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Electronic Supplementary Information (ESI)

Selective Complexation of *n*-Alkanes with Pillar[5]arene Dimer in Organic Media

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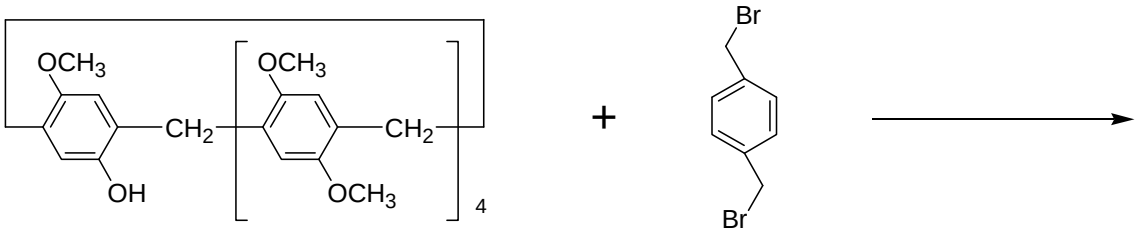
Experimental section

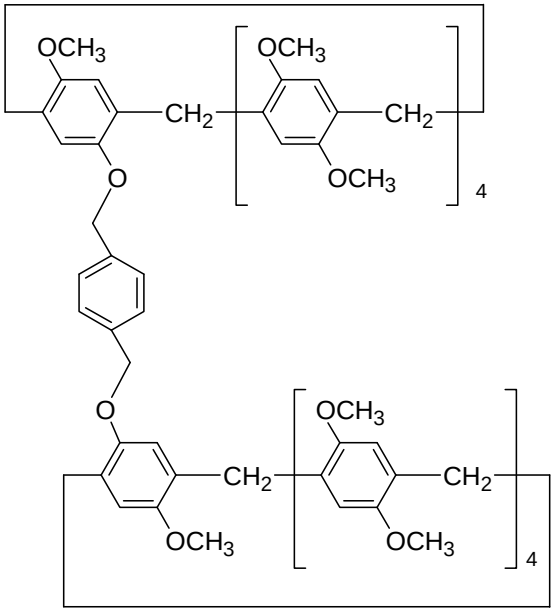
Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer.

1OH-Pillar was synthesized according to the previous paper.[S1]

Pillar[5]arene Dimer (2). Under a nitrogen atmosphere **1OH-Pillar** (300 mg, 0.410 mmol) was dissolved in DMF (5 mL). Sodium hydride (39.4 mg, 1.64 mmol) was added and the reaction mixture was stirred. Then, 1,4-bis(bromomethyl)benzene (54.1 mg, 0.205 mmol) was added and the reaction mixture was heated at 80 ^{o}C for 48 h. After removal of the solvent, the resulting solid was dissolved in chloroform and water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated to give a solid. Column chromatography (silica gel; chloroform : acetone =





18 : 1) afforded a white solid (**3**, 0.220 g, 0.140 mmol, Yield: 69%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.47 (s, 4H, phenyl protons of linker), 6.87, 6.82, 6.78, 6.77, 6.74, 6.71, 6.66 (m, 10H, phenyl protons of pillar[5]arene), 4.90 (s, 4H, methylene protons of linker), 3.84, 3.79, 3.78, 3.75, 3.65, 3.64, 3.62, 3.61, 3.36 (m, 74H, methylene bridge and methoxy protons of pillar[5]arene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.1, 150.9, 150.8, 150.0, 137.5, 128.6, 128.4, 128.2, 128.0, 127.5, 115.3, 114.2, 114.1 (C of phenyl), 70.5 (C of methylene of linker), 55.9, 55.8, 55.5 (C of methoxy), 29.9, 29.7, 29.6 (C of methylene bridge of pillar[5]arene). HRFABMS Calcd for C96H103O20 $[M+H]^+$: 1575.7043, found 1575.7045.

