Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPLEMENTARY MATERIAL

Pyridyl-Cyclodextrin for Ultra-Hydrosolubilization of [60]Fullerene

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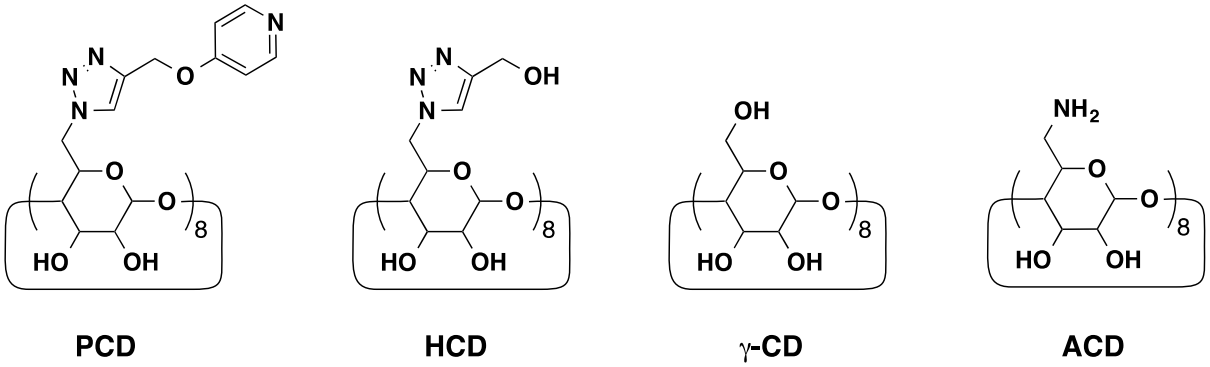
General information

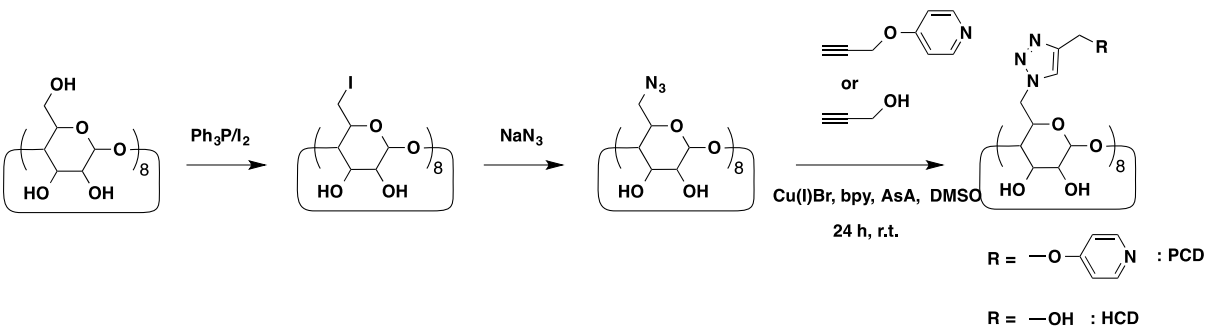
All chemicals and reagents were used as received from commercial sources without any purification. ^{1}H, ^{13}C NMR, HMQC and HMBC spectra were recorded on a JNM ECX-400 spectrometer (JEOL Ltd.) using, unless otherwise noted, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt as an internal reference. The MALDI-TOF MS was measured with a SpiralTOF JMS-S3000 instrument (JEOL Ltd.). UV-vis spectra were measured using a V-670 spectrometer (JASCO Co.). AFM images were obtained with a SPI3800N/SPA400 instrument (SI Inc.). The molecular mechanics simulations were carried out using Materials Studio (version 4.0; Accerlys Software Inc.) with Universal force field.

Synthesis details

Scheme S1. Chemical structures of cyclodextrin derivatives



Scheme S2. General synthetic procedures for PCD and HCD



6-azide-γ-cyclodextrin (N_3CD), 4-(prop-2-ynloxy)pyridine (PP) and amino-functionalized CD (ACD) were synthesized according to the references.[1-3]

6-[4-(4-methoxypyridyl)-1*H*-1,2,3-triazol-4-yl]-γCD (PCD)

To N_3CD (350 mg, 0.234 mmol) in degassed DMSO (2 mL) was added PP (312 mg, 2.34 mmol), Cu(I)Br (17 mg, 0.12 mmol), 2,2'-bipyridyl (36 mg, 0.23 mmol), L-ascorbic acid (20 mg, 0.12 mmol). The mixture was placed in a glass bottle, and was purged with nitrogen. The solution

