Electronic Supplementary Information

Self-organization of dipyridylcalix[4]pyrrole into a supramolecular cage for dicarboxylates

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1. Synthesis

5-methyl-5-(4-pyridyl)dipyrromethane

4-acetylpyridine (2.6 ml, 24 mmol) and pyrrole (4.5 ml, 75 mmol) were suspended in water (160 ml) and the mixture was stirred under hydrochloric acid for 1 hour at room temprature. After neutralized with sodium bicarbonate, 5-methyl-5-(4-pyridyl)dipyrromethane was precipitated and dried *in vac*. The residue was further purified by silica column chromatography (1.1 g, 19%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 3H, CH_3), 5.95 (m, 2H, pyrrole-CH), 6.18 (m, 2H, pyrrole-CH), 6.70 (m, 2H, pyrrole-CH), 7.02 (d, 2H, pyridine-CH), 7.82 (s, 2H, pyrrole-NH), 8.50 (d, 2H, pyridine-CH)
FAB-MS m/z = 238.2 ($M+H^+$)

5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole (1)

5-methyl-5-(4-pyridyl)dipyrromethane (300 mg, 1.3 mmol) was dissolved in acetone (500 ml). BF_3•OEt_2(0.5 ml, 4.1 mmol) was added to the solution and stirred for 24 h. After neutralized with triethylamine, the solution was concentrated *in vac.* and the mixture of $CHCl_3$/water was poured. The organic layer was separated, washed with water, dried i*n vac.* the residue was purified by silica column chromatography (eluent; chloroform : ethyl acetate = 1 : 2) (31 mg, 9% (Rf 0.23: *cis*), 84 mg, 24% (Rf 0.33: *trans*)) ^{1}H NMR (400 MHz, CD_3CN) δ 1.47 (s, 6H, CH_3), 1.62 (s, 12H, CH_3), 5.62 (d, 4H, pyrrole-CH), 5.84 (d, 4H, pyrrole-CH), 6.82 (d, 4H, pyridine-CH), 7.82 (s, 4H, NH), 8.38 (d, 4H, pyridine-CH). ESI-MS m/z = 555.1120 ($M+H^+$)

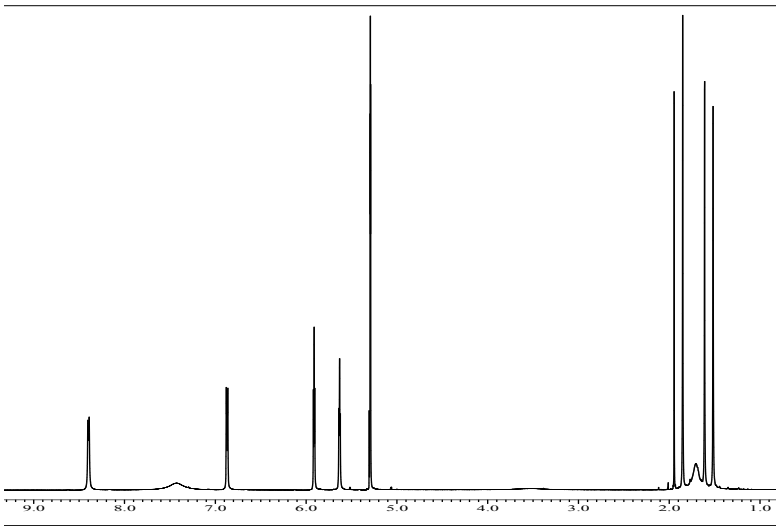


Fig.S1 ^{1}H NMR spectrum of *cis*-1 (400 MHz, CD_2Cl_2).

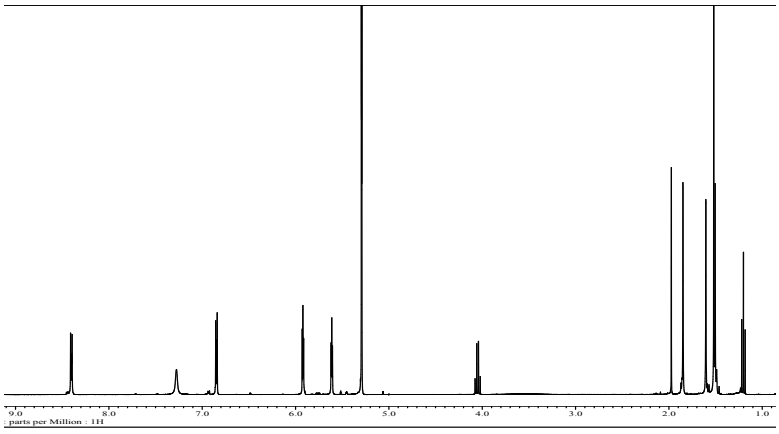


Fig.S2 ^{1}H NMR spectrum of *trans*-1 (400 MHz, CD_2Cl_2).

