Electronic Supplementary Information

A Novel Molecular Tube Fully Modified at One End: Selective Inclusion of *cis*-Unsaturated Fatty Acid Esters

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9. Reference

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1. Materials and Methods

Boron trifluoride diethyl ether complex and dichloromethane were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Tetrabutylammonium fluoride was purchased from Sigma-Aldrich (Japan). Tetramethylammonium fluoride and 1,4-dioxane were purchased from Wako Pure Chemical Industries, Ltd. (Japan). These reagents were used without further purification. ¹H and ¹³C NMR spectra were recorded on a JEOL NMR system (400 MHz). The following abbreviations were used for chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR signal assignments were based on additional 2D-NMR spectroscopy (e.g., COSY and HSQC). Infrared (IR) spectra were obtained with a Spectrum 100FT-IR spectrometer (Perkin Elmer). MALDI-TOF MS spectra were measured by Bruker Autoflex III. Melting points were measured with BUCHI Melting point B-545. Elemental analysis was performed with Perkin Elmer 240C. HPLC was performed using a Shimadzu Prominence HPLC system equipped with a Soft 400 ELSD detector.

1-1. Synthesis of 1



Scheme S1. Synthesis of 1.

1 was prepared according to our previously reported method.^[1] The structure was confirmed by the ¹H NMR spectrum.



Figure S1. ¹H NMR spectrum of 1 in chloroform-*d* at 25 °C.

1-2. Synthesis of 2



Scheme S2. Synthesis of 2.

1 (20 mg, 4.4 μ mol) and tetramethylammonium fluoride (TMAF, 8.6 mg, 92 μ mol) were dissolved in 1,4-dioxane (2.0 mL). The reaction mixture was stirred for 8 h at 100 °C. After the solvent was removed in vacuo, the resulting solid was purified by silica gel column chromatography (chloroform/methanol, in a gradient 10:1 to 6:1) to give compound **2** (8.0 mg, 48% yield).

1-3. Synthesis of 3



Scheme S3. Synthesis of 3.

1 (0.1 g, 22 μ mol) was dissolved in dichloromethane (10.0 mL). Into this solution, boron trifluoride diethyl ether complex (60 μ L, 0.48 mmol) was added, and the reaction mixture was stirred for 4 h at room temperature. After the solvent was removed in vacuo, the resulting solid was washed with acetone (10 mL×3) and hexane (10 mL×3), and dried at 80 °C in vacuo to give compound **3** (60 mg, 91% yield).

1-4. Spectral Data of 2

 $R_{\rm f}$ 0.5 (CHCl₃/MeOH = 4/1); mp: 273 °C (decomp); ¹H NMR (400 MHz, methanol- d_4): δ 0.07 (d, J = 2.8 Hz, 42H), δ 0.88 (s, 63H), δ 3.34-3.46 (m, 28H), δ 3.63-3.85 (m, 35H), δ 4.07 (d, J = 8.8 Hz, 7H), δ 4.15-4.25 (m, 28H), δ 4.93 (m, 28H), δ 5.21-5.25 (m, 28H), δ 7.14-7.18 (m, 14H), δ 7.23-7.27 (m, 7H), δ 7.66 (s, 7H); ¹³C NMR (100 MHz, methanol- d_4): δ -5.74, -4.47, 19.26, 26.63, 61.84, 72.90, 73.18, 75.33, 75.43, 77.44, 77.50, 83.22, 83.45, 84.34, 85.00, 103.76, 129.19, 129.64, 129.82, 131.38, 138.99, 139.01; MALDI-TOF MS: m/z = 3808 [M+Na]⁺; Anal. Calcd for C₁₅₂H₂₈₀O₇₀Si₇•6H₂O: C, 56.15; H, 7.56. Found: C, 56.24: H, 7.59; FT-IR (cm⁻¹): 3406, 2926, 2855, 1462, 1360, 1251, 1158, 1083, 1039, 833, 777.