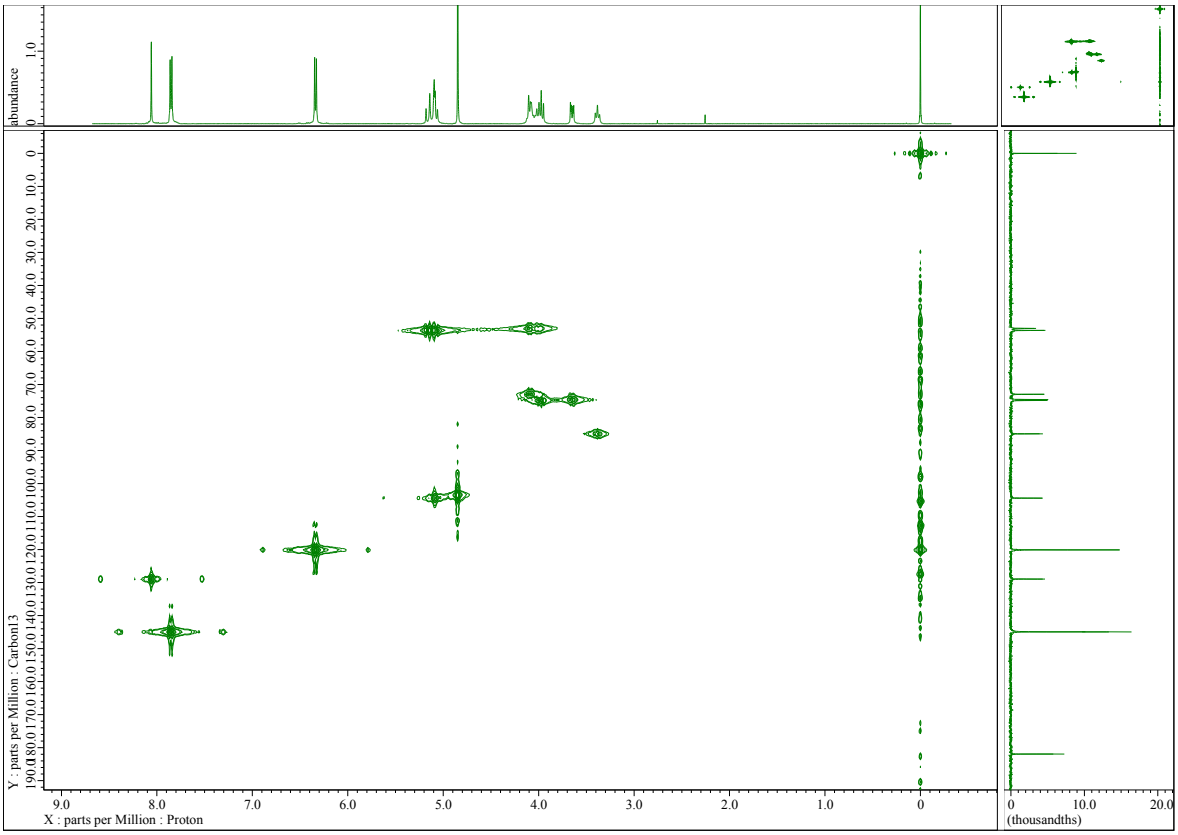
was stirred at room temperature for 24 h. The resulting brownish solution was precipitated by excess amount of acetone and the precipitate was collected through filtration. The product was dissolved in water and the solution was passed through a chelating resin (DIAION^{TM} CR20, Mitsubishi Chemical Corp.) to extract the remaining copper ion. The resulting solution was freeze-dried, and the pale-yellow powder was yielded of 543 mg (92%): ^{1}H NMR (400 MHz, D_2O) δ 3.38 (t, *J* = 9.2 Hz, 8H, H-4), 3.65 (dd, *J* = 10.0, 3.6 Hz, 8H, H-2), 3.95–4.11 (overlap, 32H, H-3, 5, 6), 5.06–5.18 (overlap, 24H, H-1, OCH_2), 6.34 (d, *J* = 8.0 Hz, 16H, pyridyl), 7.85 (d, *J* = 7.6 Hz, 16H, pyridyl), 8.06 (s, 8H, triazole); ^{13}C NMR (100 MHz, D_2O) δ 181.94 (triazole), 144.94 (pyridyl), 144.91 (pyridyl), 128.94 (triazole), 120.09 (pyridyl), 104.43 (C-1), 84.94 (C-4), 74.84 (C-3), 74.57 (C-2), 72.97 (C-5), 53.62 (OCH_2), 53.01 (C-6); MALDI-TOFMS *m/z* calcd for $C_{112}H_{128}N_{32}O_{40}$ $[M + Na]^+$ 2583.8858, found 2583.8829 (mass accuracy of 1.10 ppm)