The cage (2) of 5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole

Cis-5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole **1** (7.2 mg, 0.013 mmol) was dissolved in CH_2Cl_2 and $Pd(II)(OTf)_2(PEt_3)_2$ (8.3 mg, 0.013 mmol) was added into the solution. The mixture was sttired at room temprature for 1 h. The solution was concentrated and dried *in vac.* ^1H NMR (400 MHz, CD_3CN) δ 1.18 (m, 36H, ethyl-CH_3), 1.49 (s, 12H, CH_3), 1.63 (s, 24H, CH_3), 1.98 (m, 24H, P-CH_2), 5.34 (d, 8H, pyrrole-CH), 5.93 (d, 8H, pyrrole-CH), 7.02 (d, 8H, pyridine-CH), 7.68 (s, 8H, NH), 8.55 (d, 4H, pyridine-CH)

ESI-MS m/z = 2393.47 ($M+H^+$)

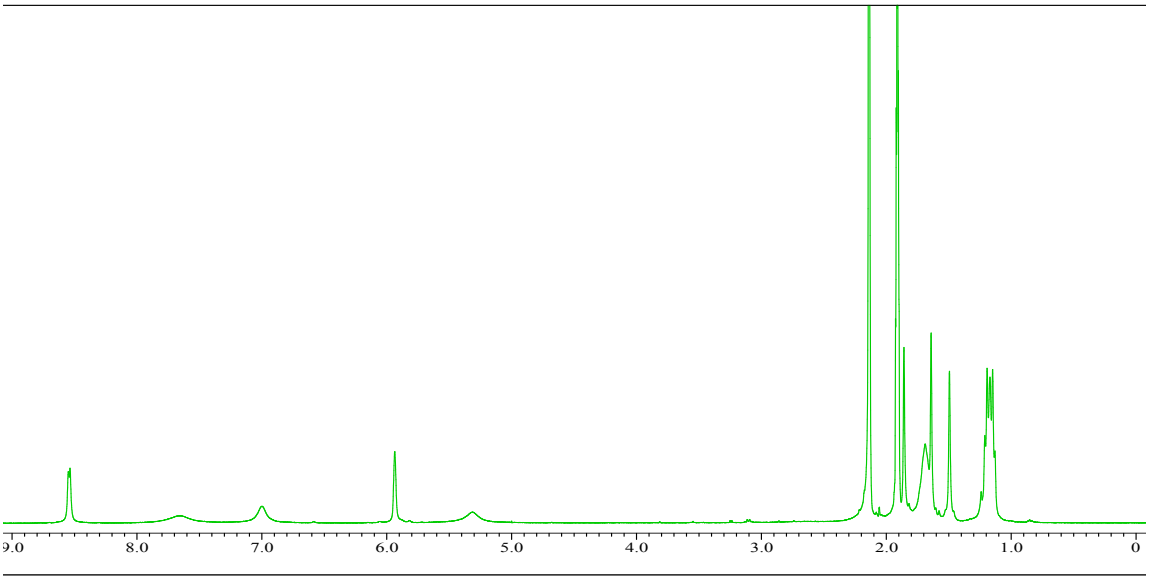


Fig.S3 ^1H NMR spectrum of cage molecule **2** (400 MHz, CD_3CN).

2. ^{1}H NMR titration experiments

The cage (**2**) of 5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole was dissolved in an NMR tube (2.0 mM, acetonitrile-d_3 (500 μl)). To the solution, aliquots of $(TBA)_2$ suberate (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.3, 1.5, 1.7, 2.0 equiv.) were added with a microsyringe, and those ^{1}H NMR spectra were observed.