Figure S2. ¹H NMR spectrum of **2** in methanol- d_4 at 25 °C.



Figure S3. ¹³C NMR spectrum of **2** in methanol- d_4 at 25 °C.



Figure S4. HPLC chromatogram of **2**. Column: NACALAI TESQUE, COSMOSIL 5SL-II Packed Column (250 mm \times 4.6 mm i.d.); mobile phase: chloroform/methanol = 2/1 (v/v); flow rate: 1.5 ml min⁻¹; temperature: 25 °C; detector: ELSD.

1-5. Spectral Data of 3

mp: 270 °C (decomp); ¹H NMR (400 MHz, DMSO- d_6): δ 3.26-3.41 (m, 28H), δ 3.58-3.70 (m, 28H), δ 4.02 (t, J = 9.6 Hz, 14H), δ 4.21 (d, J = 9.6 Hz, 14H), δ 4.63 (s, 14H), δ 4.84 (m, 14H), δ 5.04 (d, J = 9.6 Hz, 14H), δ 7.13 (d, J = 8.0 Hz, 14H) , δ 7.22 (t, J = 7.2 Hz, 7H) , δ 7.52 (s, 7H); ¹³C NMR (100 MHz, DMSO- d_6): δ 59.91, 71.32, 73.58, 75.20, 81.68, 83.14, 101.42, 127.80, 128.20, 137.55; MALDI-TOF MS: m/z = 3008 [M+Na]⁺; Anal. Calcd for C₁₄₀H₁₈₂O₇₀•9H₂O: C, 53.43; H, 6.41. Found: C, 53.43: H, 6.44; FT-IR (cm⁻¹): 3389, 2920, 1360, 1322, 1247, 1155, 1083, 1010, 948, 854, 754, 700.



Figure S5. ¹H NMR spectrum of **3** in DMSO- d_6 at 25 °C.



Figure S6. ¹³C NMR spectrum of **3** in DMSO- d_6 at 25 °C.

1-6. Determination of Association Constants by NMR Titration

A solution of the host molecule $(5.0 \times 10^{-4} \text{ M}, 0.5 \text{ mL})$ was titrated in a NMR tube with increasing amounts of guest stock solution (200 mM). 6 or more solutions with different host-guest concentration ratios were analyzed. Four of ¹H NMR spectra obtained are shown in each figure. The titration curves (changes in the chemical shift of the host protons ($\Delta\delta$) against the guest/host concentration ratio) were analyzed by a non-linear least-squares curve fitting method to give the association constants between the hosts and the guests.

1-7. Experimental Procedure for Job Plots

Job plots were carried out by monitoring the changes in the chemical shift of the host protons ($\Delta\delta$) in a series of solutions with varying host/guest ratios but the total concentrations of the host and guest being kept constant (0.4 or 2.0 mM). The relative concentration of the host-guest complex estimated from the $\Delta\delta$ ·[host] value was plotted against ([host]/{[host] + [guest]}).

2. MALDI-TOF MS Spectra of the Products Obtained by the Desilylation of 1 under Various Conditions



Figure S7. MALDI-TOF MS spectra of the products of the desilylation of **1** with TMAF in 1,4-dioxane at 100 °C for (a) 2 h and (b) 18 h.



Figure S8. MALDI-TOF MS spectrum of the product of the desilylation of **1** with TBAF (14 eq.) in THF for 8 h at 60 °C.

3. ¹H-NMR Spectral Changes Observed for 2 upon Addition of Long-Chain Fatty Acid Esters in Methanol-*d*₄ and Titration Curves for Their Complex Formation



Figure S9. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl myristate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl myristate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S10. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl palmitate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl palmitate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S11. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl stearate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl stearate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S12. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl elaidate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl elaidate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S13. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl linoelaidate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl linoelaidate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S14. ¹H NMR titration curve for complex formation between **2** and methyl oleate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S15. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl linoleate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl linoleate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S16. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl eicosapentaenoate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl eicosapentaenoate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.



