Electric Supplementary Information (ESI)

Supramolecular Polymers with Alternating Pillar[5]arene and Pillar[6]arene Units from Highly Selective Multiple Host-Guest Complexation System and Monofunctionalized Pillar[6]arene

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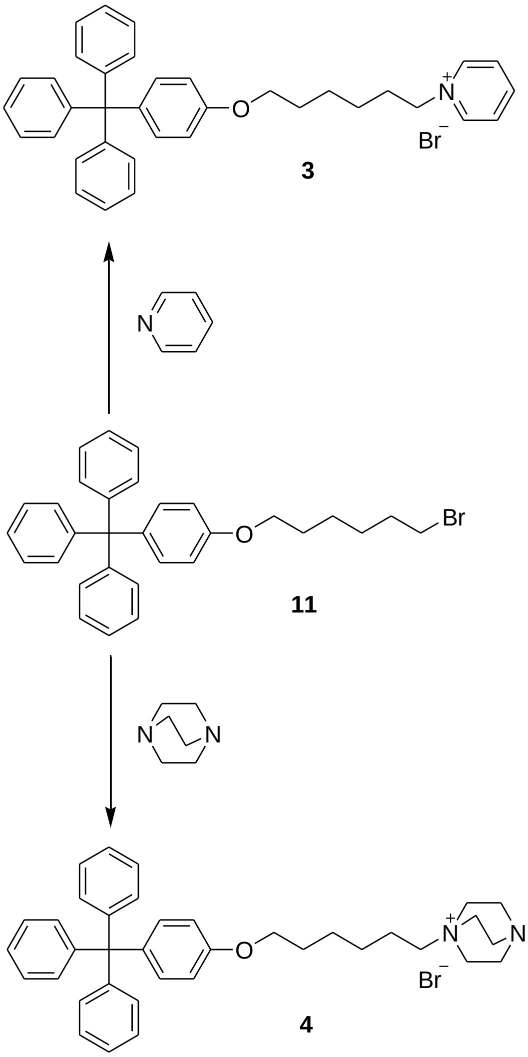
Experimental Section

Determination of association constants. ^{1}H NMR titrations were done with solutions which had a constant concentration of guest (1 mM) and varying concentrations of host. By the non-linear curve-fitting methods, the association constants for **1-3**, **1-4**, and **2-4** complexes in $CDCl_3$ were determined to be $1350 \pm 75\ M^{-1}$, $90.3 \pm 11\ M^{-1}$ and $552 \pm 65\ M^{-1}$, respectively, for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:[S1]

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

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

Model Compounds



3. To a solution of pyridine (10 mL), **11**[S2] (200 mg, 0.401 mmol) was added. The mixture was heated at 80 °C for 12h under nitrogen. The resulting solution was concentrated under *vacuo*. The residue was poured into diethyl ether and the precipitate was collected by filtration (light pink solid, **3**, 223 mg, 0.386 mmol, Yield: 96%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.44 (d, J = 6.3 Hz, 2H, pyridyl), 8.38 (t, J = 7.7 Hz, 1H, pyridyl), 8.01 (t, J = 6.5 Hz, 2H, pyridyl), 7.15-7.26 (m, 15 H, phenyl), 7.10 (d, J = 6.9 Hz, 2H, phenyl), 6.73 (d, J = 6.9 Hz, 2H, phenyl), 5.06 (t, J = 7.5 Hz, 2H, methylene), 3.90 (t, J = 5.7 Hz, 2H, methylene), 2.09 (m, 2H, methylene), 1.76 (m, 2H, methylene), 1.54 (m, 2H, methylene), 1.48 (m, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 156.9, 147.1, 145.1, 139.0, 132.2, 131.1, 128.4, 127.5, 125.9, 113.3 (C of phenyl and pyridyl), 67.4 (C of methylene), 64.3 (sp3 carbon of triryl), 61.9, 31.8, 28.9, 25.7, 25.6 (C of methylene). LRFABMS: *m*/*z* Calcd for $C_{36}H_{36}NO$ [M−Br]$^+$: 498.2797, found 498. HRFABMS: *m*/*z* Calcd for $C_{36}H_{36}NO$ [M−Br]$^+$: 498.2797, found 498.2796. Melting point (T_m): 193 °C.

4. To a solution of **11** (303 mg, 0.608 mmol) in acetone (20 mL), 1,4-dizazbicyclo[2.2.2]octane (DABCO, 0.670 g, 2.74 mmol) was added. The mixture was refluxed for 12h under nitrogen. The resulting solution was concentrated under *vacuo*. The residue was poured into diethyl ether and the precipitate was collected by filtration (white solid, **4**, 361 mg, 0.591 mmol, Yield: 97%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.15-7.29 (m, 15 H, phenyl), 7.10 (d, J = 8.6 Hz, 2H, phenyl), 6.75 (d, J = 8.0 Hz, 2H, phenyl), 3.93 (t, J = 6.0 Hz, 2H, methylene), 3.66 (t, J = 7.4 Hz, 6H, DABCO), 3.60 (t, J = 8.3 Hz, 2H, methylene), 3.25 (t, J = 8.3 Hz, 6H, DABCO), 1.78 (m, 4H, methylene), 1.44-1.60 (m, 4H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 156.9, 147.0, 139.0, 132.2, 131.1, 127.4, 125.8, 113.2 (C of phenyl), 67.4, 64.4 (C of methylene), 64.3 (sp3 carbon of triryl), 52.5, 45.4 (C of DABCO), 29.1, 26.2, 25.8, 22.1 (C of methylene). LRFABMS: *m*/*z* Calcd for $C_{37}H_{43}N_2O$ [M−Br]$^+$: 531.3375, found 531. HRFABMS: *m*/*z* Calcd for $C_{37}H_{43}N_2O$ [M−Br]$^+$: 531.3375, found 531.3376. Melting point (T_m): 217 °C.

8. Monofunctionalized pillar[5]arene **8** can be prepared by two different approaches. **8** was already prepared by co-cyclization approach.[S3] In this study, we synthesized **8** from mono-deprotected pillar[5]arene **7**. Under a nitrogen atmosphere **7** (434 mg, 0.589 mmol) was dissolved in acetone (5 mL). Potassium carbonate (162 mg, 1.17 mmol) was added and the reaction mixture was stirred. Then, 1,6-dibromohexane (719 mg, 2.95 mmol) was added and the reaction mixture was refluxed for 48h. After filtration, the filtrate was evaporated to give a solid. Column chromatography (silica gel; ethyl acetate: hexane = 1 : 6) afforded a white solid (**8**, 296 mg, 0.330 mmol, 56%).

5. To a solution of **8** (200 mg, 0.224 mmol) in acetone (20 mL), DABCO (124 mg, 1.11 mmol) was added. The mixture was refluxed for 12h under nitrogen. The resulting solution was concentrated under *vacuo*. The residue was poured into diethyl ether and the precipitate was collected by filtration (light pink solid, **5**, 143 mg, 0.141 mmol, Yield: 63%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.83-6.88 (m, 10H, phenyl), 3.90 (t, 2H, J = 6.3 Hz, methylene), 3.65-3.76 (m, 43 H, methyl, methylene bridge and DABCO), 3.54 (m, 2H, methylene), 3.25 (t, J = 7.5 Hz, 6H, DABCO), 1.85-1.93 (m, 4H, methylene), 1.68 (m, 2H, methylene), 1.51 (m, 2H, methylene). ^{13}C NMR (acetone-*d*$_6$, 125 MHz, ppm): δ 151.1, 150.8, 150.4, 150.0, 128.7, 128.6, 128.3, 115.3, 115.0, 114.8, 114.6, 114.3, 114.0 (C of phenyl), 67.6, 64.1 (C of methylene), 58.9, 56.6, 56.5, 56.3, 56.1, 55.9, 55.9, 55.7 (C of methyl), 52.3, 45.4 (C of DABCO), 30.2, 29.7, 29.5, 29.4 (C of methylene bridge), 28.9, 25.8, 25.1, 21.0 (C of methylene). LRFABMS: *m*/*z* Calcd for $C_{56}H_{71}N_2O_{10}$ $[M{-}Br]^+$: 931.5109, found 931. HRFABMS: *m*/*z* Calcd for $C_{56}H_{71}N_2O_{10}$ $[M{-}Br]^+$: 931.5109, found 931.5107. Melting point (T_m): 111 ^{o}C.