6-[4-hydroxymethyl-1*H*-1,2,3-triazol-4-yl]-γCD (HCD)

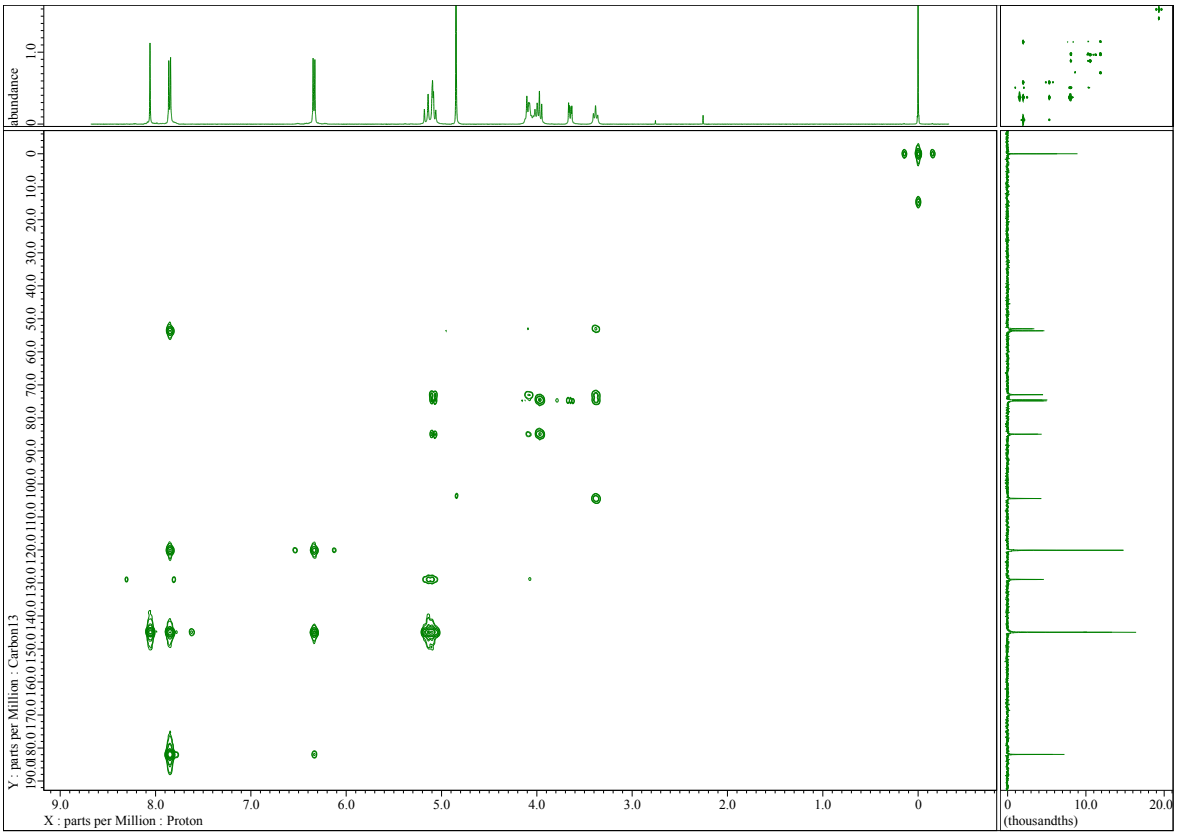
HCD was synthesized through the same procedure for PCD with N_3CD (200 mg, 0.134 mmol), DMSO (1 mL), 2-propyn-1-ol (72 μL, 1.2 mmol), Cu(I)Br (9 mg, 0.06 mmol), 2,2'-bipyridyl (19 mg, 0.12 mmol) and L-ascorbic acid (21 mg, 0.12 mmol). The resulting solution was freeze-dried, and the white powder was yielded of 188.4 mg (72%): ^{1}H NMR (400 MHz, D_2O) δ 3.42 (t, *J* = 9.2 Hz, 8H, H-4), 3.63 (dd, *J* = 10.0, 3.6 Hz, 8H, H-2), 3.94 (t, *J* = 9.6 Hz, 8H, H-3), 4.15–4.17 (m, 22H, H-5, 6), 4.44 (dd, *J* = 20.8, 13.2 Hz, 16H, OCH_2), 5.14 (d, *J* = 4.0 Hz, 8H, H-1), 7.88 (s, 8H, triazole); ^{13}C NMR (100 MHz, D_2O) δ 149.48 (triazole), 128.14 (triazole), 104.16 (C-1), 84.86 (C-4), 74.91 (C-3), 74.56 (C-2), 72.74 (C-5), 57.06 (OCH_2), 52.92 (C-6); MALDI-TOFMS *m/z* calcd for $C_{72}H_{104}N_{24}O_{40}$ $[M + Na]^+$ 1967.6734, found 1967.6747 (mass accuracy of 0.64 ppm)

