Electronic Supplementary Information

1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) as a novel and effective solvent to facilely prepare cyclodextrin-assembled materials

*Toshiyuki Kida, Shin-ichiro Sato, Hiroaki Yoshida, Ayumi Teragaki and Mitsuru Akashi**

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan

Contents

1. Materials and methods

α-, β- and γ-CD were purchased from Wako Pure Chemical Industries Ltd. (Japan) and dried overnight at 80 °C under a reduced pressure before use. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HFMP) and 2,2,2-trifluoroethanol (TFE) were purchased from Wako Pure Chemical Industries Ltd. (Japan).

The solubilities of CDs in fluorinated alcohols were determined by visually estimating the saturation concentration through the addition of a prescribed amount of CD into a fluorinated alcohol (2 mL) and subsequent stirring for 1 h.

The ^{1}H-NMR titrations were performed at 25 ^{o}C in D_2O. A solution of the CD molecule (0.6 mL, 1.0 mM) was titrated in a NMR tube with increasing amounts of HFIP stock solution (0.5 mL, 150 mM) as follows (in μL): 0, 2.0, 4.0, 8.0, 40, 60, 80. The titration curve (changes in the chemical shift of the β-CD proton (Δδ) against the HFIP/β-CD concentration ratio) was analyzed by a non-linear least-squares curve fitting method to generate an association constant of the β-CD-HFIP complex. A Job plot was carried out by monitoring the changes in the chemical shift of the β-CD proton (Δδ) in a series of solutions with varying β-CD/HFIP ratios but the total concentration of β-CD and HFIP being kept constant (2.0 mM). The relative concentration of the β-CD-HFIP complex estimated from the Δδ • [β-CD] value was plotted against ([β-CD]/{[β-CD] + [HFIP]}).

Electrospinning was performed with a Nanofiber Electrospinning Unit (Kato Tech Co., Ltd., Japan). The solution was pumped through a single-use blunt-end 18-gauge cannula at a flow rate of 0.16 mL/min, and the collection distance between the cannula and the rotating drum target (diameter: 10 cm, width: 33 cm) was 10 cm. The drum substrate was covered with aluminum foil and rotated at a rate of 2.0 m/min during the electrospinning of the solutions. A voltage of 25 kV was applied between the cannula and the substrate. The viscosities of the CD/HFIP solutions at different CD concentrations were measured by a viscometer, TOKIMEC TV-20 (Toki Sangyo, Japan).

The morphologies and X-ray diffraction (XRD) patterns of the CD structures obtained via electrospinning were measured by a scanning electron microscope (SEM) (JSF-6701F, JEOL Ltd., Japan) and a Rigaku X-ray diffractometer (Rigaku, Japan), respectively.