9. To a solution of **2** (500 g, 0.468 mmol) in anhydrous dichloromethane (50 mL), boron tribromide (0.0395 mL, 0.421 mmol) was added. The mixture was stirred at 25 ^{o}C for 1 min under nitrogen. Then, water was added into the mixture. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated. Column chromatography (silica gel; hexane : ethyl acetate = 4 : 1) afforded a white solid (**9**, 224 mg, 0.215 mmol, Yield: 46%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.80 (s, 1H, phenyl), 6.75 (s, 1H, phenol), 6.74 (s, 1H, phenyl), 6.72 (s, 1H, phenyl), 6.67 (s, 1H, phenyl), 6.65 (s, 1H, phenyl), 6.64 (s, 2H, phenyl), 6.63 (s, 2H, phenyl), 6.61 (s, 1H, phenyl), 6.56 (s, 2H, phenyl), 3.69-4.01 (m, 34H, methylene adjacent to O atom and methylene bridge), 1.17-1.42 (m, 33H, methyl). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.3, 150.5, 150.4, 150.3, 148.1, 147.8, 130.1, 129.3, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.3, 126.5, 124.4, 118.6, 115.4, 115.3, 115.1, 115.0, 114.8, 114.4, 114.1 (C of phenyl), 64.8, 64.2, 64.1, 64.0, 63.8 (C of methylene adjacent O atom), 31.3, 31.0, 30.7, 30.4, 30.3, 29.6 (C of methylene bridge), 15.1, 15.0, 14.9, 14.6 (C of methyl). LRFABMS: *m*/*z* Calcd for $C_{64}H_{80}O_{12}$ $[M]^+$: 1040.5650, found 1040. HRFABMS: *m*/*z* Calcd for $C_{64}H_{80}O_{12}$ $[M]^+$: 1040.5650, found 1040.5666. Melting point (T_m): 75 ^{o}C.

6. Under a nitrogen atmosphere **9** (100 mg, 0.0959 mmol) was dissolved in acetone (1 mL). Potassium carbonate (394 mg, 2.90 mmol) was added and the reaction mixture was stirred. Then, 1,6-dibromohexane (0.234 mg, 0.959 mmol) was added and the reaction mixture was refluxed for 24h. After filtration, the filtrate was evaporated to give a solid. Column chromatography (silica gel; ethyl acetate: hexane = 1 : 6) afforded a white solid (**10**, 81.0 mg, 0.0673 mmol, Yield: 54%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.62-6.71 (s, 12H, phenyl), 3.78-3.82 (m, 34H, methylene adjacent to O atom and methylene bridge), 3.30 (t, 2H, J = 6.6 Hz, methylene adjacent to O atom), 1.76 (br, 2H, methylene), 1.66 (br, 2H, methylene), 1.36 (br, 4H, methylene), 1.25-1.30 (m, 33H, methyl). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.5, 150.4, 150.3, 127.9, 127.8, 115.4, 115.3, 115.2, 115.0 (C of phenyl), 68.2 (C of methylene linker), 64.0 (C of methylene adjacent to O atom), 33.8, 32.6 (C of methylene), 31.2, 31.0, 30.9, 30.8, 30.7 (C of methylene bridge) 29.4, 27.9, 25.3 (C of methylene), 15.2 (C of methyl). To a solution of pyridine (10 mL), **10** (100 mg, 0.0829 mmol) was added. The mixture was heated at 80 ^{o}C for 24h under nitrogen. The resulting solution was concentrated under *vacuo* (light brown solid, **6**, 72.0 mg, 0.0561 mmol, Yield: 68%). ^{1}H NMR (acetone-d_6, 500 MHz, ppm): δ 7.37 (br, 1H, pyridyl), 6.56-7.07 (m, 14H, pyridyl and phenyl), 6.35 (br, 2H, pyridyl), 3.59-4.10 (m, 34H, methylene adjacent to O atom and methylene bridge), 2.95 (br, 2H, methylene), 1.75 (br, 2H, methylene), 1.56 (br, 2H, methylene), 1.22-1.46 (m, 35H, methylene and methyl), 0.86 (br, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.0, 150.7, 150.5, 150.3, 150.2, 150.0, 144.3, 142.7, 129.2, 129.1, 129.0, 127.7, 127.0, 126.9, 117.2, 116.9, 116.2, 116.1, 115.9, 115.7, 114.3, 113.8 (C of phenyl and pyridyl), 65.5, 65.1, 64.8, 64.5, 64.1, 63.8 (C of methylene adjacent to O atom), 58.6 (C of methylene adjacent to N atom), 32.5 (C of methylene bridge), 31.9 (C of methylene), 30.6, 30.2, 29.8, 29.7, 29.1 (C of methylene bridge), 27.5, 22.6, 21.5 (C of methylene), 15.3 (C of methyl). LRFABMS: *m*/*z* Calcd for $C_{75}H_{96}NO_{12}$ $[M{-}Br]^{+}$: 1202.6933, found 1202. HRFABMS: *m*/*z* Calcd for $C_{75}H_{96}NO_{12}$ $[M{-}Br]^{+}$: 1202.6933, found 1202.6925. Melting point (T_m): 109 ^{o}C.