HMQC and HMBC spectra of new compounds, PCD and HCD

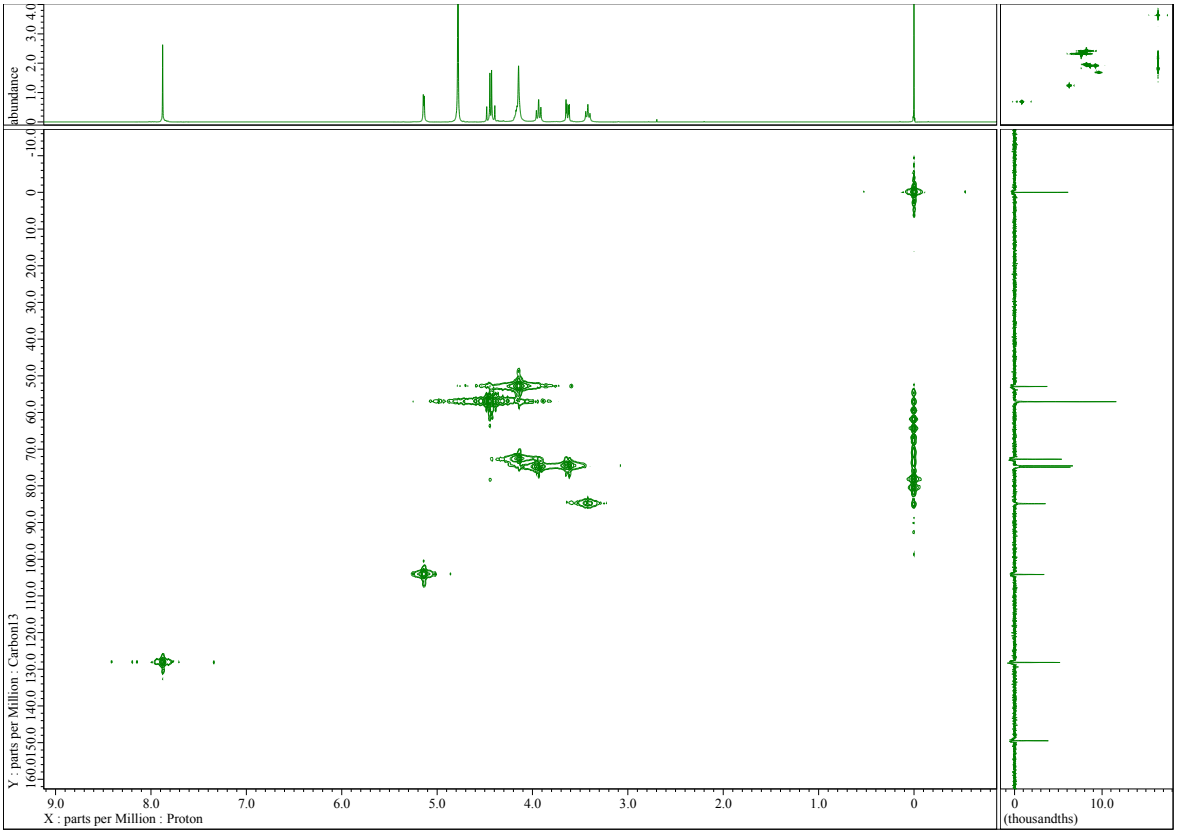
HMQC spectra of PCD



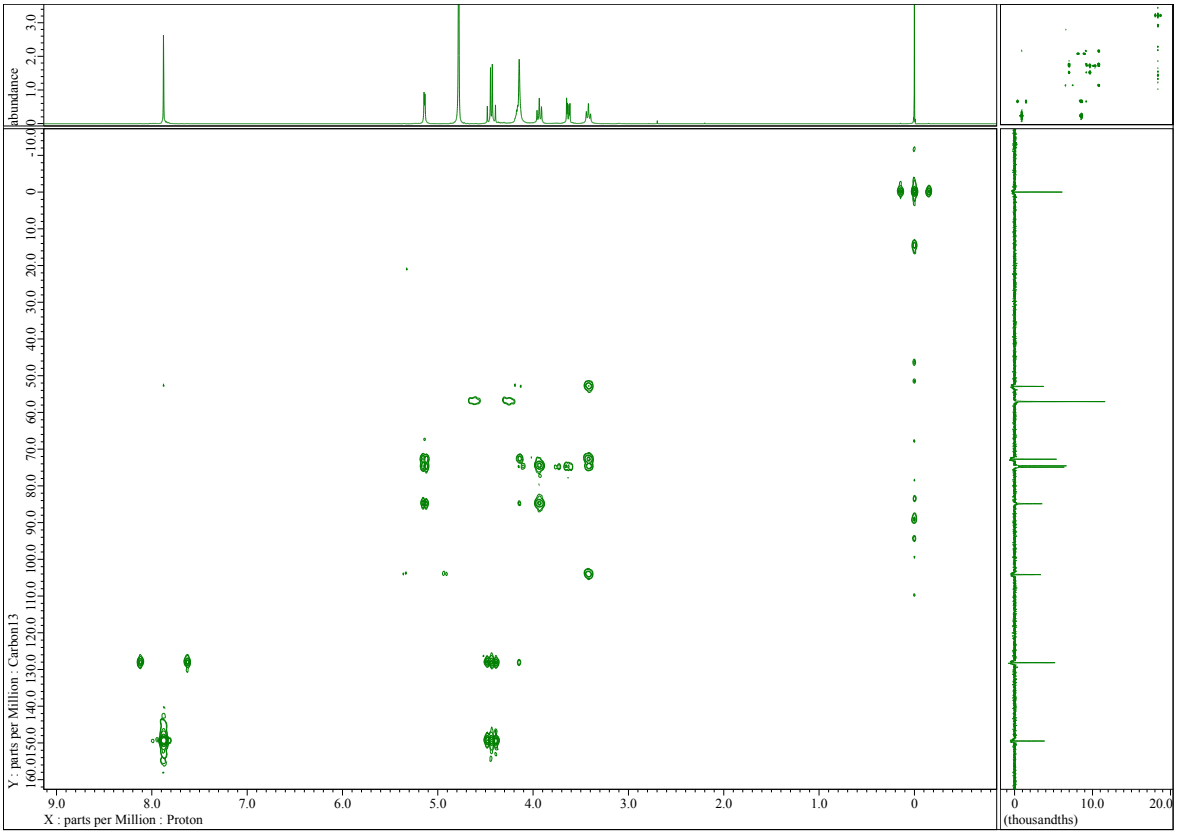
HMBC spectra of PCD



HMQC spectra of HCD



HMBC spectra of HCD



Experimental details

Preparation of the C_{60}–CDs inclusion complex[4-6]

C_{60}–CDs inclusion complex were prepared by solid-state mechanochemical process using ball milling. In a typical way, mixtures of C_{60} and CD derivative of each 1.4×10^{-5} mol were placed in an agate capsule together with two agate-mixing balls. They were mixed vigorously by mixing at 30 Hz for 20 min using a mixer mill (MM400, Retsch Co. Ltd.). The solid mixtures were dissolved in 1 mL of water following centrifugation (17970×g, 20 min), all nondispersed C_{60} were removed from the solutions.

Estimation of the maximum concentration of C_{60} in the inclusion complexes with CD derivatives

In as-prepared C_{60}-dissolved sample of CD derivatives, only the sample of PCD did not indicate any precipitation after more than two months at 4 °C even though the solution was concentrated until apparently judging its solution behavior. Concentration of C_{60} in this condition was estimated from absorbance at 332 nm in UV–vis spectra after diluting the concentrated sample. As for other host molecules, spectral measurements were carried out using as-prepared samples without any intervals after mechanochemical complexation because the samples could not keep the dispersibility in such high concentration of the inclusion complexes with forming precipitation of them subsequently.

Table S1 Comparison of the maximum concentration of C_{60} with various CD derivatives

Compound	Solubilizing ability for C_{60}	Maximum concentration of C_{60}
PCD	◎	72.7 mM
HCD	○	1.1 mM
γ–CD	○	0.8 mM