2. ^{1}H NMR spectra of CDs regenerated from the CD/HFIP solutions

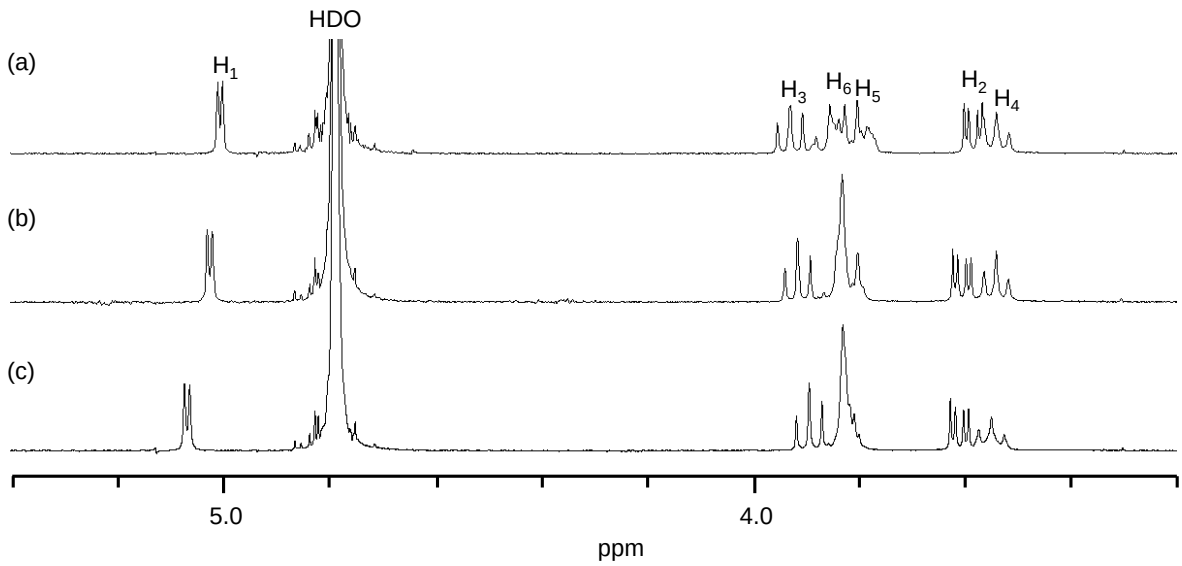

Fig. S1 ^{1}H NMR spectra of (a) α-, (b) β- and (c) γ-CD regenerated by evaporating HFIP from the corresponding HFIP solutions (solvent: D_2O, CD concentration: 1.0×10^{-3} mol/L).

3. ^{1}H-NMR spectral changes observed for CDs upon addition of HFIP

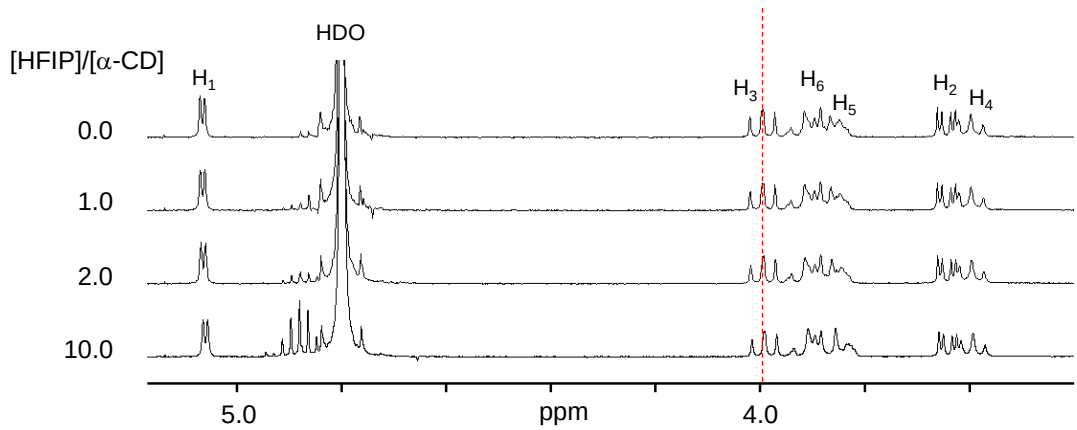

Fig. S2 ^{1}H-NMR spectral changes observed for α-CD (1.0×10^{-3} mol/L) upon addition of HFIP in D_2O at 25 °C.