^{1}H and ^{13}C NMR spectra of 3

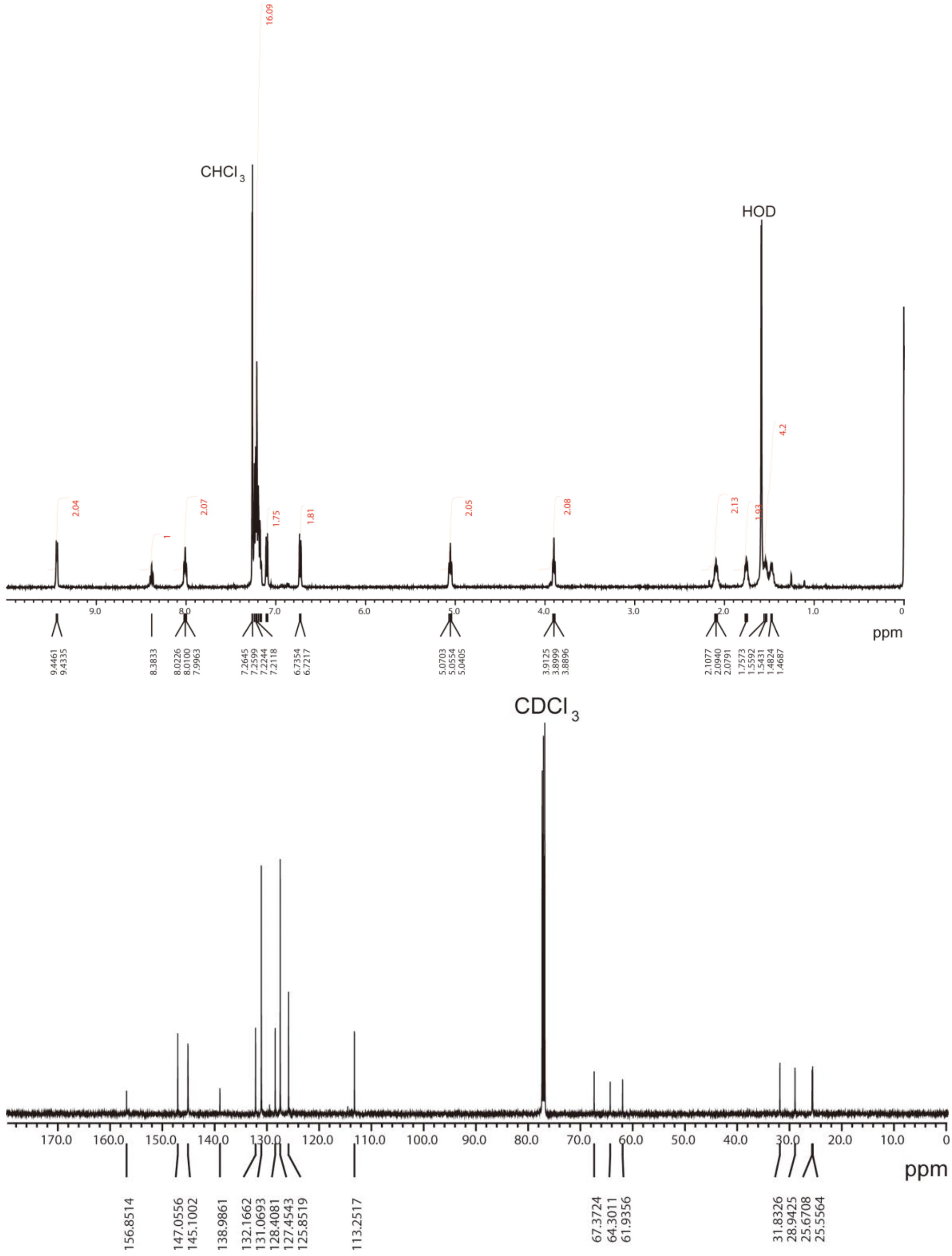


Fig. S1 ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of 4

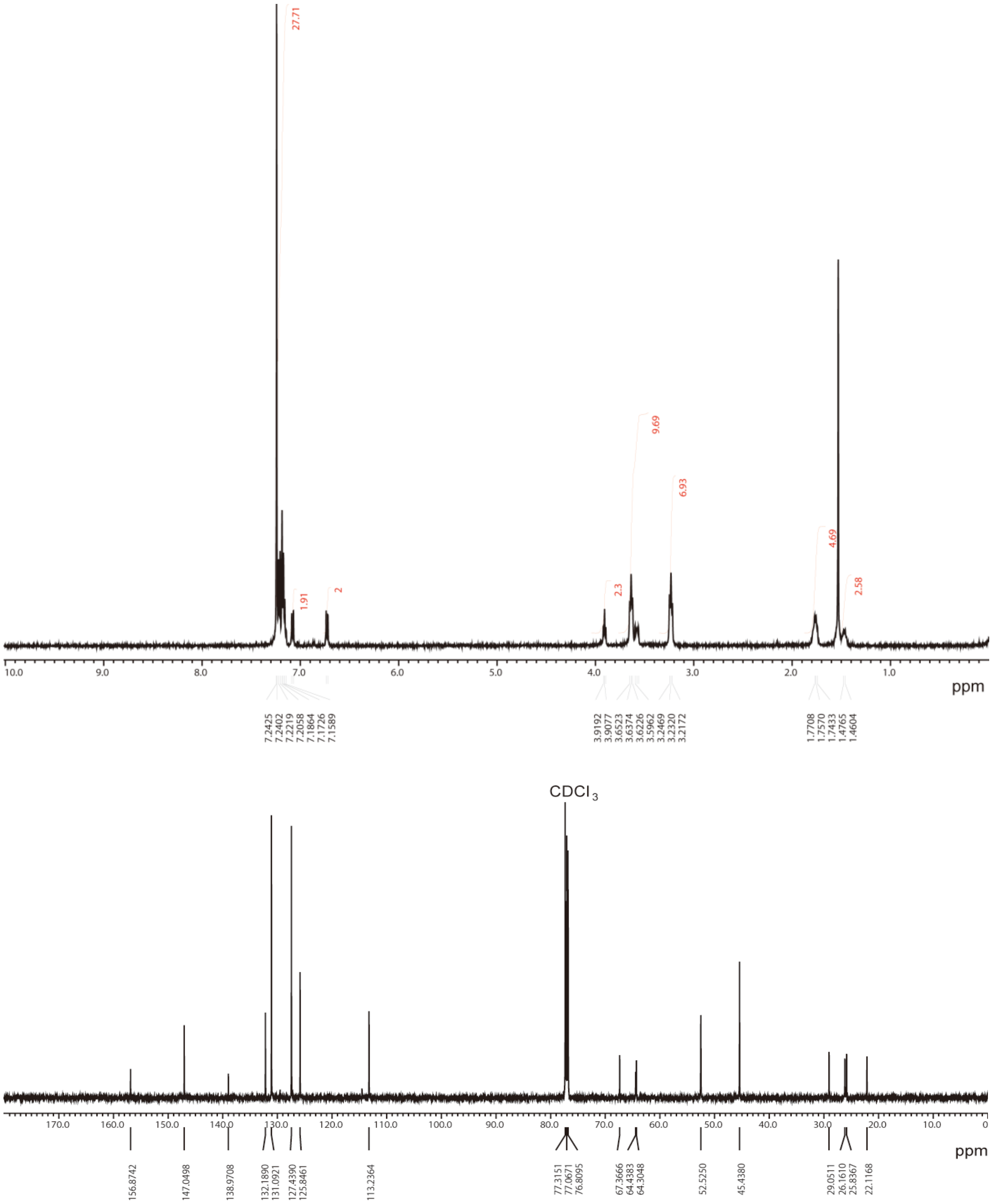


Fig. S2 ^{1}H and ^{13}C NMR spectra of **4** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of 5

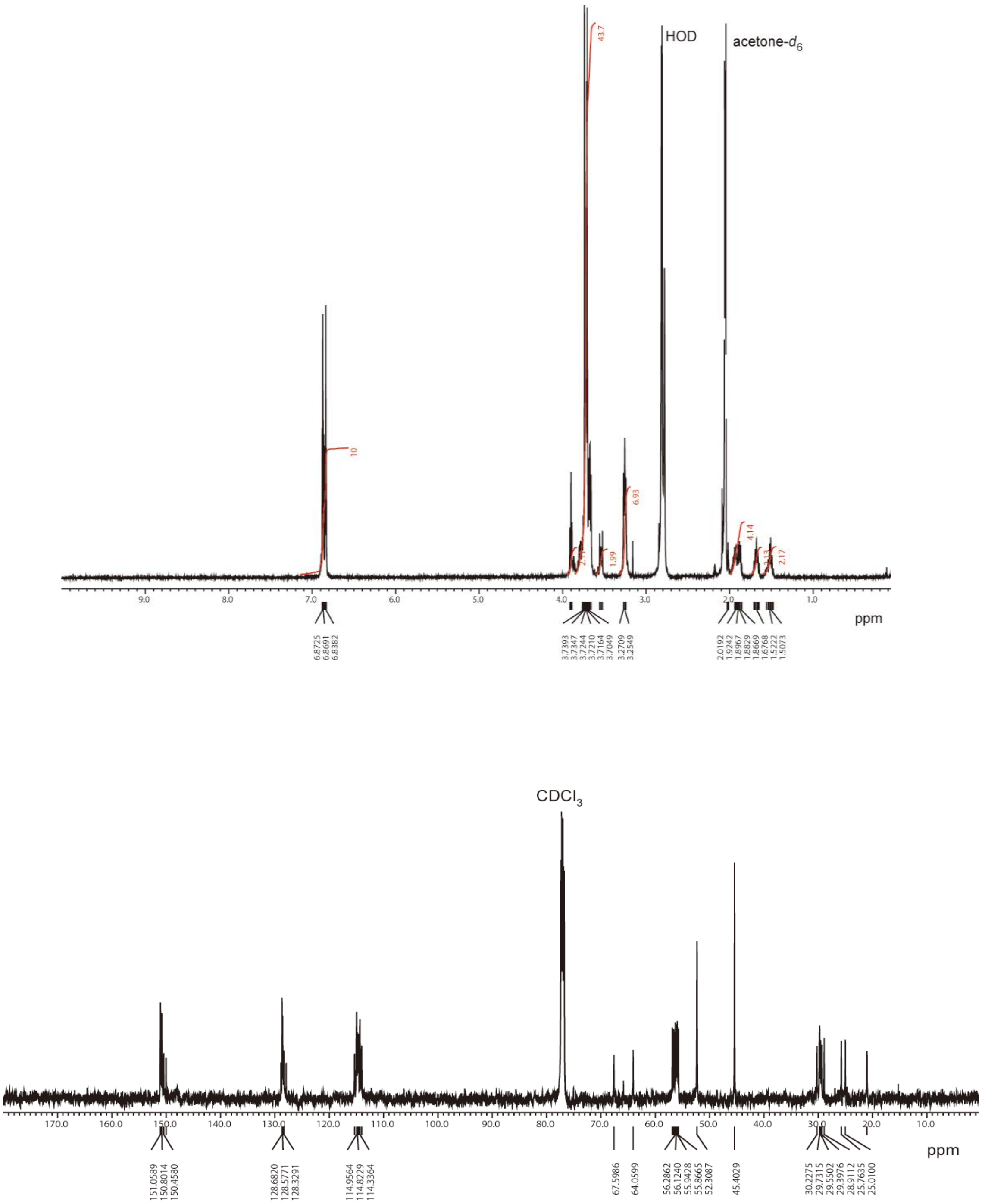


Fig. S3 ^{1}H NMR spectrum of **5** in acetone-d_6 and ^{13}C NMR spectrum of **5** in CDCl$_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of 9