Determination of association constants for *n*-alkane complexes. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of *n*-alkane and varying concentrations of **2**. By the non-linear curve-fitting methods, the association constants (K_1) for **2**-*n*-hexane and **2**-*n*-octane complexes are estimated to be 98 ± 12 M^{-1} and 62 ± 10 M^{-1}, respectively, for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:[S2]

$$\Delta\delta_{obs} = \frac{\Delta\delta_{11}}{2K[G]_0}\left[1 + K[H]_0 + K[G]_0 - \{(1 + K[H]_0 + K[G]_0)^2 - 4K^2[H]_0[G]_0\}^{1/2}\right]$$

Where $\Delta\delta_{obs}$ is the chemical shift change of *n*-alkane protons at $[H]_0$, $\Delta\delta_{11}$ is the chemical shift change of the *n*-alkane proton resonance when the guest *n*-alkane is completely complexed, $[G]_0$ is the fixed initial concentration of the guest *n*-alkane, and $[H]_0$ is the initial concentration of the host **2**.

References

S1) T. Ogoshi, K. Demachi, K. Kitajima and T. Yamagishi, *Chem. Commun.*, 2011, 7164.

S2) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931.

^{1}H NMR spectrum of pillar[5]arene dimer (2)

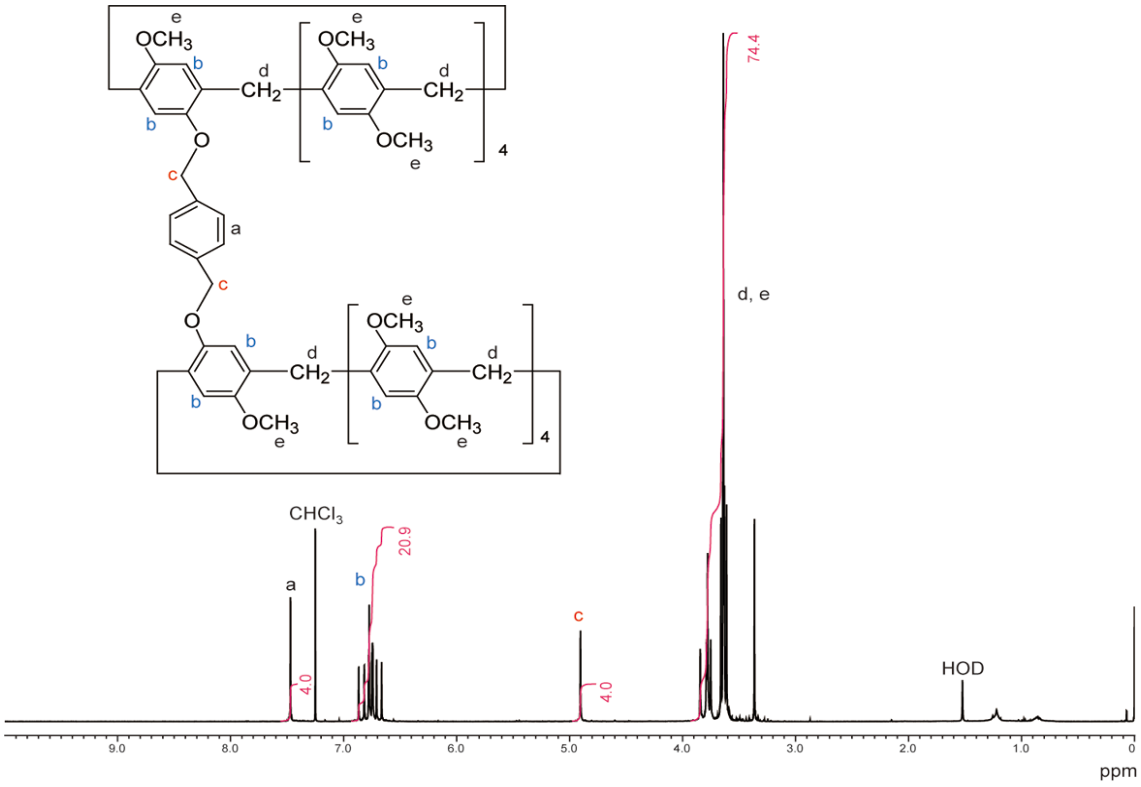


Figure S1. ^{1}H NMR spectrum of pillar[5]arene dimer (**2**) in $CDCl_3$ at 25 ^oC.

