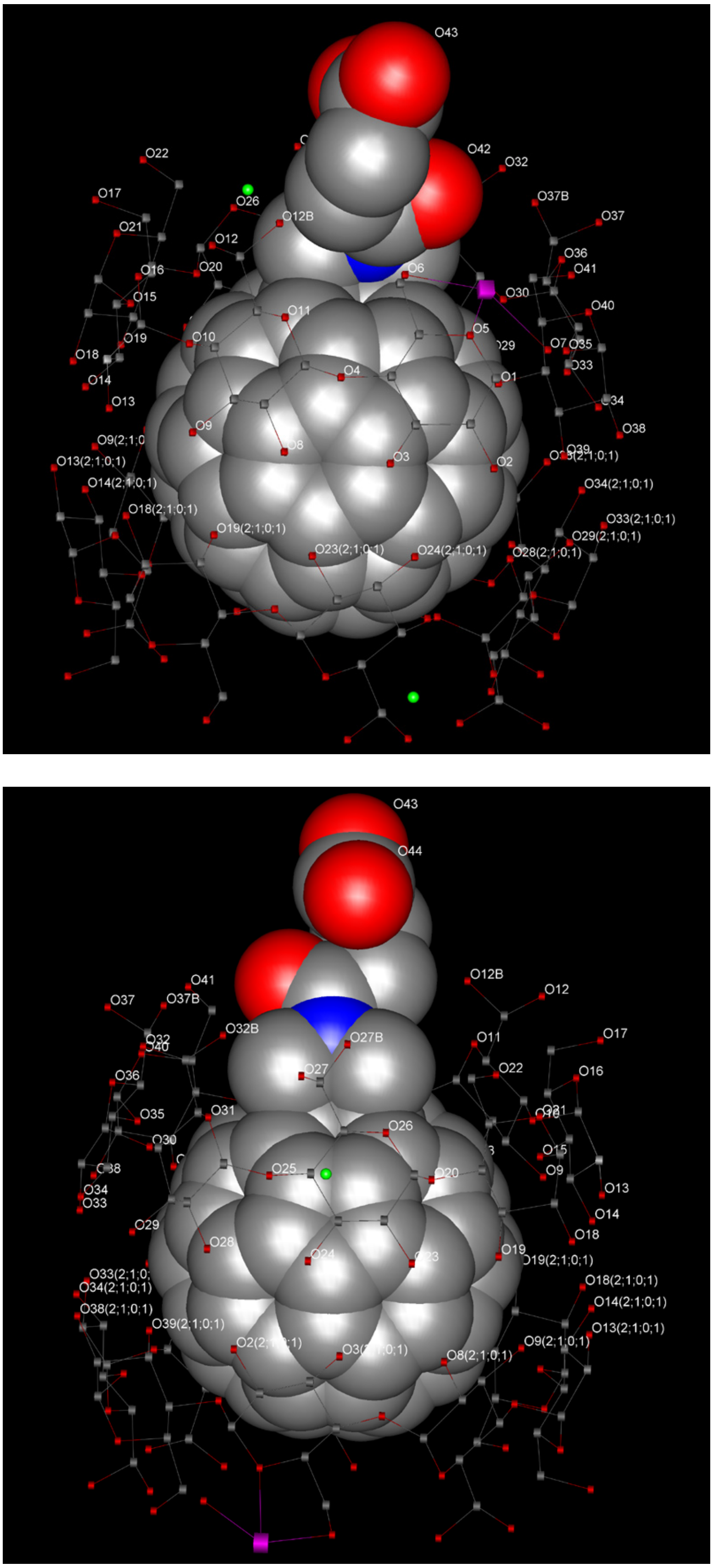


Fig. S1 Structure of the crystal of the **3**•γ-CDx complex Oxygen atom numbers are given. (A) one side view and (B) another side view.