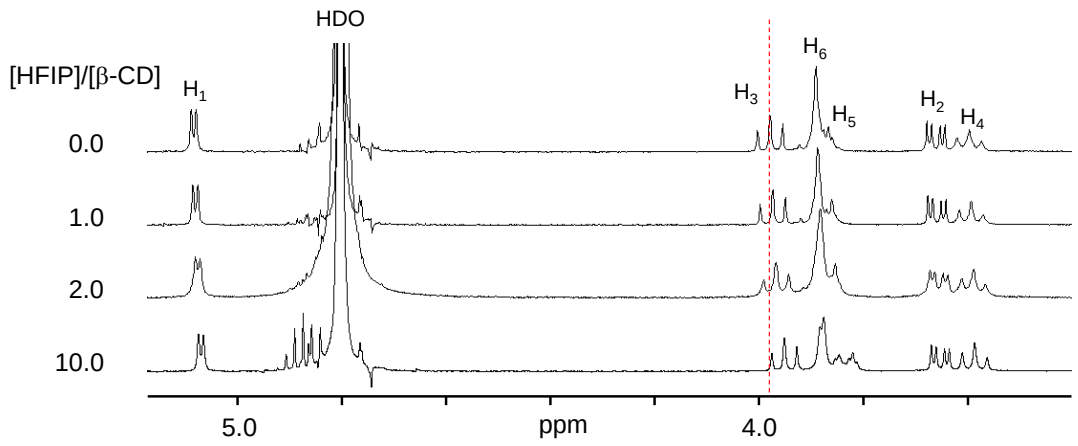

Fig. S3 ^{1}H-NMR spectral changes observed for β-CD (1.0×10^{-3} mol/L) upon addition of HFIP in D_2O at 25 °C.

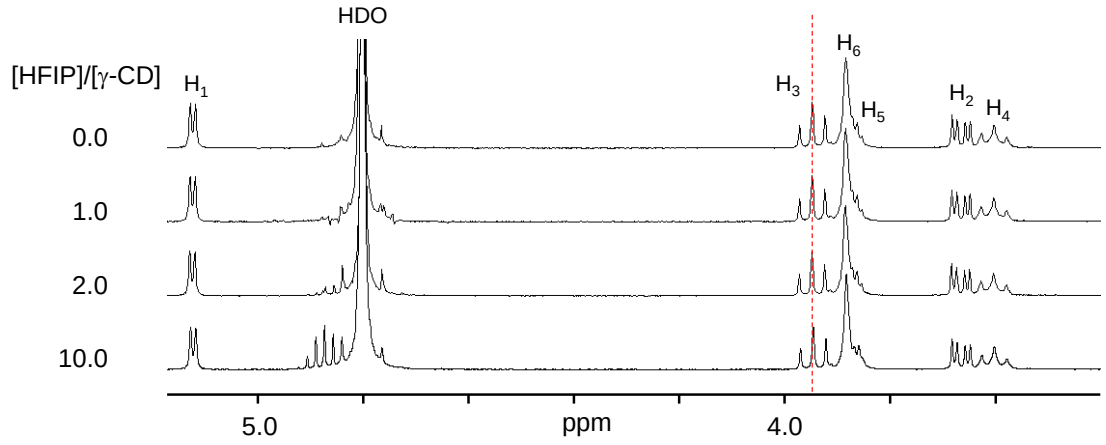

Fig. S4 ^{1}H-NMR spectral changes observed for γ-CD (1.0×10^{-3} mol/L) upon addition of HFIP in D_2O at 25 °C.

4. ^{1}H-NMR titration curve for complex formation between β-CD and HFIP in D_2O

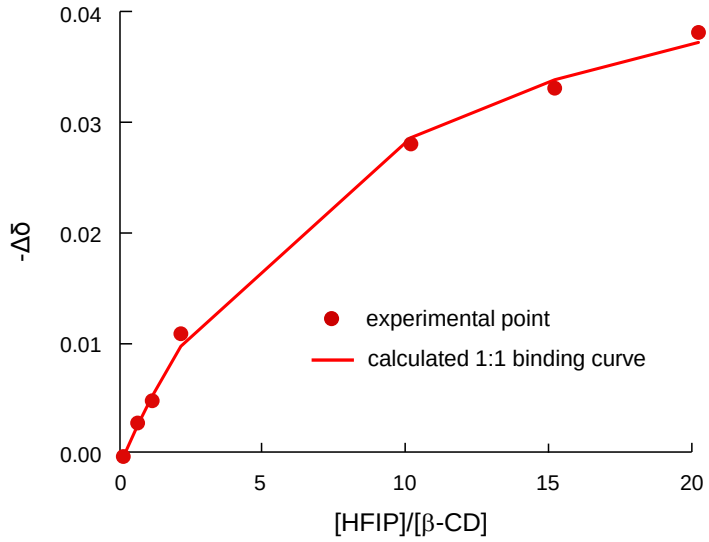

Fig. S5 ^{1}H-NMR titration curve for complex formation between β-CD and HFIP in D_2O. [β-CD] = 1.0×10^{-3} mol/L. At 25 °C. The H_3 proton signal of β-CD at 3.98 ppm was used for the titration.