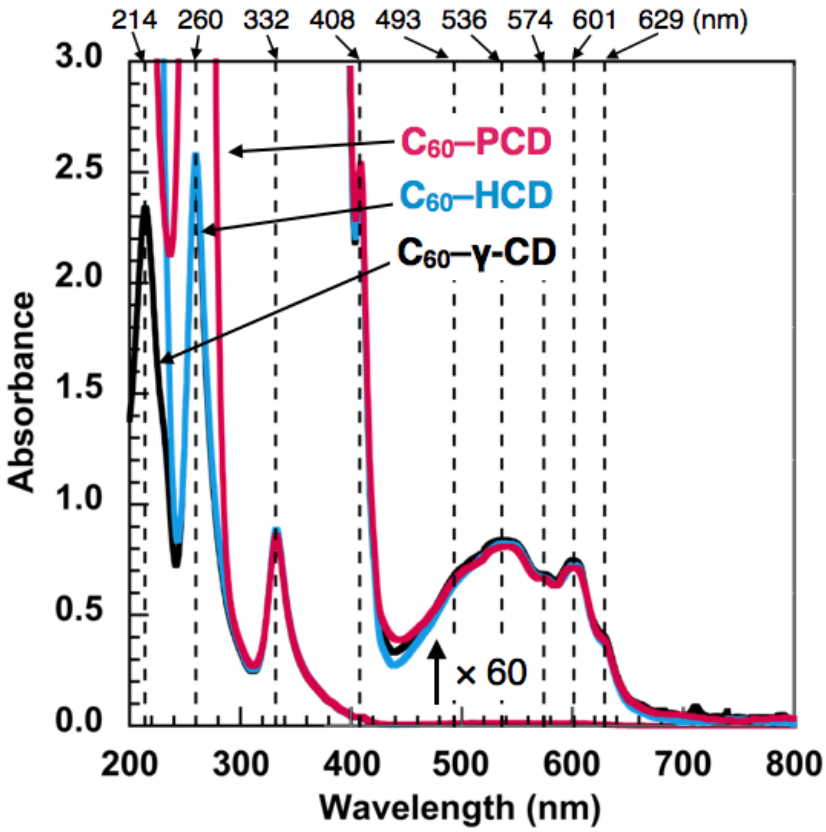


Figure S1 UV-vis absorption spectra of the extracted C_{60} with PCD, HCD and γ-CD, in which the concentration of C_{60} were fixed at 2.0×10^{-5} M. Cell length = 1 cm.

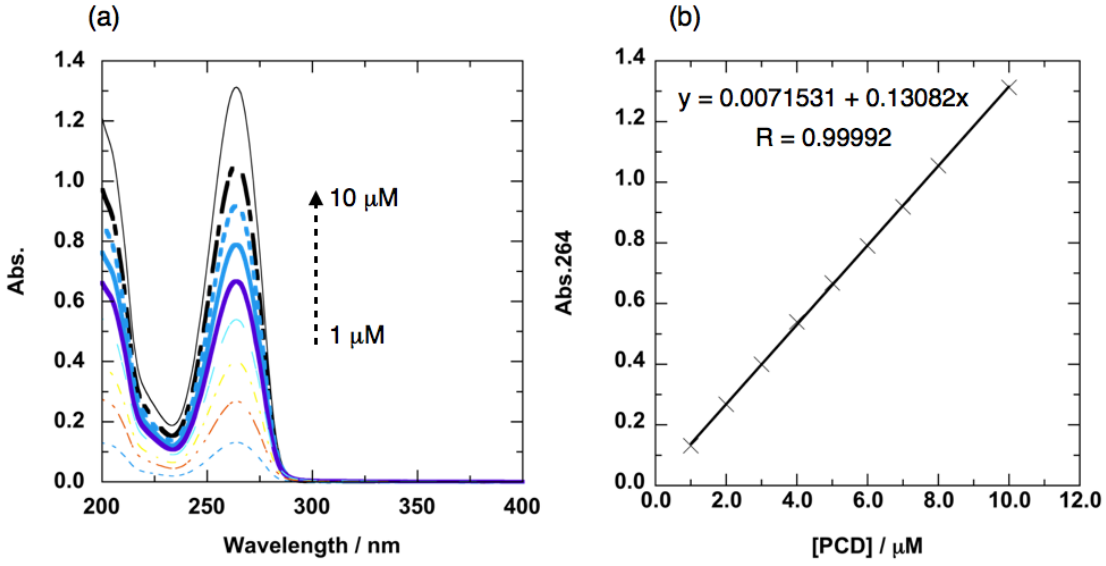


Figure S2 (a) UV-vis absorption spectra of different concentration of PCD in water. (b) Plots of absorbance at 264 nm of PCD against for the concentration. Cell length = 1 cm.