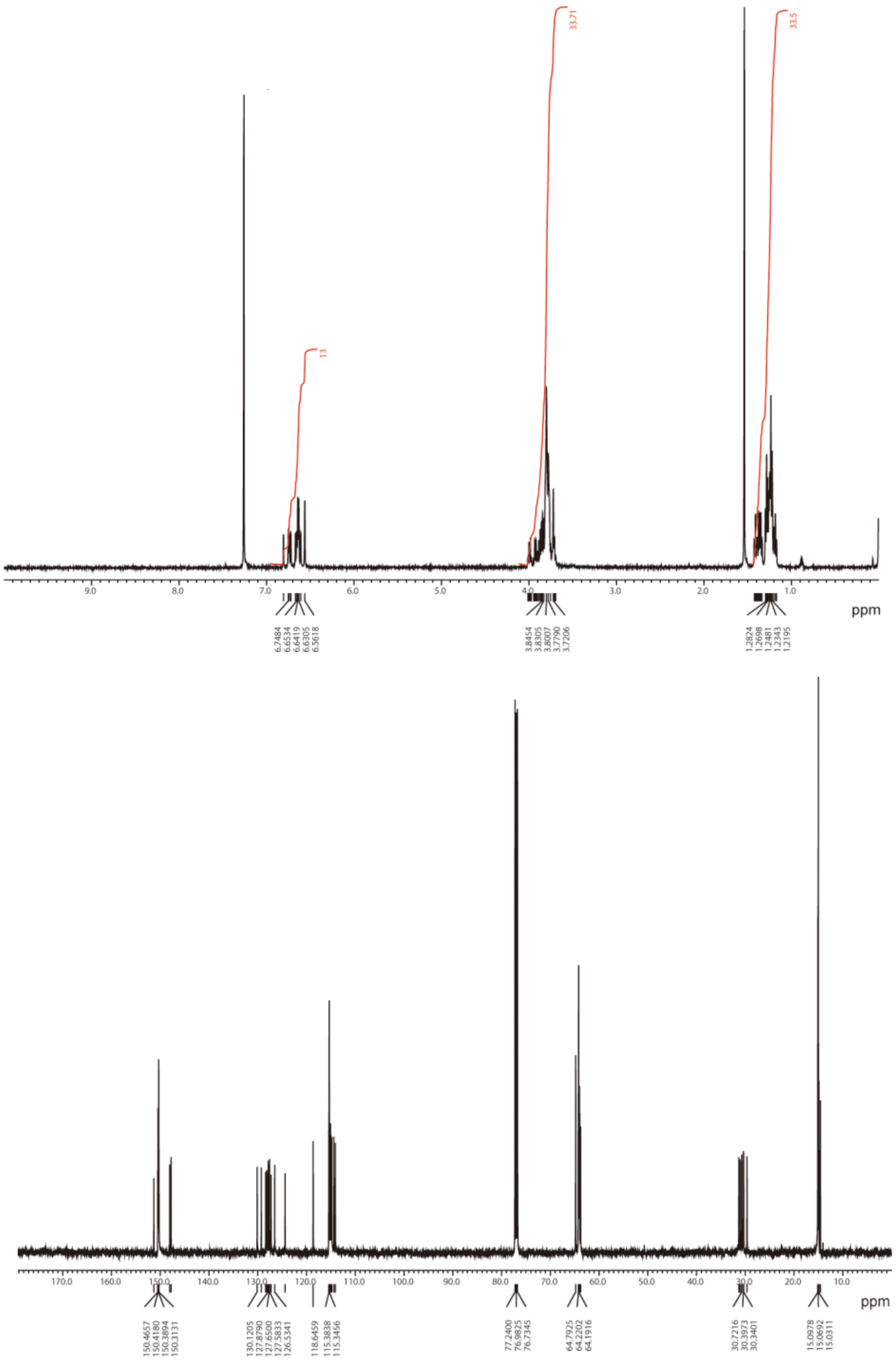


Fig. S4 ^{1}H and ^{13}C NMR spectra of **9** in $CDCl_3$ at 25 ^oC

^{1}H and ^{13}C NMR spectra of 10

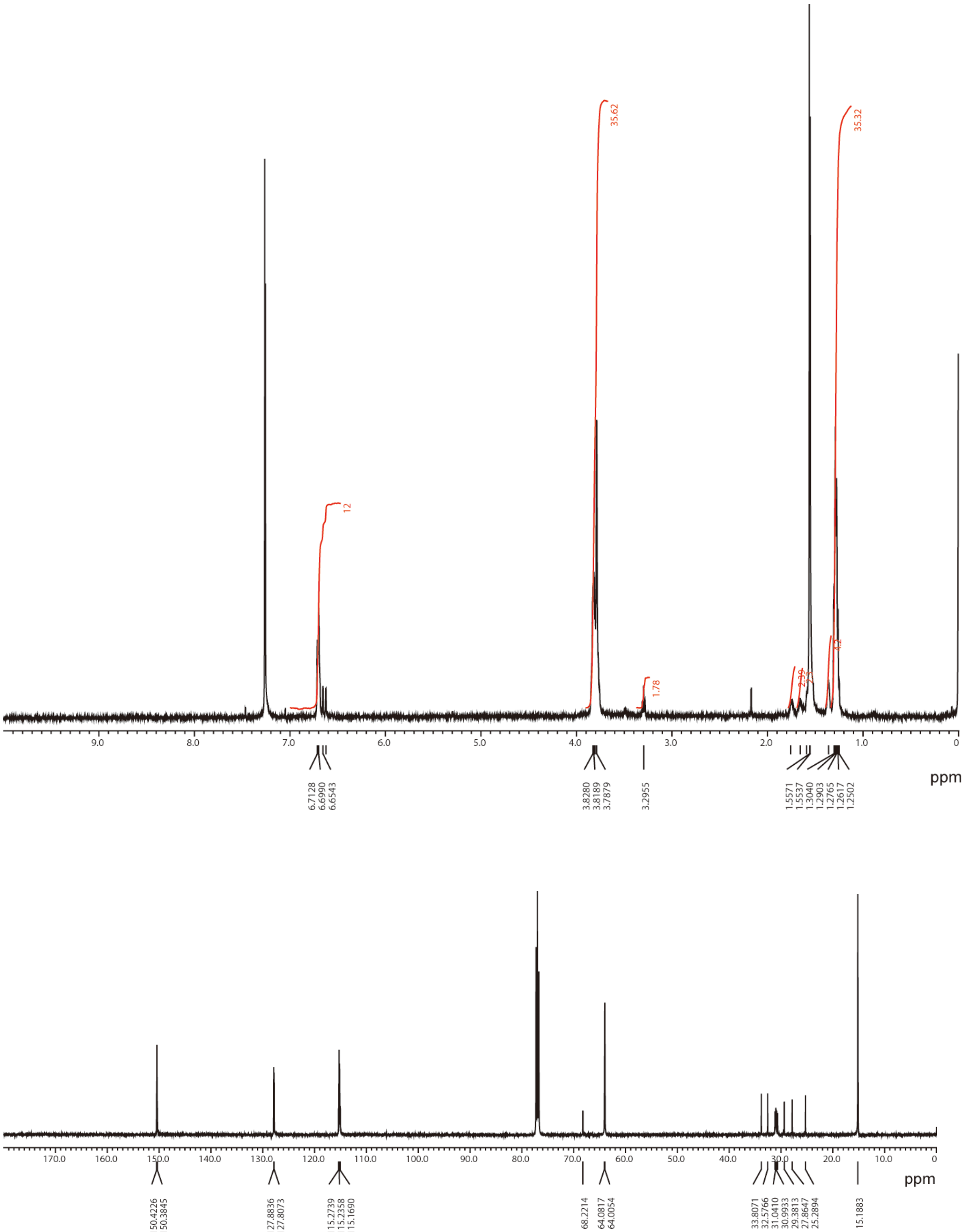


Fig. S5 ^{1}H and ^{13}C NMR spectra of **10** in $CDCl_3$ at 25 °C.