5. Job plot for a complex between β-CD and HFIP in D_2O

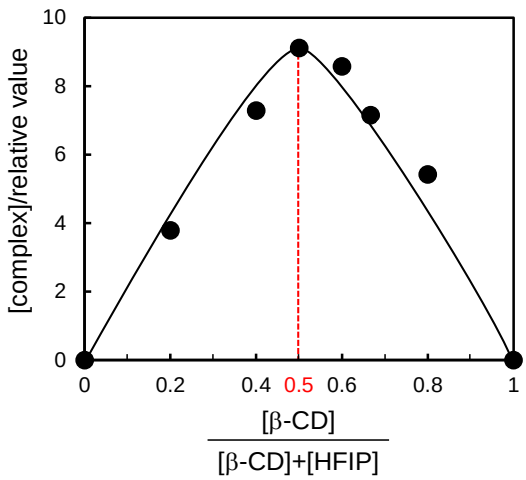

Fig. S6 Job plot for a complex between β-CD and HFIP in D_2O at 25 °C.

6. Photographs of CD/HFIP solutions and CD crystalline solids obtained from the HFIP solutions

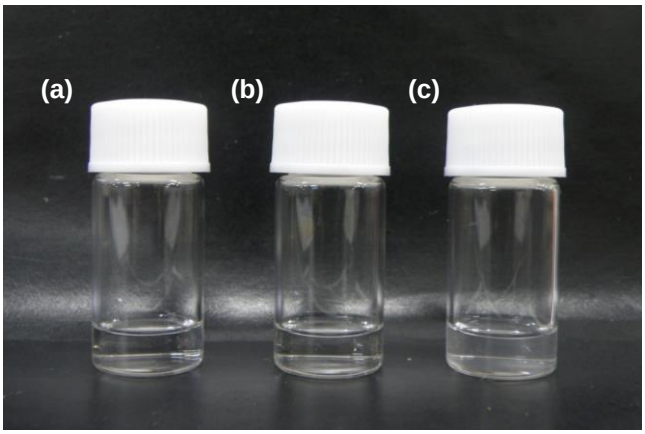

Fig. S7 Photographs of HFIP solutions of (a) α-, (b) β- and (c) γ-CD (0.1 mol/L).

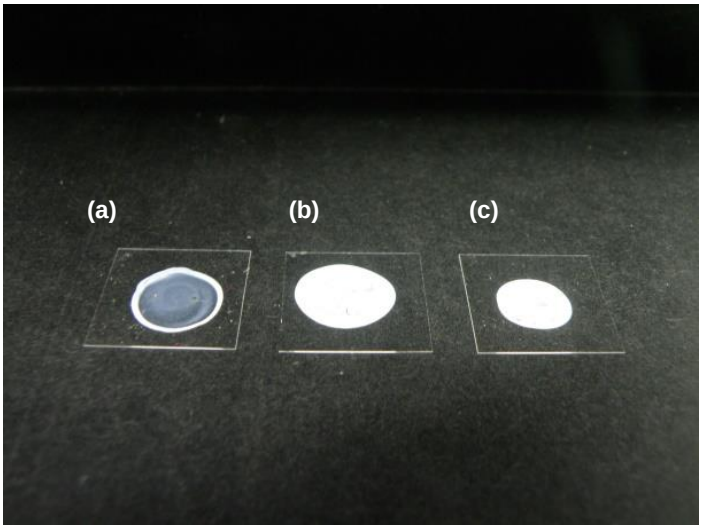

Fig. S8 Photographs of (a) α-, (b) β- and (c) γ-CD crystalline solids obtained after drying the HFIP solutions on a glass plate at ambient temperature.