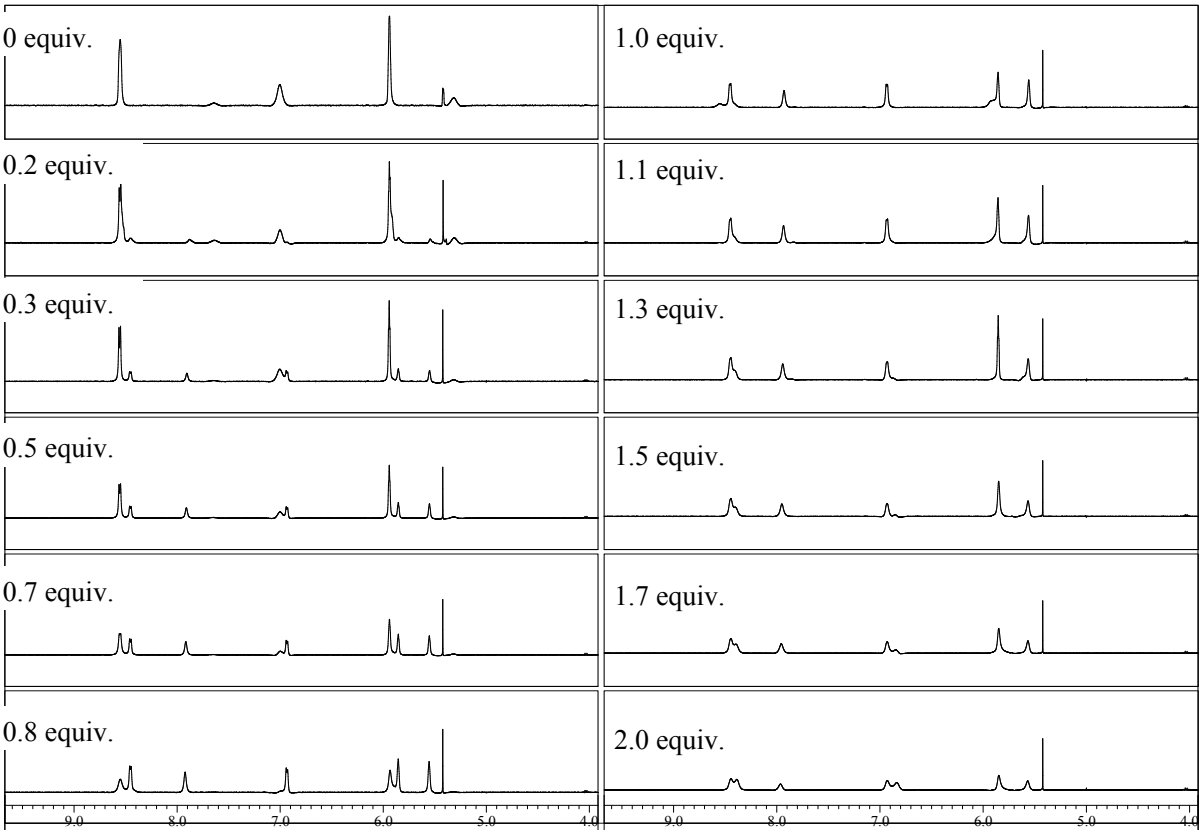


Fig. S4 ^{1}H NMR titration experiments of **2** with suberate (400 MHz, CD_3CN).

Pimelate, azelate, and acetate (TBA salts) were also added by the similar method, and ^{1}H NMR spectra of those complexes were observed.

3. Job plots

Stock solutions of the host **2** (1.0 mM) and $(TBA)_2$ azelate (1.0 mM) were prepared separately in acetonitrile-d_3. ^{1}H NMR spectrum (600 MHz) was taken for each of 10 different solutions containing a total of 500 μL of the host **2** and $(TBA)_2$ azelate in an NMR tube in the following ratios: 50:450, 100:400, 150:350, 200:300, 250:250, 300:200, 350:150, 400:100, 450:50, 500:0. At the peak of pyridine moiety, three new peaks appeared by adding azelate (Fig.S5). As three types of complex (complex A, complex B, complex C) were considered, Job plots were constructed from the integration ratio of the each complex peak. Job plots were plotted as [complex A] against mole fraction of host, [complex B] against mole fraction of host, [complex C] against mole fraction of host, and [total complex] against mole fraction of host. From the results of Job plot, 2: 1 (host: guest) component (A), 1: 1 (host: guest) component (B), and 1: 3 (host: guest) component (C) have been suggested (Fig.S6). Since Job's plot from total complex gave a peak at 0.7, we concluded that 2: 1 component (A) mainly existed in case of azelate.