^{1}H and ^{13}C NMR spectra of 6

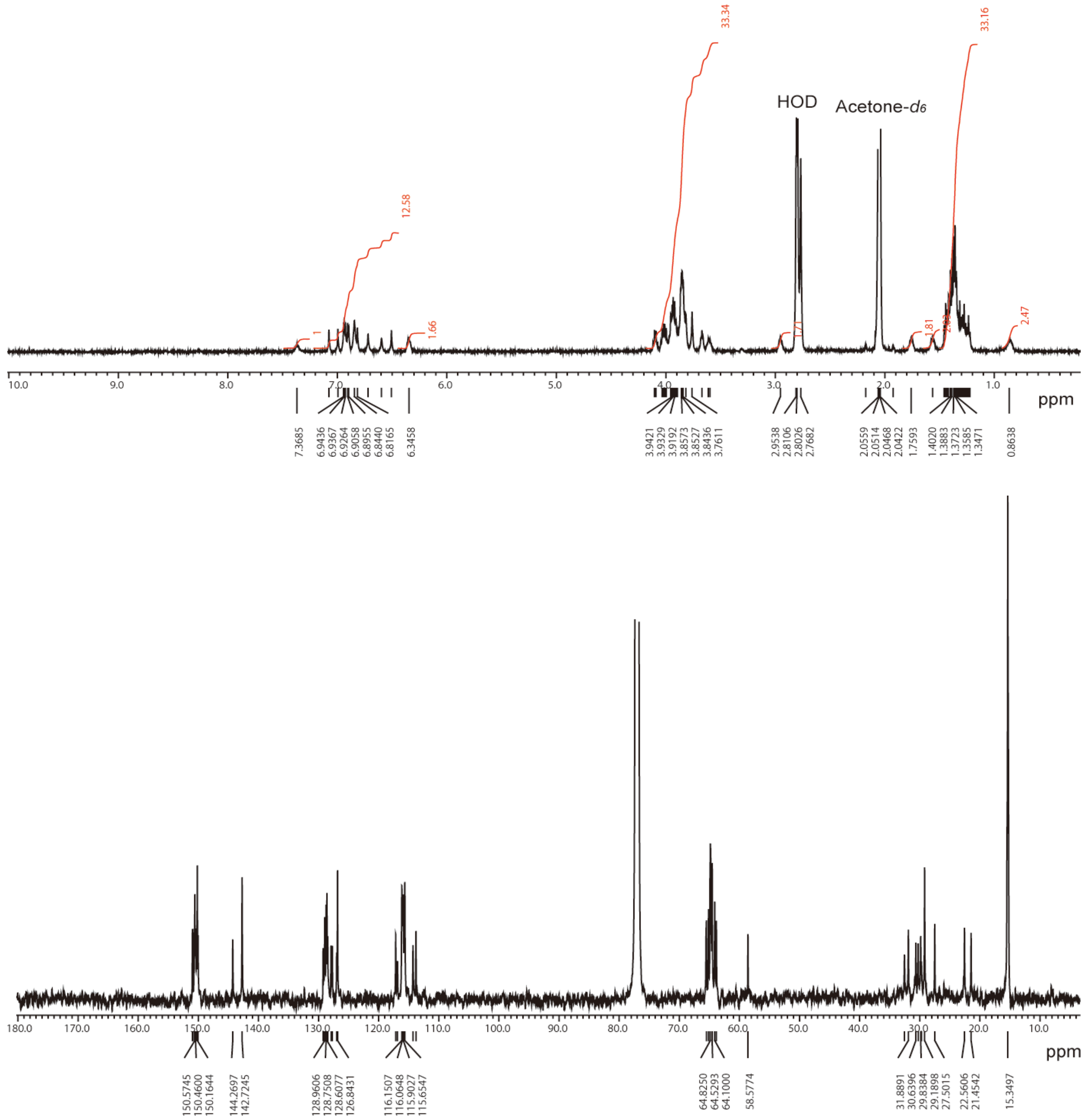


Fig. S6 ^{1}H NMR spectrum of **6** in acetone-d_6 and ^{13}C NMR spectrum of **6** in $CDCl_3$ at 25 °C.

Job Plot for 1-3 Complex

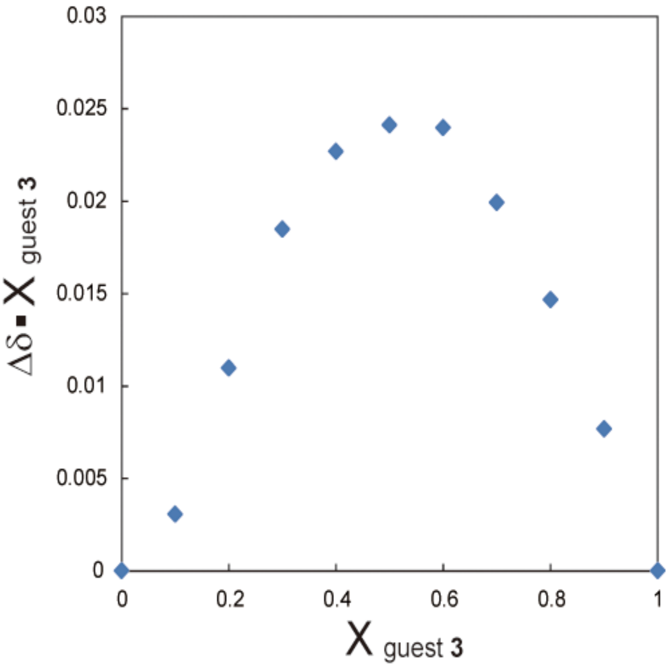


Fig. S7 Job plot between **1** (host) and **3** (guest) was collected by plotting the Δδ in chemical shift of the proton signal of pyridinium moiety (**Fig. 2b**, peak b) of **3** observed by ^{1}H NMR spectroscopy against the change in the mole fraction of the guest ($X_{\text{guest } \mathbf{3}}$). Concentration: [**1**] + [**3**] = 10 mM. The plot indicates a 1:1 binding between the host and guest.

ESIMS for a mixture of 1 and 3

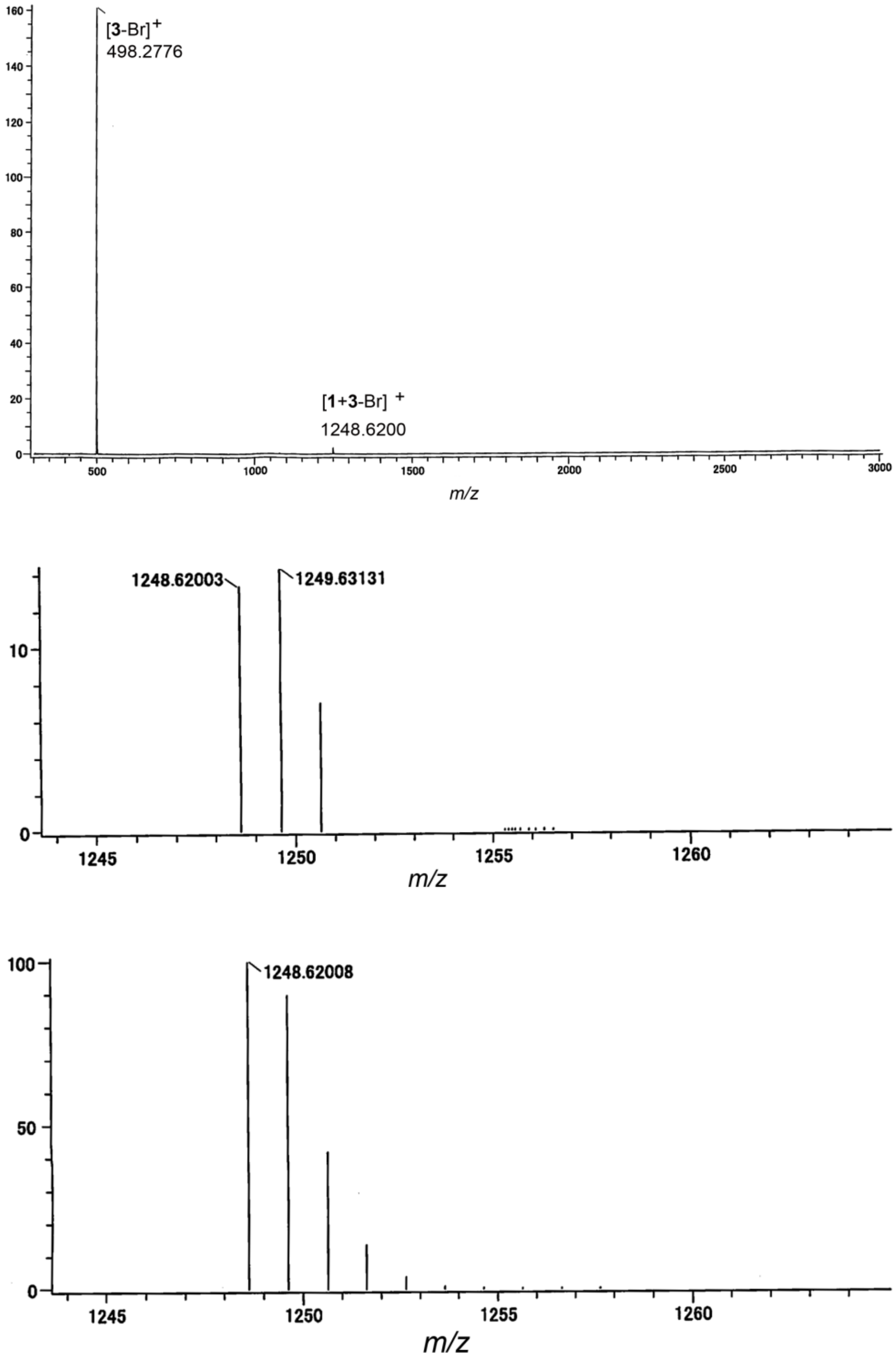


Fig. S8 ESI mass spectra of a mixture of **1** and **3**. Detection of the peak corresponding to [**1** + **3** –Br]$^+$ indicates formation of the 1:1 complex.

Job Plot for 2-3 Complex

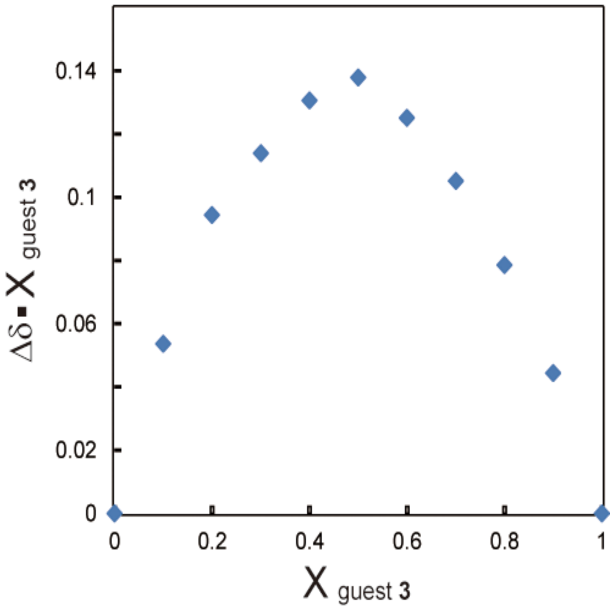


Fig. S9 Job plot between **2** (host) and **3** (guest) was collected by plotting the Δδ in chemical shift of the proton signal of pyridinium moiety (**Fig. 2c**, peak b) of **3** observed by ^{1}H NMR spectroscopy against the change in the mole fraction of the guest ($X_{guest\ \mathbf{3}}$). Concentration: [**2**] + [**3**] = 10 mM. The plot indicates a 1:1 binding between the host and guest.