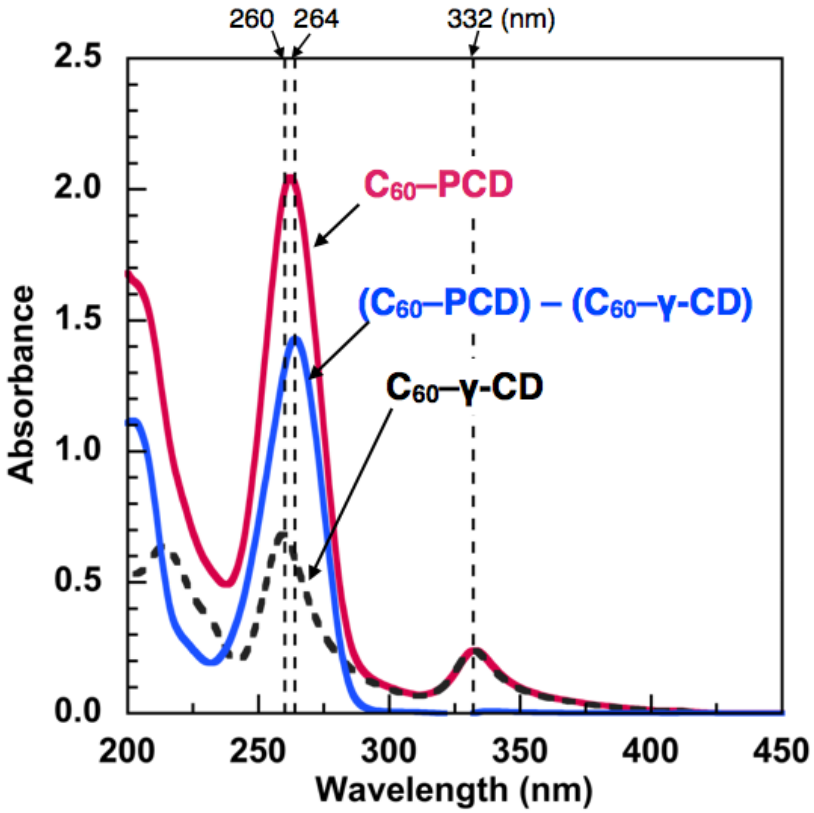


Figure S3 UV-vis absorption spectra of C_{60}–PCD and C_{60}–γCD. In this figure, 100 times dilution of the extracted C_{60}–PCD solution was represented. C_{60}–γCD was set with the same concentration as diluted C_{60}–PCD by comparing absorbance at 332 nm. To estimate the PCD concentration in the inclusion complex, the difference spectrum was obtained by subtracting the spectrum of C_{60}–γCD from that of C_{60}–PCD. Cell length = 0.1 cm.

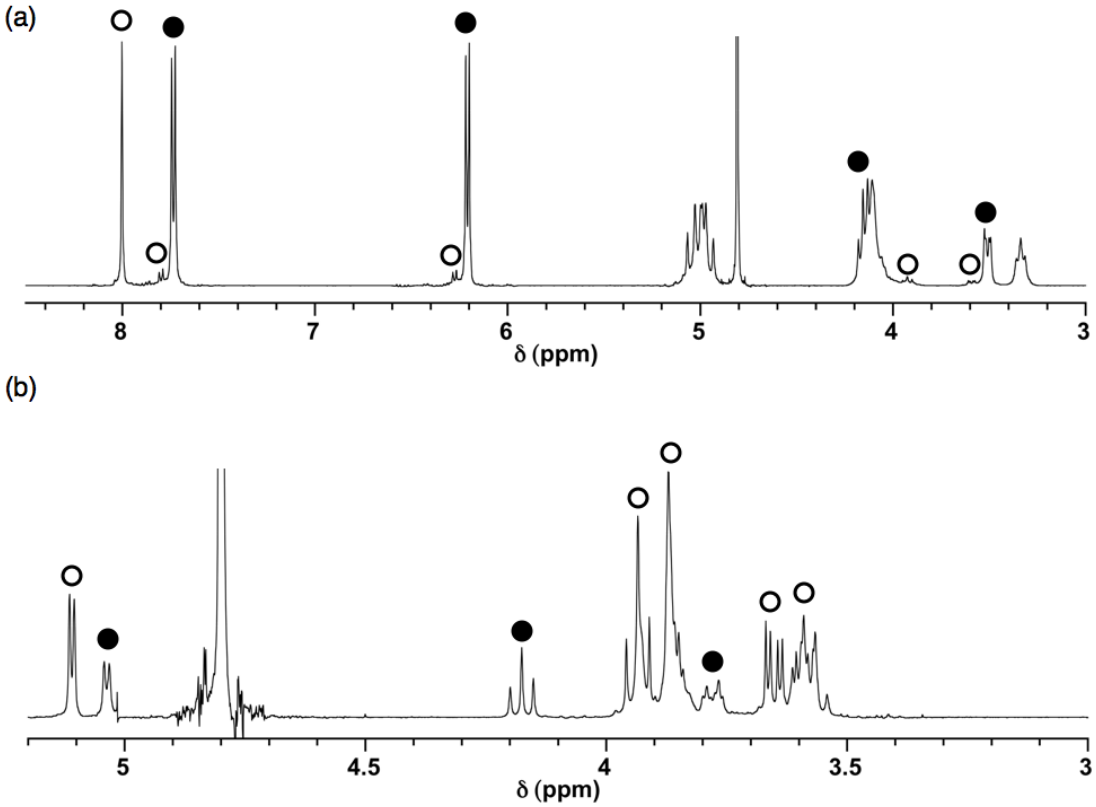


Figure S4 ^{1}H NMR spectra of (a) C_{60}–PCD and (b) C_{60}–γCD in D_2O (400 MHz, HOD as internal reference). White and black circles represent a free CDs and the complex, respectively.