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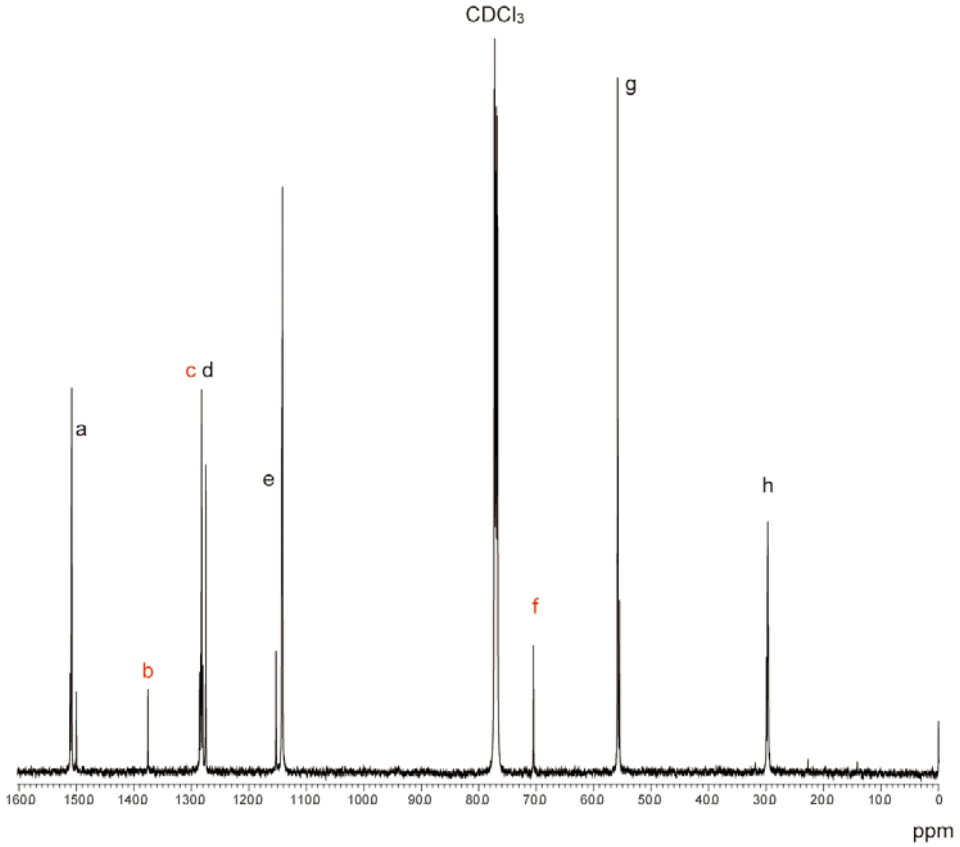
^{13}C NMR spectrum of pillar[5]arene dimer (2)



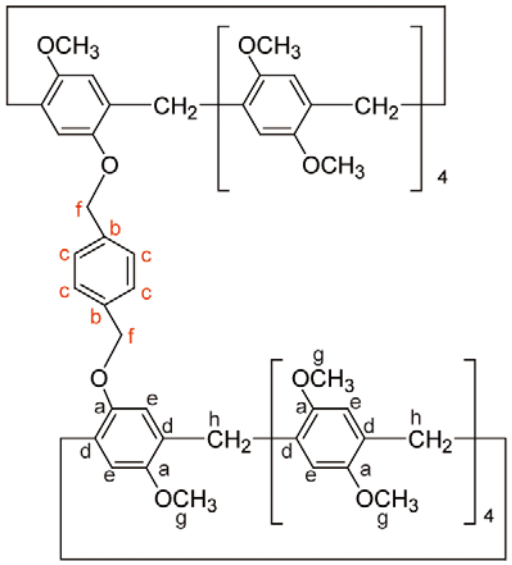


Figure S2. ^{13}C NMR spectrum of pillar[5]arene dimer (**2**) in $CDCl_3$ at 25 ^{o}C.