^{1}H NMR spectra of a mixture of 1 and 3 in acetone-d_6

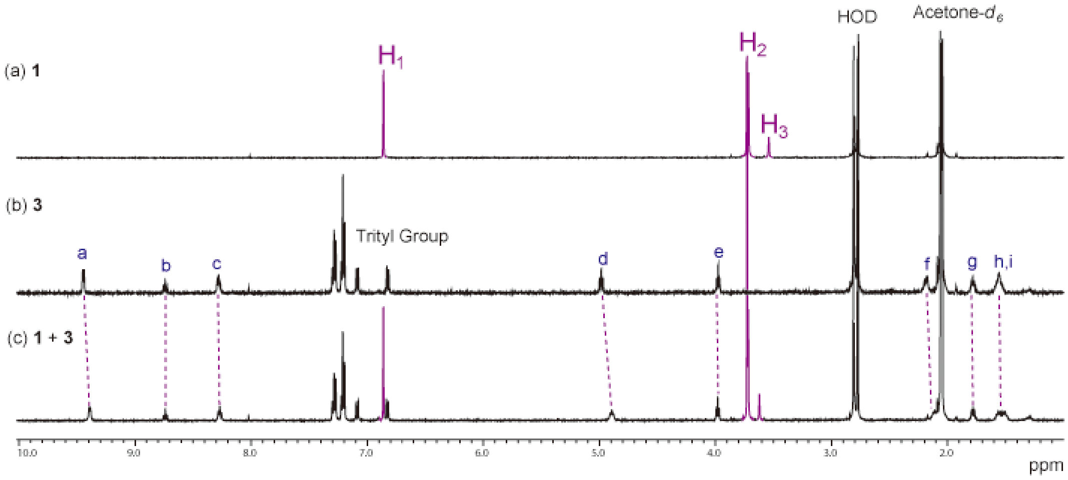


Fig. S10 ^{1}H NMR spectra of (a) **1**, (b) **3**, (c) a mixture of **1** and **3** at 1 mM in acetone-d_6 at 25 °C. Only small shifts were observed for the proton signals of the pyridinium and methylene of **3** upon addition of **1**. This observation suggests very weak binding between host **1** and guest **3**. Due to the weak binding, an association constant could not be calculated for this complex.

Job Plot for 2-4 Complex

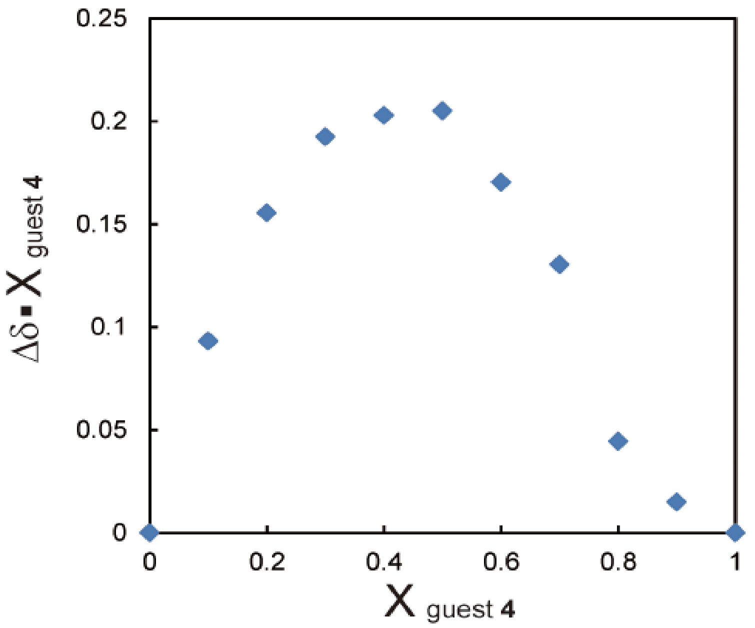


Fig. S11 Job plot between **2** (host) and **4** (guest) was collected by plotting the Δδ in chemical shift of the proton signal of DABCO moiety (**Fig. 2g**, peak b) of **4** observed by ^{1}H NMR spectroscopy against the change in the mole fraction of the guest ($X_{\text{guest } \mathbf{4}}$). Concentration: [**2**] + [**4**] = 10 mM. The plot indicates a 1:1 binding between the host and guest.

ESIMS for a mixture of 2 and 4

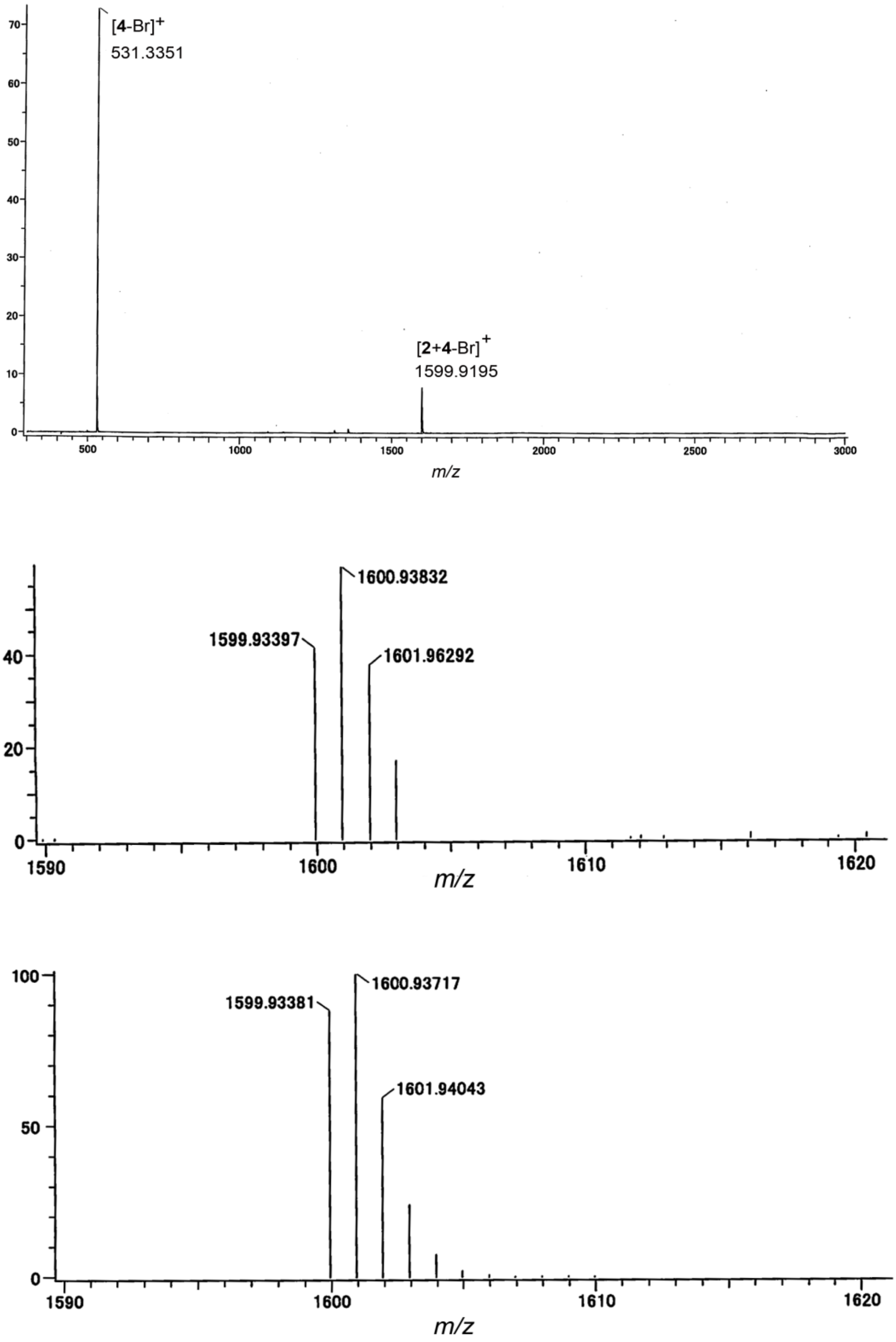


Fig. S12 ESI mass spectra of a mixture of **2** and **4**. Detection of the peak corresponding to [**2** + **4** –Br]$^+$ indicates formation of the 1:1 complex.