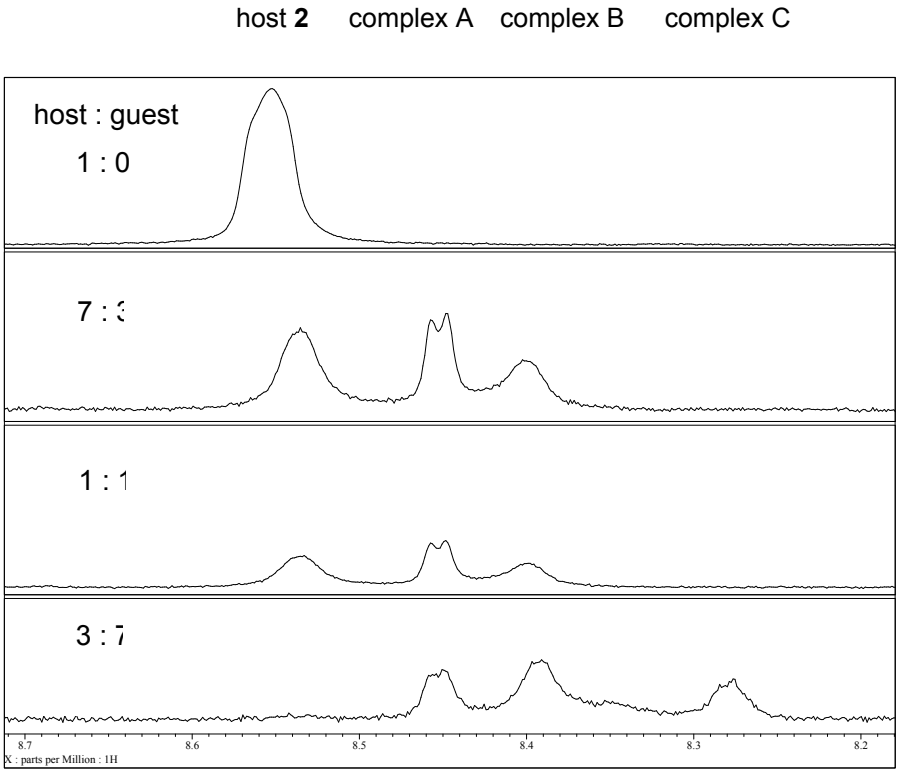


Fig. S5 ^{1}H NMR spectra of the pyridine moiety of host **2** with azelate (600MHz, CD_3CN).