7. XRD patterns of CD solids obtained by the freeze-drying of CD/HPIC solutions

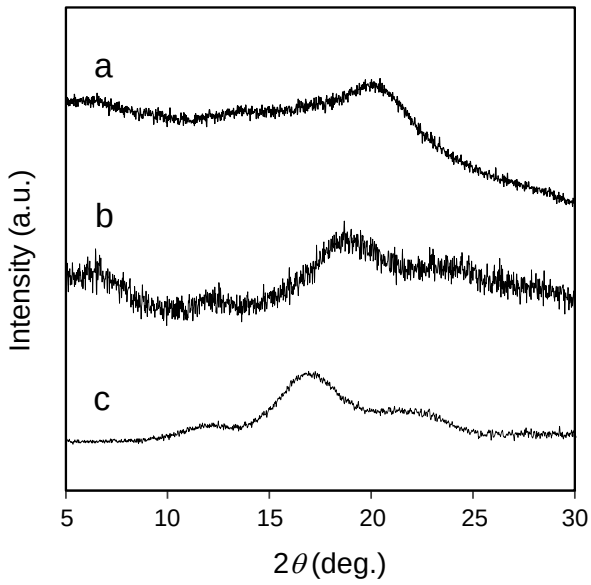

Fig. S9 XRD patterns of (a) α-, (b) β- and (c) γ-CD solids obtained by the freeze-drying of HFIP solutions (0.1 mol/L).

8. XRD patterns of the micrometer-sized CD beads formed by electrospinning of HFIP solutions

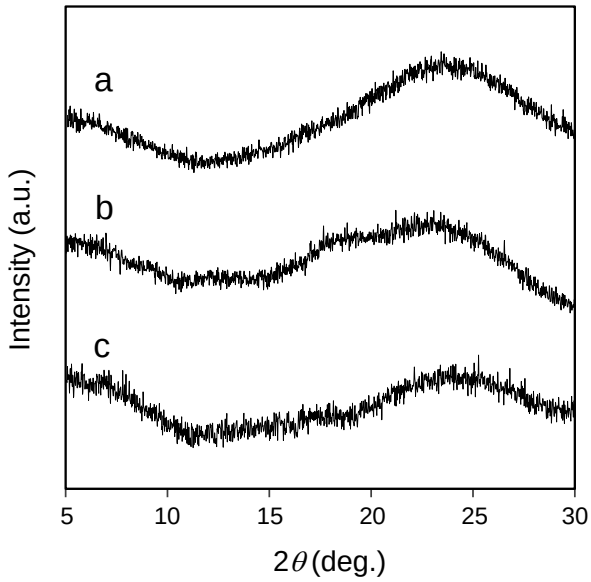

Fig. S10 XRD patterns of (a) α-, (b) β- and (c) γ-CD beads formed by electrospinning of HFIP solutions (2.5 wt%).

9. SEM image of β-CD structures formed by electrospinning of a 10 wt% β-CD/HFIP solution

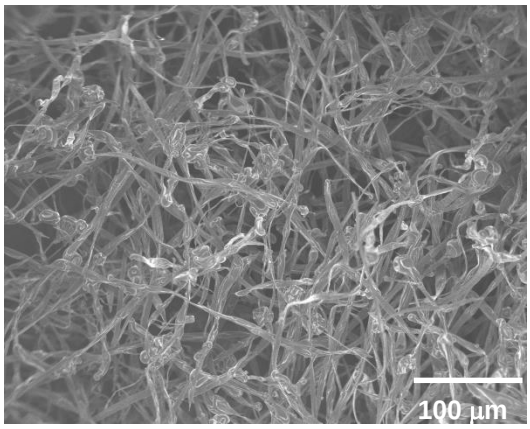

Fig. S11 SEM image of β-CD structures formed by electrospinning of a β-CD/HFIP solution (10 wt%).