Figure S17. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl docosahexaenoate in methanol- d_4 at 25 °C. (b) ¹H NMR titration curve for complex formation between **2** and methyl docosahexaenoate in methanol- d_4 at 25 °C. The proton signal of **2** at 4.2 ppm was used for titration.

4. Job Plots for Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-d₄



Figure S18. Job plot for complex between 2 and methyl elaidate in methanol- d_4 at 25 °C.



Figure S19. Job plot for complex between 2 and methyl oleate in methanol- d_4 at 25 °C.



Figure S20. Job plot for complex between 2 and methyl linoleate in methanol- d_4 at 25 °C.



Figure S21. Job plot for complex between **2** and methyl docosahexaenoate in methanol- d_4 at 25 °C.

5. NOESY Spectra of Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-d4



Figure S22. The partial 400 MHz NOESY spectrum of a complex of 2 with methyl linoleate in methanol- d_4 at 25 °C.



Figure S23. The partial 400 MHz NOESY spectrum of a complex of **2** with methyl docosahexaenoate in methanol- d_4 at 25 °C.

6. ¹H-NMR Spectral Changes Observed for 2 or 3 upon Addition of Long- Chain Fatty Acid Esters in Methanol-d₄/DMSO-d₆ (7/3) and Titration Curves for Their Complex Formation



Figure S24. (a) ¹H NMR spectral changes observed for **2** (5.0×10^{-4} M) upon addition of methyl elaidate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. (b) ¹H NMR titration curve observed for **2** (5.0×10^{-4} M) upon addition of methyl elaidate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. The proton signal of **2** at 7.6-7.7 ppm was used for titration.



Figure S25. (a) ¹H NMR spectral changes observed for **2** $(5.0 \times 10^{-4} \text{ M})$ upon addition of methyl oleate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. (b) ¹H NMR titration curve observed for **2** $(5.0 \times 10^{-4} \text{ M})$ upon addition of methyl oleate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. The proton signal of **2** at 7.6-7.7 ppm was used for titration.



Figure S26. (a) ¹H NMR spectral changes observed for **3** (5.0×10^{-4} M) upon addition of methyl elaidate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. (b) ¹H NMR titration curve for complex formation between **3** and methyl elaidate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. The proton signal of **3** at 7.6-7.7 ppm was used for titration.



Figure S27. (a) ¹H NMR spectral changes observed for **3** $(5.0 \times 10^{-4} \text{ M})$ upon addition of methyl oleate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. (b) ¹H NMR titration curve for complex formation between **3** and methyl oleate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C. The proton signal of **3** at 7.6-7.7 ppm was used for titration.

7. Job Plots for Complexes between 3 and Long-Chain Fatty Acid Esters in Methanol- d_4 /DMSO- d_6 (7/3)



Figure S28. Job plot for complex between 3 and methyl elaidate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C.



Figure S29. Job plot for complex between 3 and methyl oleate in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C.

8. Association Constants between 2 or 3 and Various Long-Chain Fatty Acid Methyl Esters in Methanol-d₄/DMSO-d₆ (7/3) at 25 °C

acid methyl esters in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C.							
entry	host	guest	association constant (M ⁻¹)				
1	2	methyl elaidate	$(7.4 \pm 1.7) \times 10^2$				
2		methyl oleate	$(2.1 \pm 0.69) \times 10^3$				

methyl elaidate

methyl oleate

 $(4.2 \pm 0.27) \times 10^2$

 $(1.1 \pm 0.075) \times 10^3$

Table S1. Association constants between 2 or 3 and various long-chain fatty acid methyl esters in methanol- d_4 /DMSO- d_6 (7/3) at 25 °C.

9. Reference

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[1] S. Ito, C. Kogame, M. Akashi and T. Kida, *Tetrahedron Lett.* 2016, 57, 5243–5245.