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Partial ^{1}H NMR spectrum of a mixture of 2 and *n*-hexane

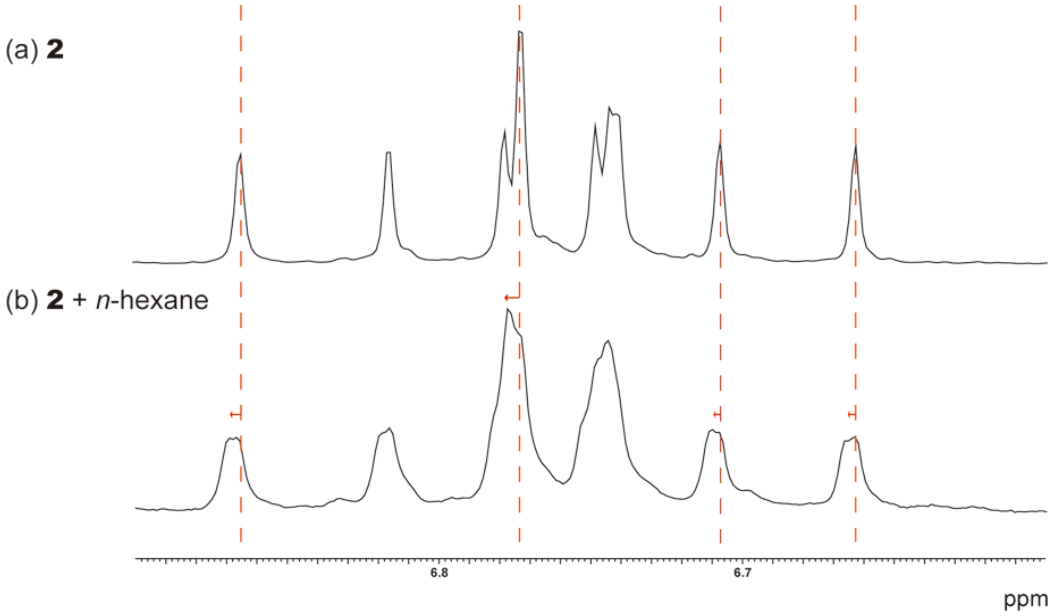

Figure S3. ^{1}H NMR spectra of (a) **2** and (b) a mixture of **2** and *n*-hexane in $CDCl_3$ at 25 ^oC; [**2**] = 2 mM, [*n*-hexane] = 20 mM. Broadening and down-field shifts of benzene proton peaks of **2** were found upon addition of *n*-hexane, indicating formation of the CH/π hydrogen bond between **2** and *n*-hexane.