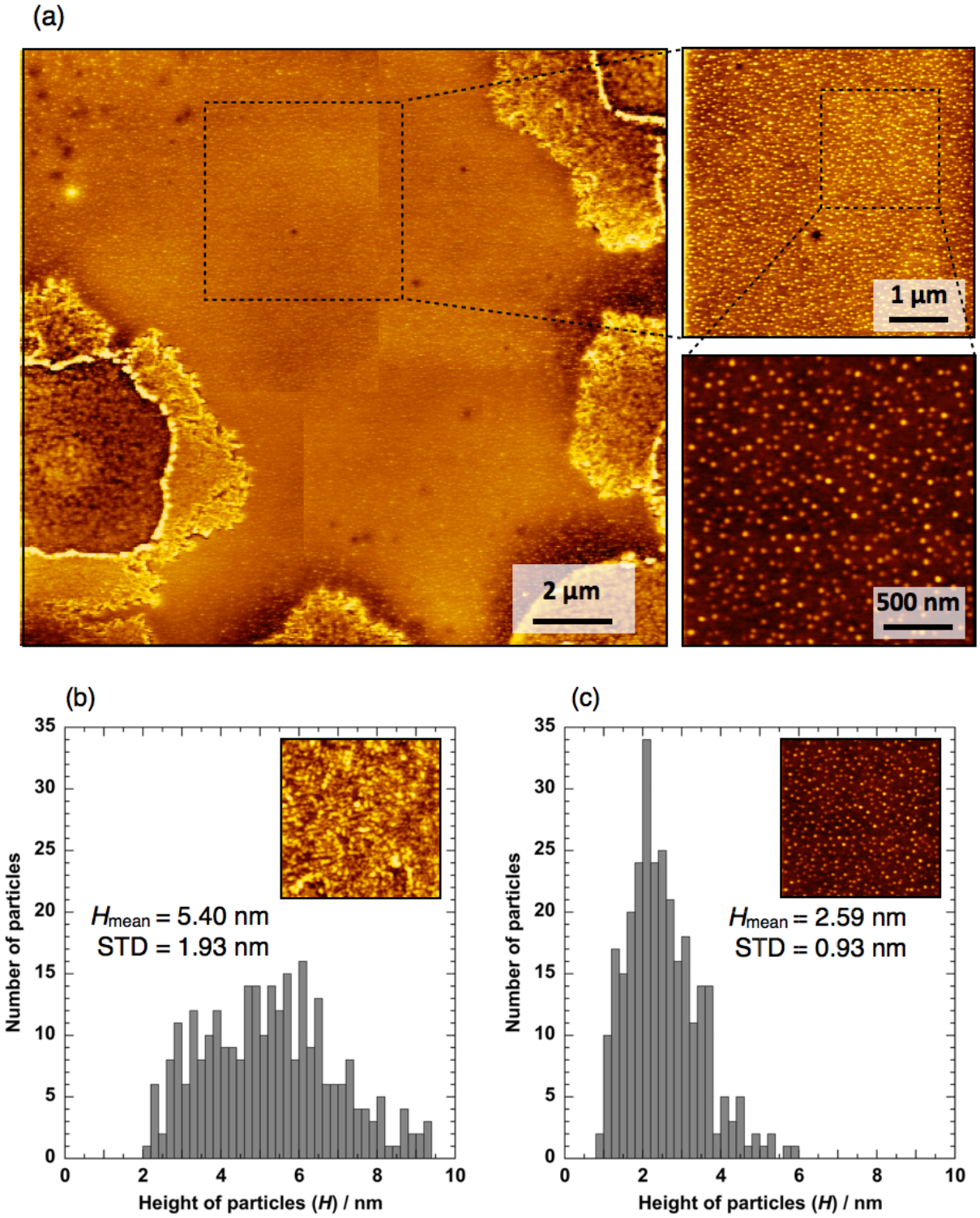


Figure S5 (a) AFM images of C_{60}–PCD complex obtained by drop-casting of the solution on mica and subsequently washed with water. From the cross-sectional analysis, the height distribution of (c) was recorded at a more thoroughly washed region than (b).

References

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