^{1}H NMR spectrum of a mixture of 1, 2, 3 and 4 in $CDCl_3$

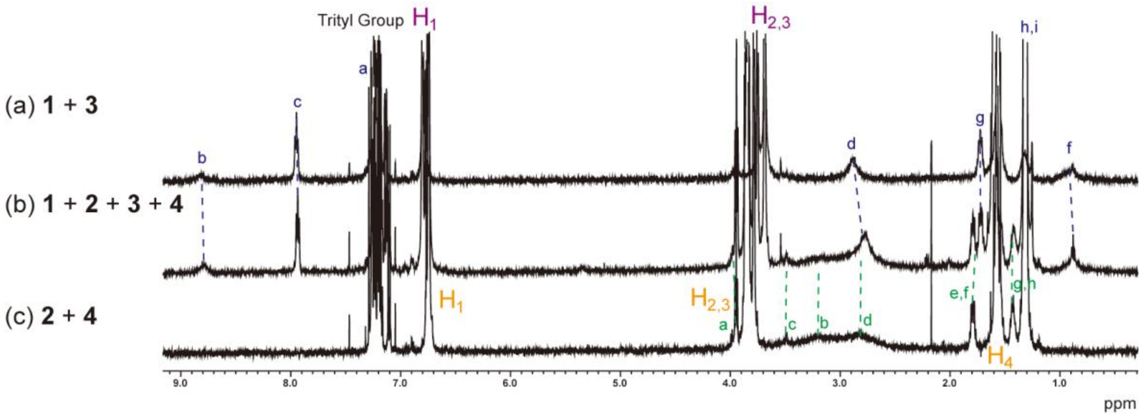


Fig. S13 ^{1}H NMR spectra of an equimolar mixture of (a) **1** and **3**, (b) **1**, **2**, **3** and **4** and (c) **2** and **4** at 1 mM in $CDCl_3$ at 25 ^{o}C. Resonances are labeled in **Fig. 1**. The peak shifts of **3** and **4** in (b) were same in those of the mixture of **1** and **3** in (a), and **2** and **4** in (c), respectively, indicating the self-sorting organization.

Variable concentration ^{1}H NMR spectra of 5

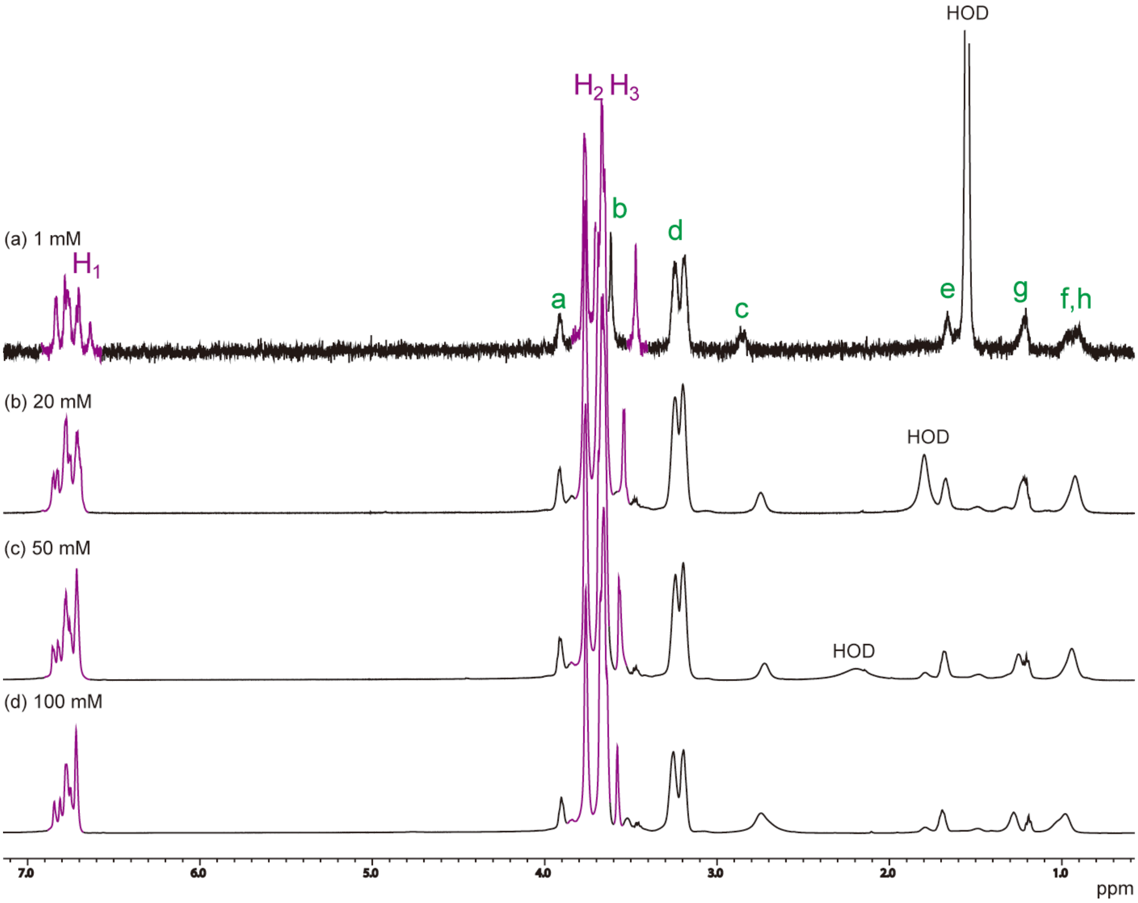


Fig. S14 Variable concentration ^{1}H NMR spectra of **5** in $CDCl_3$ at 25 ^oC. The proton resonances of **5** were independent of the concentration. These data indicate no formation of intra-/inter-molecular complex of **5** in $CDCl_3$.

Variable concentration ^{1}H NMR spectra of 6

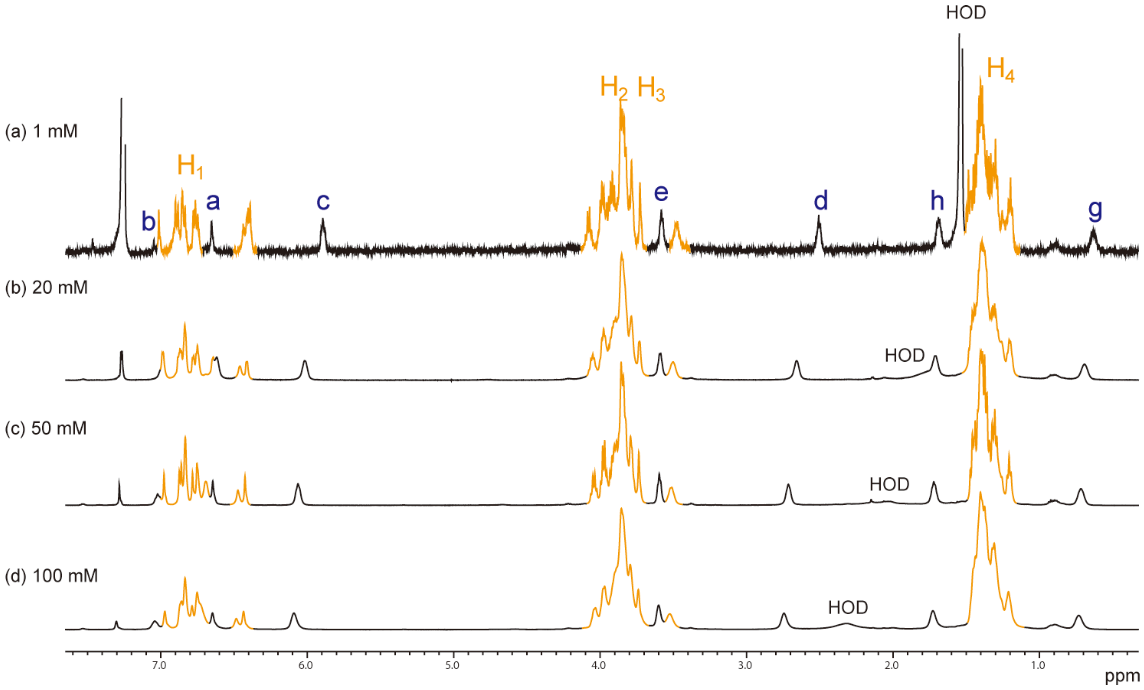


Fig. S15 Variable concentration ^{1}H NMR spectra of **6** in $CDCl_3$ at 25 °C. Proton resonances of **6** in $CDCl_3$ did not change in high and diluted concentrations. The supramolecular structure of **6** was independent of the concentration. Considering the weak association constant between pyridinium guest **2** and pillar[6]arene **3** (90.3 ± 11 M^{-1}), a self-inclusion complex or oligomers should be formed.