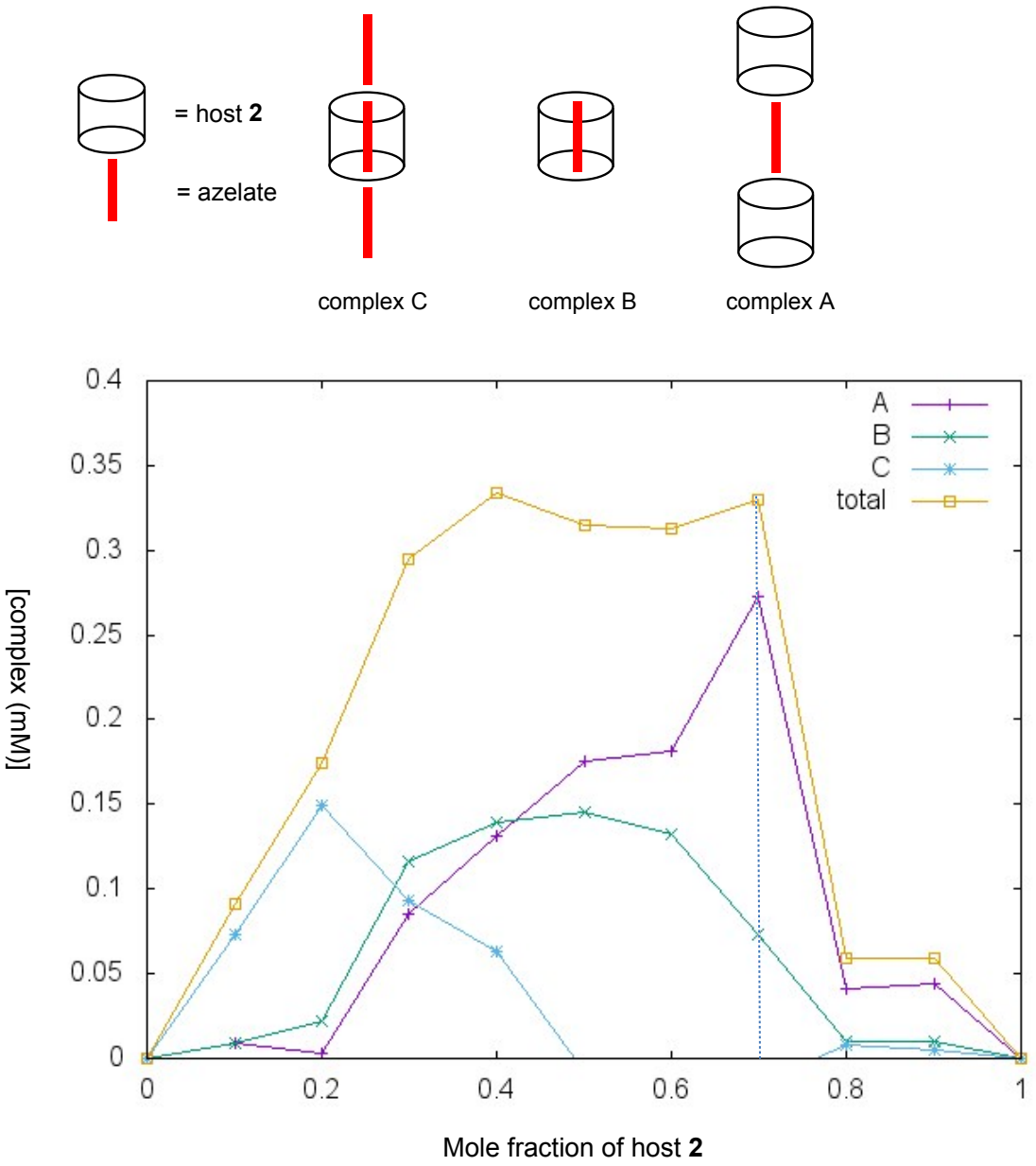


Fig. S6 Job plot and the suggested complexes for the interaction between host **2** and azelate in CD_3CN. The peak value at 0.7 shows 2:1 (host:guest) binding stoichiometry.

Job plot of host **2** and suberate was also checked in the same method. Similar three new peaks appeared by adding $(TBA)_2$ suberate (Fig.S7). Compared to azelate, Job plot of suberate showed a larger 1: 1 component (B) and a smaller 2: 1 component (A) than that of azelate. Job plot of the total complex gave a peak at 0.5 (Fig.S8). We concluded that suberate was mainly bound to the inside host by 1: 1 (host: guest) stoichiometry. The binding seemed to be stronger than azelate because the peak of free host almost disappeared at 1 equivalent of suberate. When the guest is greater than 1 equivalent, we found that the peak of complex B gradually shifted to upfield and gave the similar peak of complex C (1: 3 component). It seemed to occur a fast exchange of equilibrium between complex B and complex C because of the hydrogen bonds of extra suberate to NH protons of two calixpyrroles of host **2** from outside.