2D NOESY analysis of a mixture of 2 and *n*-hexane

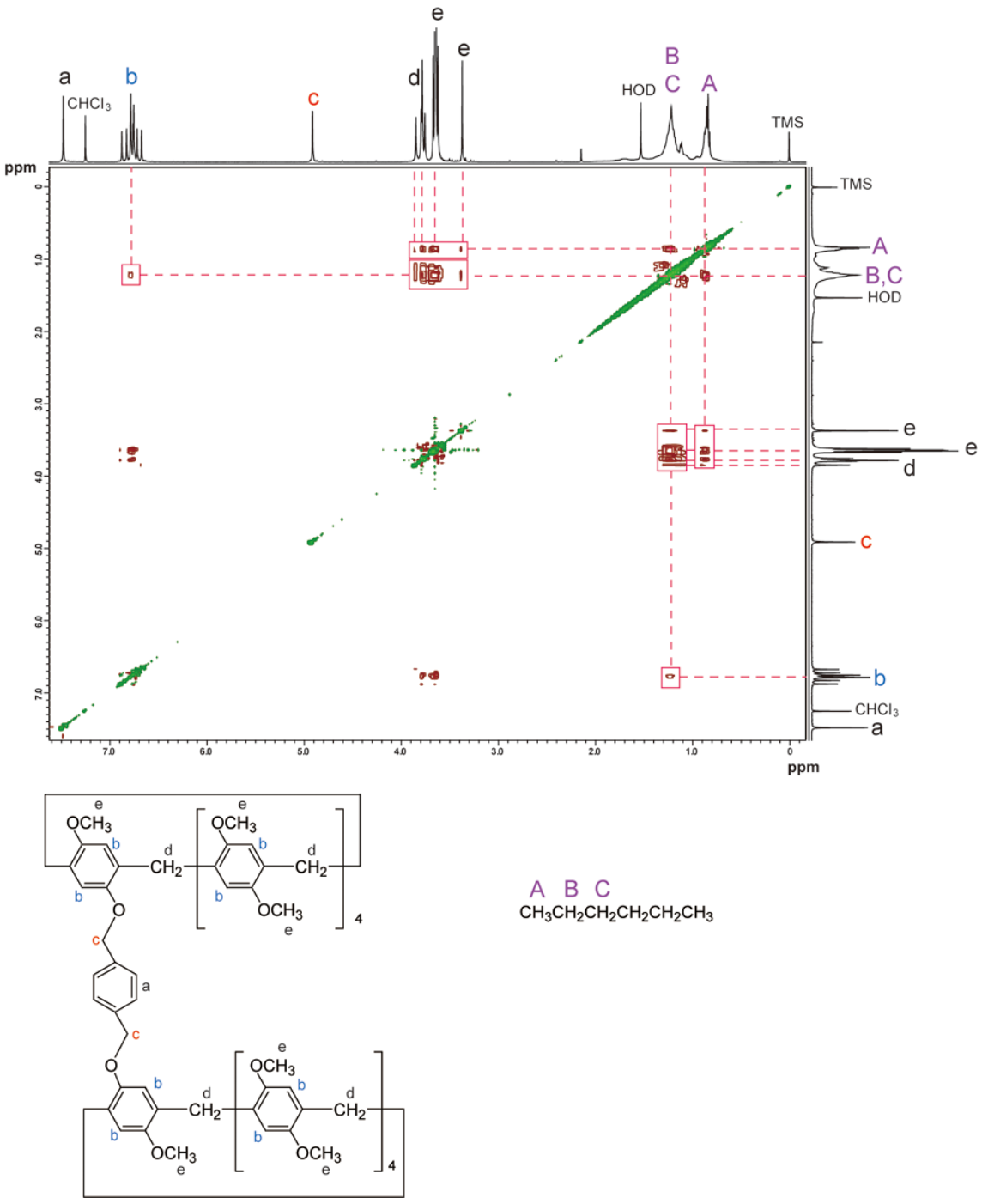

Figure S4. 2D NOESY study of a mixture of *n*-hexane (30 mM) and **2** (20 mM) in $CDCl_3$ at 25 ^{o}C; mixing time = 500 ms. NOE correlations were observed between *n*-hexane protons and protons of methylene bridge, methoxy and benzene groups of **2**, indicating that *n*-hexane was located in the pillar[5]arene cavity.