Variable concentration ^{1}H NMR spectra of a mixture of 5 and 6

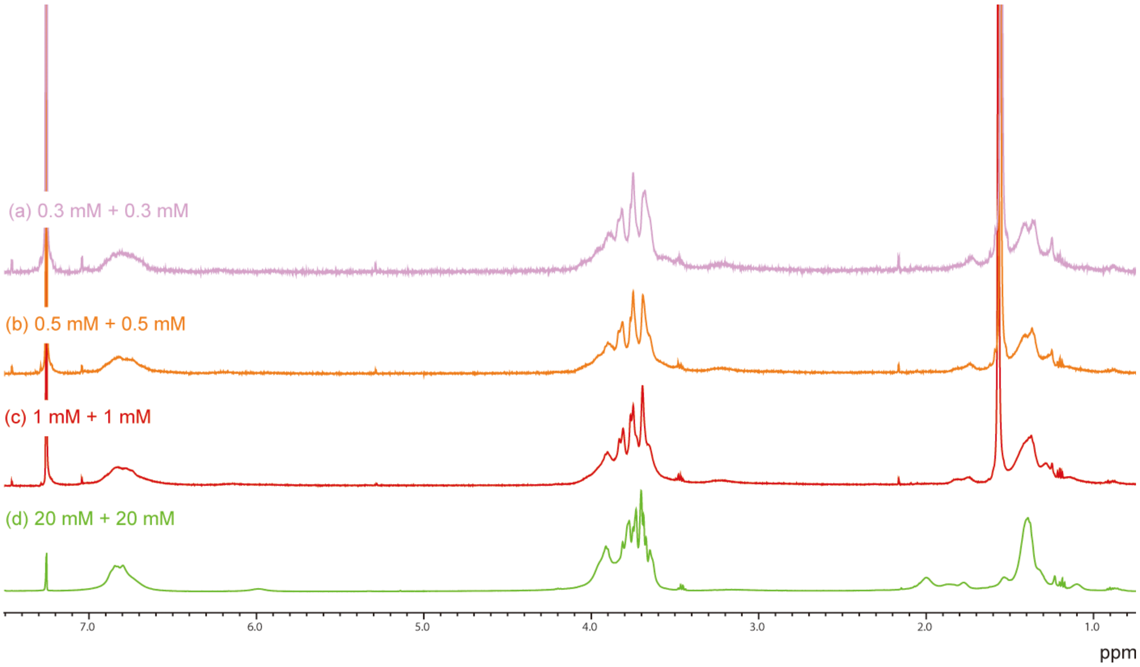


Fig. S16 Variable concentration ^{1}H NMR spectra of a 1:1 mixture of **5** and **6** in $CDCl_3$ at 25 °C. The broadening of the peaks did not change in high and diluted concentrations. The supramolecular polymer consisting of **5** and **6** was formed even in the diluted concentration investigated.

^{1}H NMR spectra of a mixture of 5 and 6 in acetone-*d*$_6$

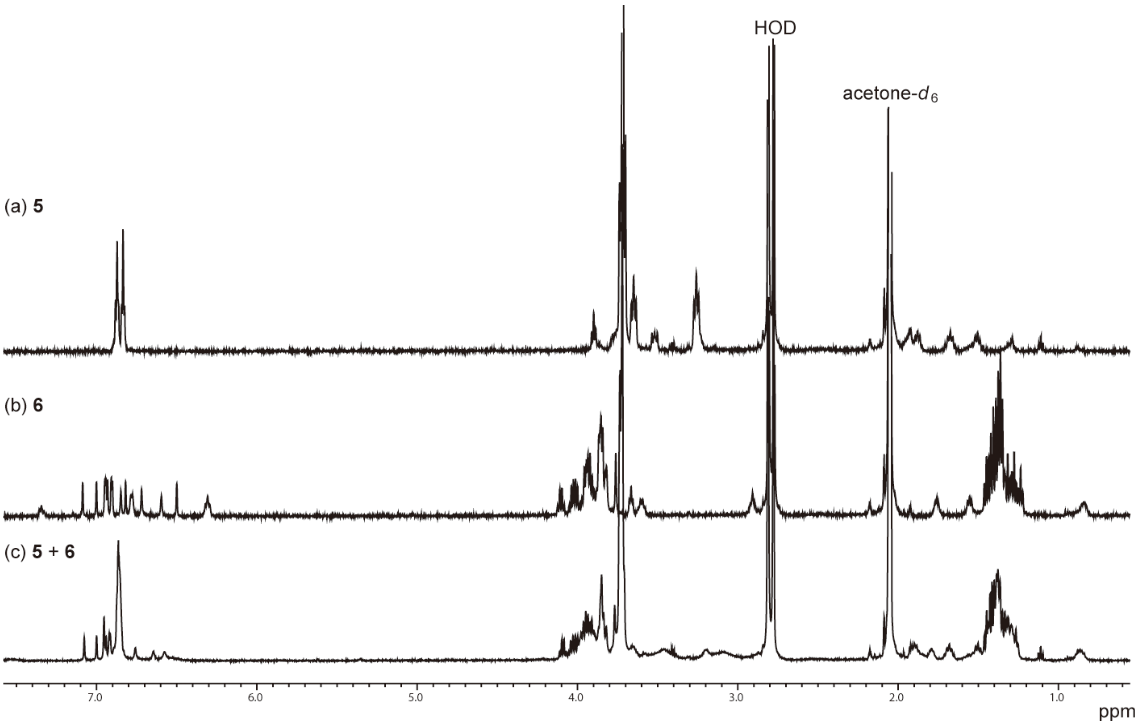


Fig. S17 ^{1}H NMR spectra of (a) **5**, (b) **6** and (c) a mixture of **5** and **6** at 1 mM in acetone-*d*$_6$ at 25 °C. The broadening was not observed in the 1:1 mixture of **5** and **6** in acetone-*d*$_6$. Since the pyridinium derivative **3** hardly formed the host-guest complex with pillar[5]arene **1** in acetone-*d*$_6$ (**Fig. S10**), formation of the supramolecular polymer did not take place in acetone-*d*$_6$.

TM-AFM images

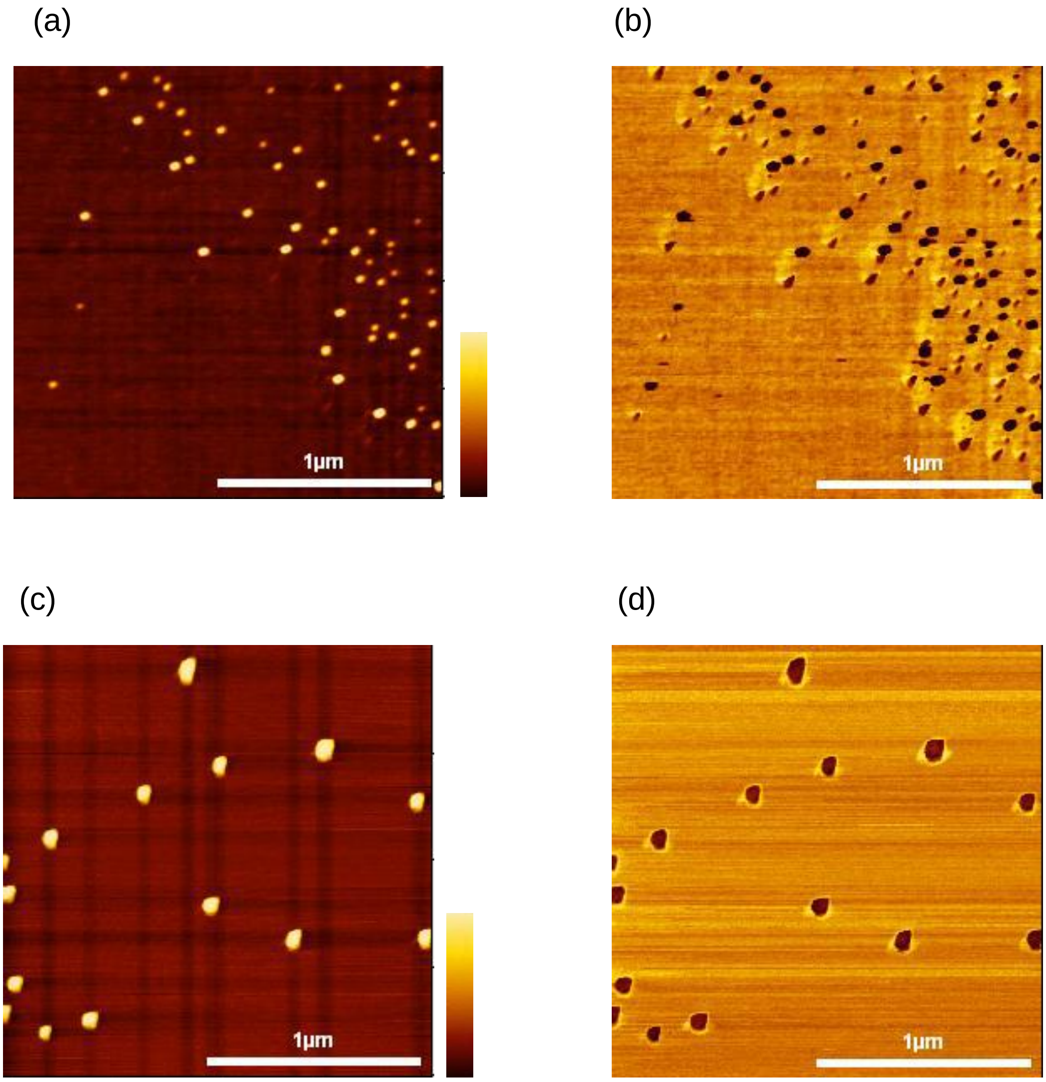


Fig. S18 TM-AFM images of (a,b) **5** and (c,d) **6**, (a,c) height images, (b,d) phase images. Spherical-shaped assemblies were observed.

References

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