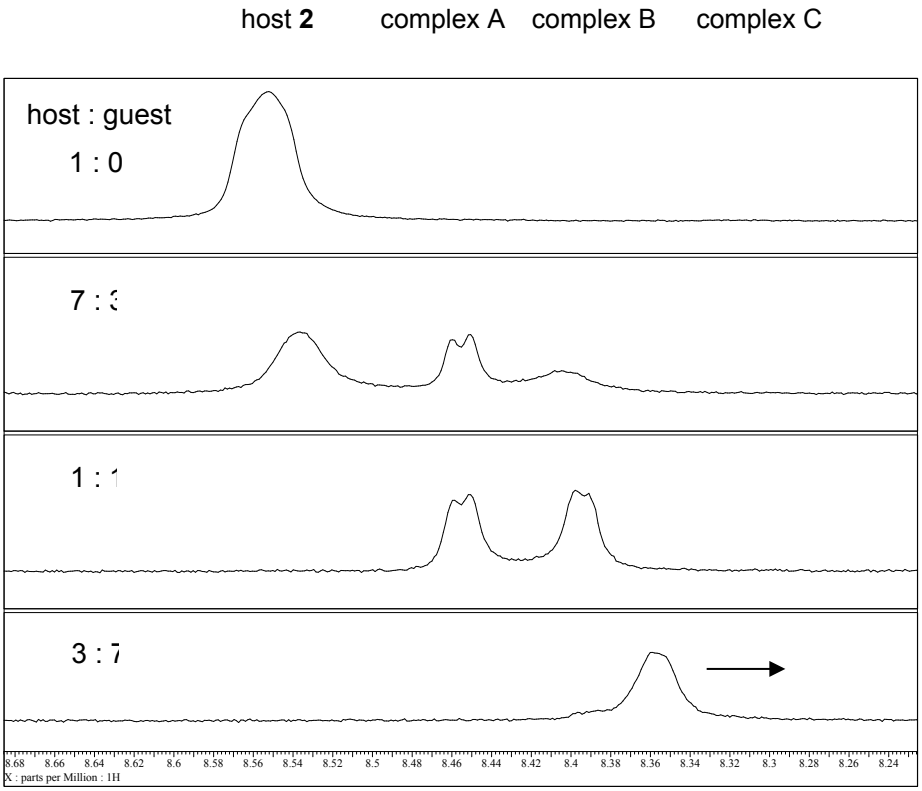


Fig. S7 ^{1}H NMR spectra of the pyridine moiety of host **2** with suberate (600MHz, CD_3CN).