2D COSY NMR of a mixture of 2 and *n*-hexane

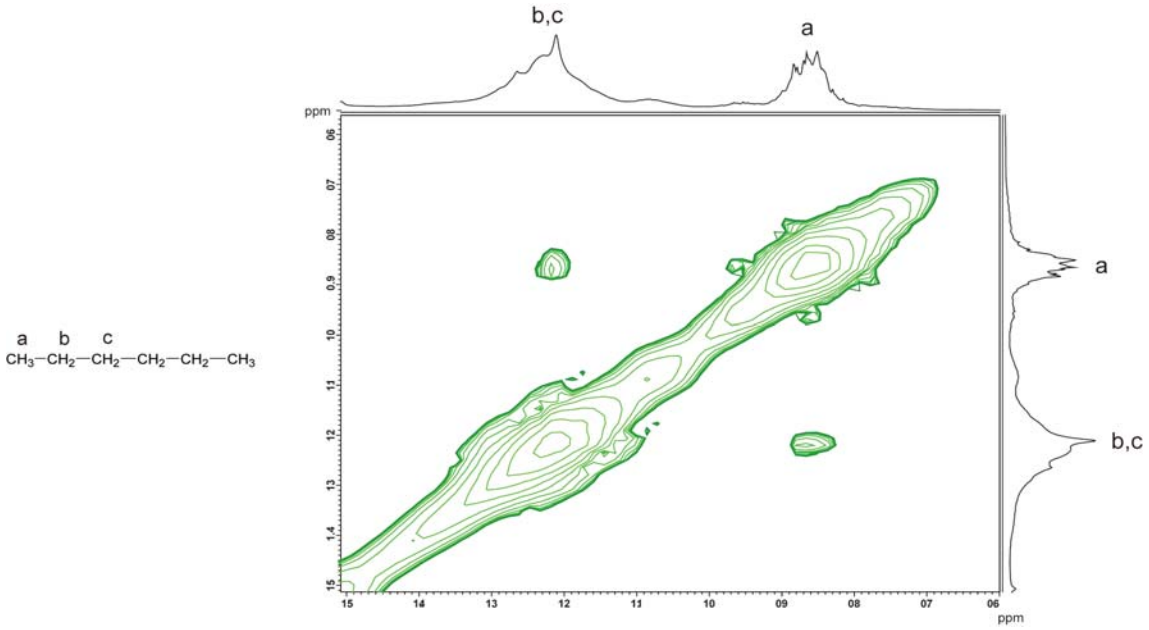

Figure S5. 2D COSY NMR of a mixture of *n*-hexane (1 mM) and **2** (25 mM) in $CDCl_3$ at 25 ^{o}C.

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Job plot for 2-*n*-hexane complex

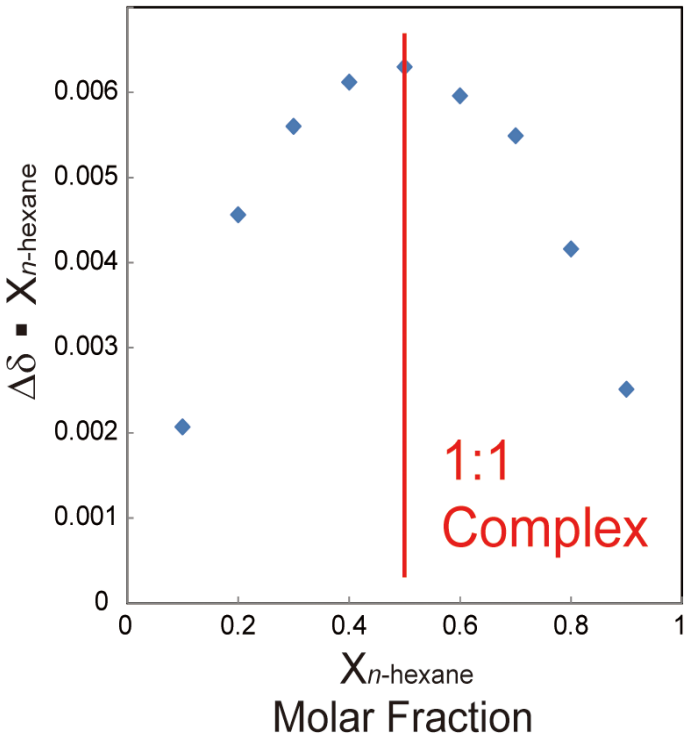

Figure S6. Job plot between pillar[5]arene dimer (host, **2**) and *n*-hexane (guest) collected by plotting Δδ in chemical shift of the methyl protons of *n*-hexane observed by ^{1}H NMR spectroscopy ($CDCl_3$) against the change in the molar fraction of the *n*-hexane ($X_{n\text{-hexane}}$); [**2**] + [*n*-hexane] = 10 mM. The plot indicates a 1:1 binding between host and guest.