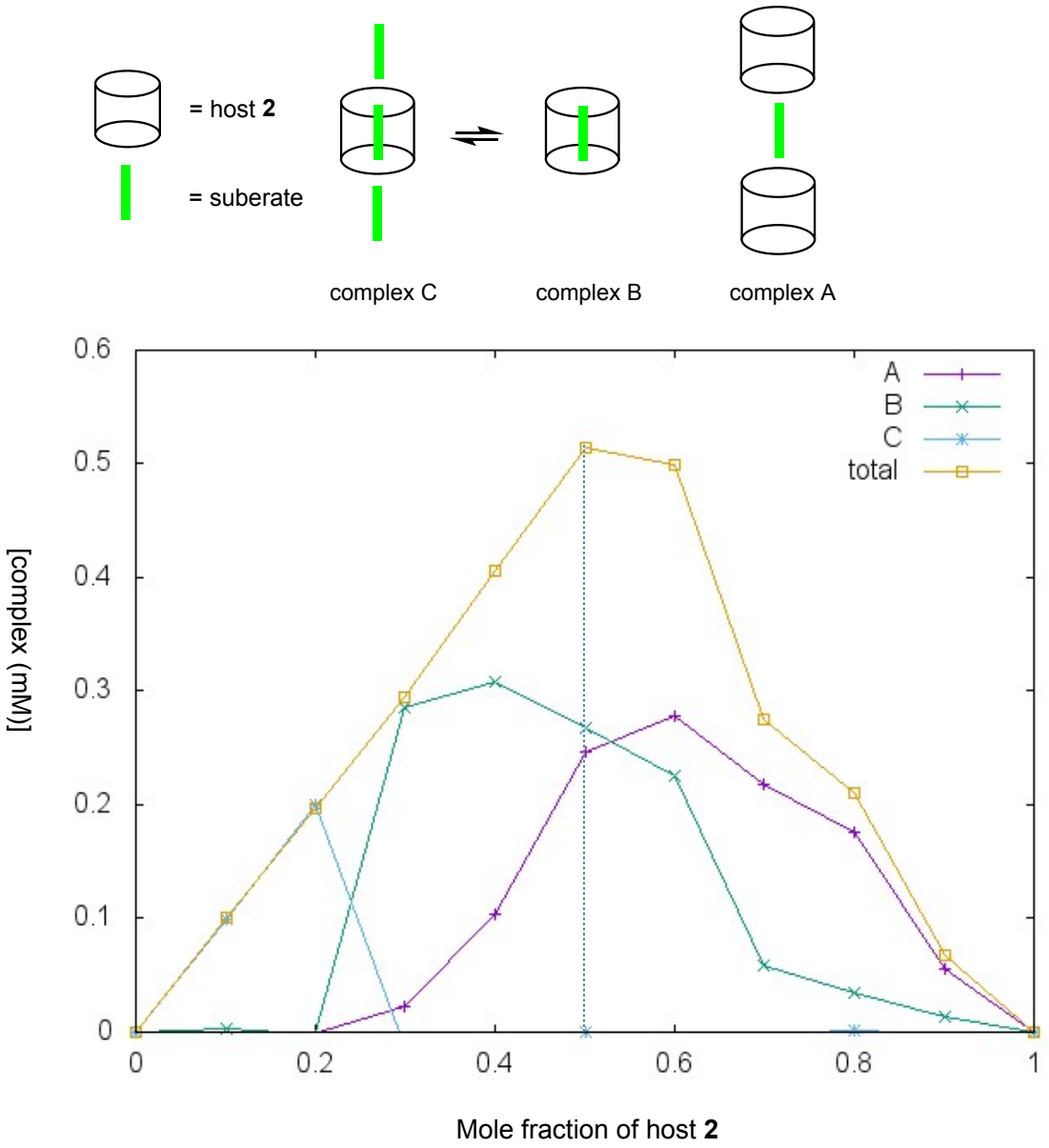


Fig. S8 Job plot and the suggested complexes for the interaction between host **2** and suberate in CD_3CN. The peak value at 0.5 shows 1:1 (host:guest) binding stoichiometry.

4. Electron spray ionization (ESI) mass spectra

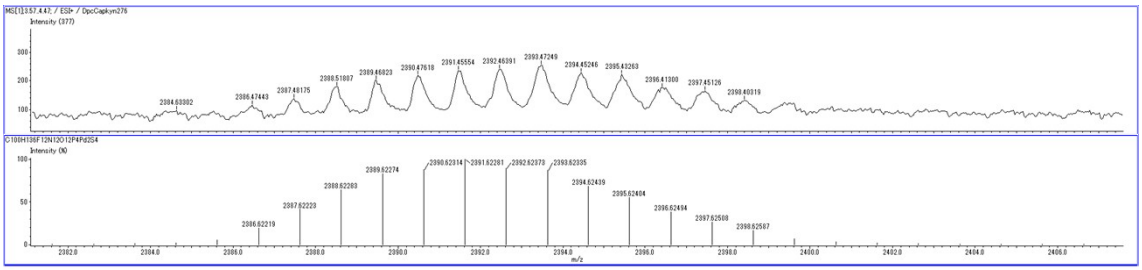


Fig. S9 ESI mass spectrum of cage 2 (up: obtained, down: calculated isotope pattern).

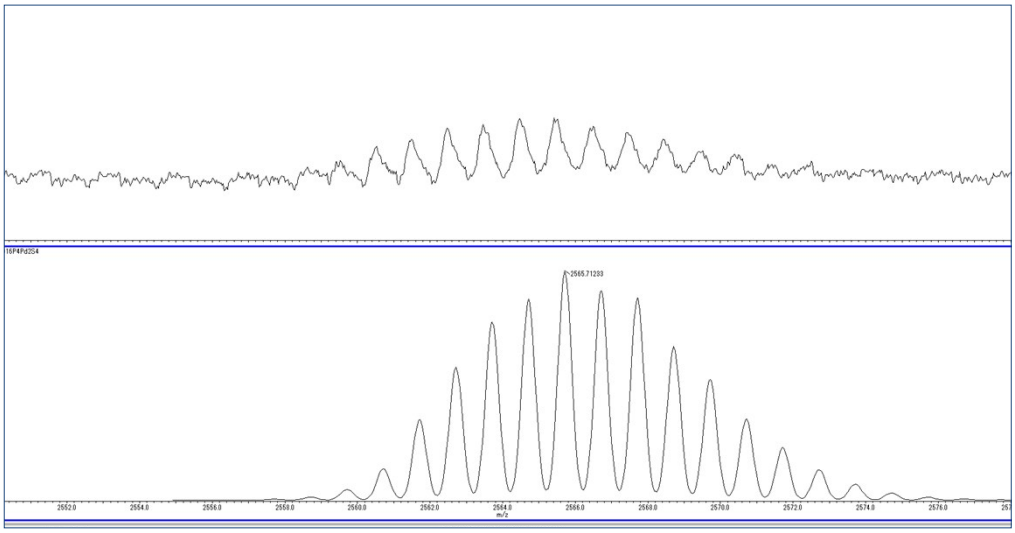
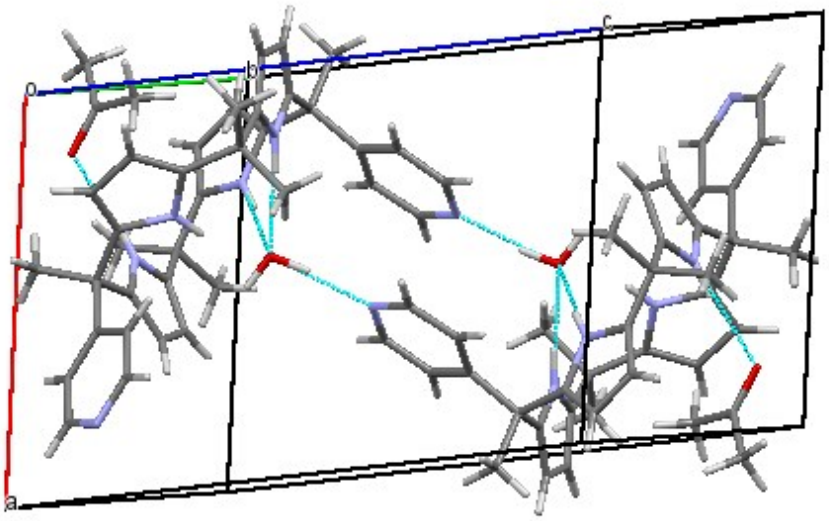


Fig. S10 ESI mass spectrum of cage **2** with suberate (up: obtained, down: calculated isotope pattern).

5. X-ray crystal structure analysis

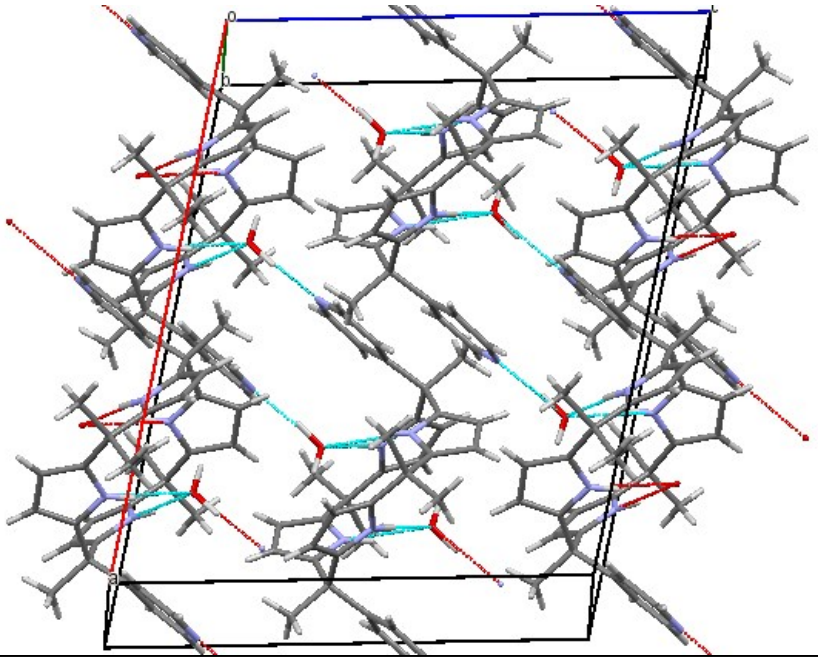
cis-5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole



Crystal data	
Chemical formula	$C_{39}H_{46}N_6O_2$
M_r	630.82
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	297
a, *b*, *c* (Å)	9.931 (3), 10.822 (3), 16.924 (5)
α, β, γ (°)	95.265 (5), 98.127 (4), 92.686 (5)
V (Å^3)	1789.7 (8)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.30 × 0.10 × 0.05
Data collection	
Absorption correction	Numerical

T_{min}, T_{max}	0.914, 0.971
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14840, 8100, 3528
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.207, 0.89
No. of reflections	8100
No. of parameters	432
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.30, -0.18

***trans*-5,15-dipyridyl-5',10,10',15',20,20'-hexamethylcalix[4]pyrrole**



Crystal data	
Chemical formula	$C_{36}H_{40}N_6O$
M_r	572.74
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	17.908 (10), 12.767 (7), 14.894 (8)
β (°)	102.821 (10)
V (Å^3)	3321 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.20 × 0.20 × 0.20
Data collection	
Absorption correction	Multi-scan

T_{min}, T_{max}	0.715, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13208, 3799, 2158
R_{int}	0.058
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.086, 0.234, 1.13
No. of reflections	3799
No. of parameters	208
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.17, -0.18