Variable-concentration ^{1}H NMR spectra of a mixture of 2 and *n*-hexane

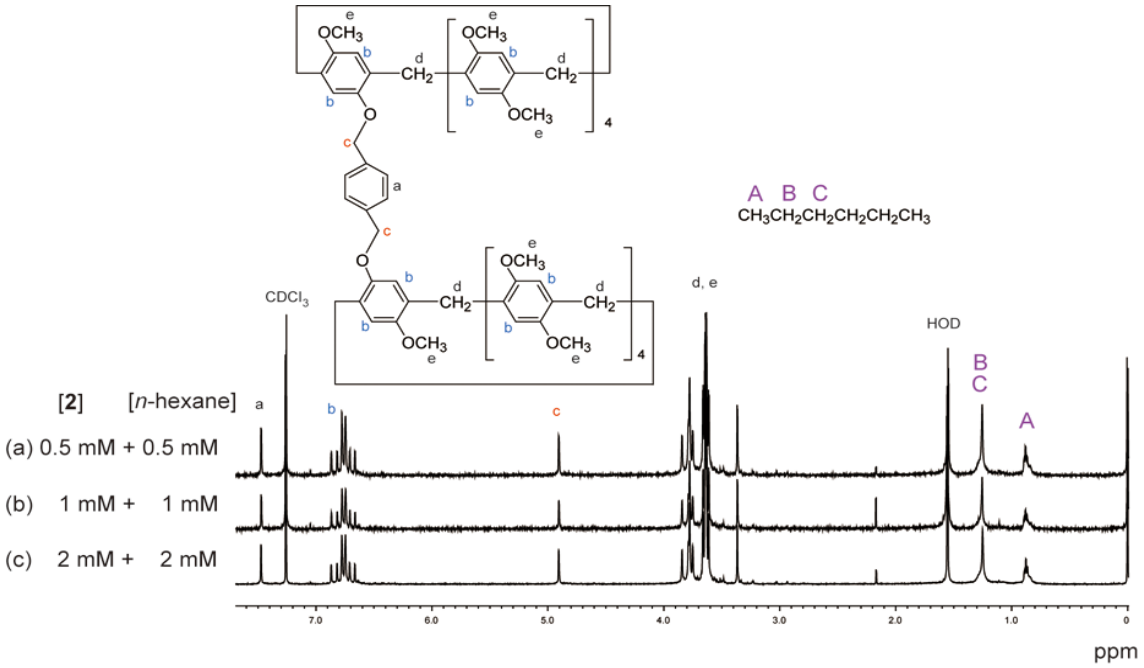

Figure S7. Variable-concentration ^{1}H NMR spectra of an equimolar mixture of *n*-hexane and **2** in $CDCl_3$ at 25 ^oC (0.5 – 2 mM). The proton peaks of **2** and *n*-hexane in $CDCl_3$ did not change in the concentration range investigated in this work, indicating that supramolecular oligomers did not form and mainly formed the 1:1 host-guest complex between **2** and *n*-hexane in the range.

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Job plot for 2-*n*-octane complex

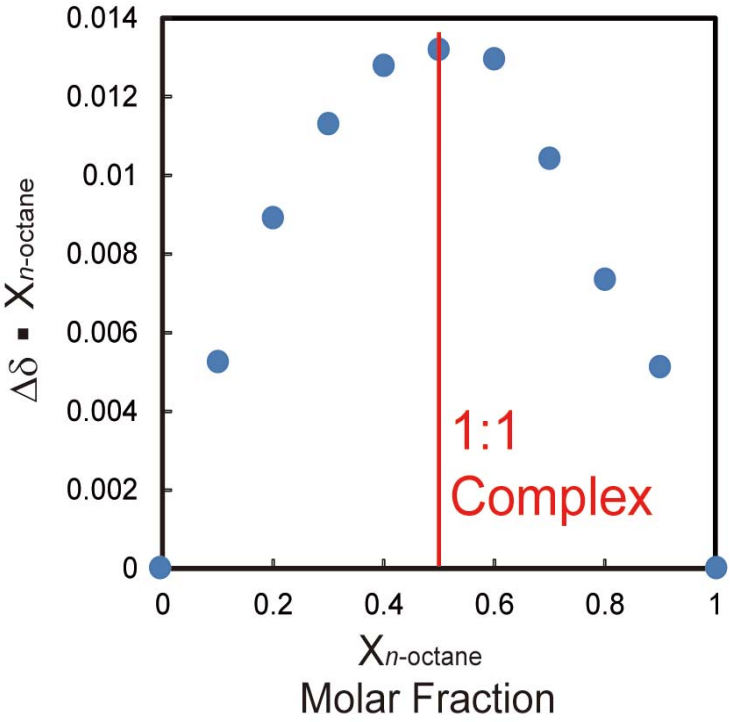

Figure S8. Job plot between pillar[5]arene dimer (host, **2**) and *n*-octane (guest) collected by plotting Δδ in chemical shift of the methylene proton of *n*-octane observed by ^{1}H NMR spectroscopy ($CDCl_3$) against the change in the molar fraction of the *n*-octane ($X_{n\text{-octane}}$); [**2**] + [*n*-octane] = 10 mM. The plot indicates a 1:1 binding between host and guest.

^{1}H NMR titration of *n*-octane with 2

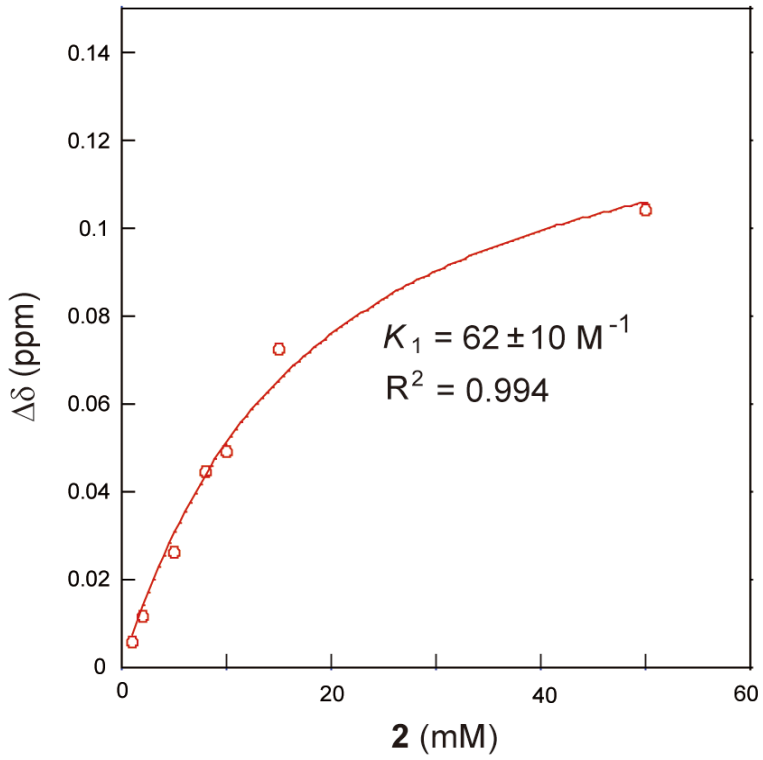

Figure S9. ^{1}H NMR titration of *n*-octane (central methylene protons) with **2** in $CDCl_3$ at 25 ^oC.