Electronic Supplementary Information (ESI)

Monofunctionalized Pillar[5]arenes: Synthesis and Supramolecular Structure

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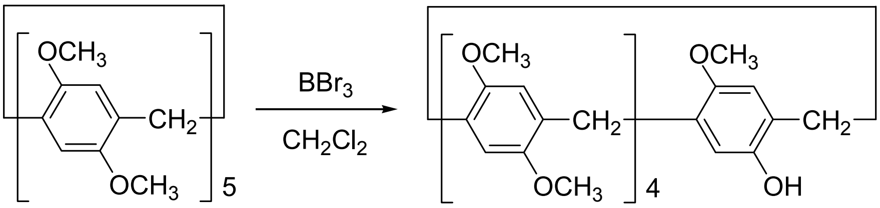
Experimental Section

Materials. All solvents and reagents were used as supplied.

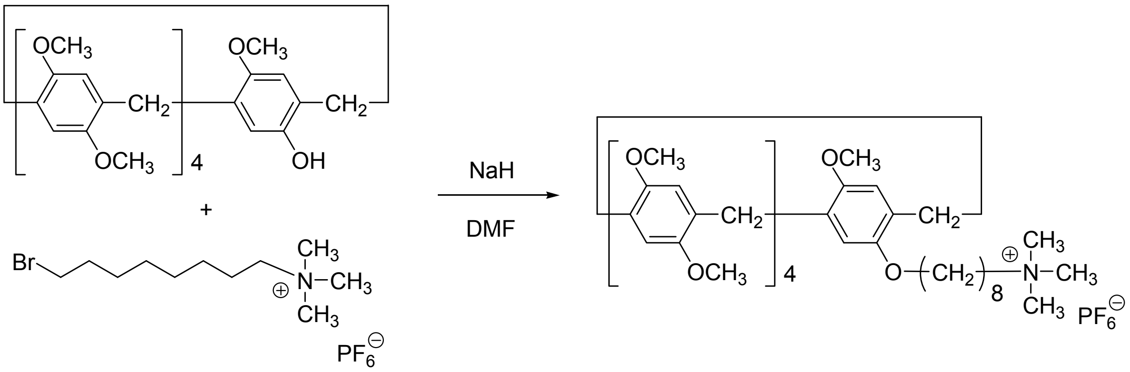
Measurements. The ^{1}H NMR spectra were recorded at 400 MHz and 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-EX400 and ECA500 spectrometers.

***N*-(8-Bromooctyl)-trimetylammonium hexafluorophosphate and per-methylated pillar[5]arene (2)** were synthesized according to the previous papers.[1,2]

3. To a solution of **2** (2.00 g, 2.68 mmol) in anhydrous dichloromethane (80 mL), boron tribromide (0.228 mL, 2.41 mmol) was added. The mixture was stirred at 25 °C for 45 minutes under nitrogen. Then, water was added into the mixture. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was poured into methanol and the resulting precipitate was collected by filtration. Column chromatography (silica gel; chloroform : acetone = 18 : 1) afforded a white solid (**3**, 0.44 g, 0.60 mmol, Yield: 22%). ^{1}H NMR (toluene-d_8, 500 MHz, ppm): δ 6.89, 6.88, 6.84, 6.83, 6.82, 6.81, 6.80, 6.76, 6.62, 6.57 (s, 10H, phenyl), 5.33 (s, 1H, phenol), 4.08, 4.05, 4.04, 4.03, 3.79 (s, 10H, methylene), 3.46, 3.41, 3.36, 3.34, 3.33, 3.31, 3.30, 3.26, 3.24 (s, 27H, methoxy). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.88, 6.73, 6.70, 6.69, 6.51, 6.60, 6.59 (s, 11H, phenyl and phenol), 3.80, 3.78, 3.75, 3.73, 3.69, 3.63, 3.60, 3.59, 3.56, 3.50 (s, 37H, methoxy and methylene bridge). ^{13}C NMR (toluene-d_8, 125 MHz, ppm): δ 151.7, 151.4, 151.3, 151.1, 150.0, 148.3, 119.7, 114.5, 114.4, 114.3, 114.2, 114.0, 113.9, 113.8, 113.5 (C of phenyl), 55.6, 55.5, 55.4, 55.3, 55.2 (C of methoxy), 30.3 (C of methylene), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 151.0, 150.9, 150.8, 147.5, 130.0, 129.3, 128.6, 128.2, 128.0, 127.6, 126.8, 125.0, 118.9, 114.5, 114.3, 114.0, 113.8, 112.9 (C of phenyl), 56.3, 56.0, 55.9, 55.8 (C of methoxy), 30.9, 30.1, 29.9, 29.6, 28.8 (C of methylene). Anal. Calcd for $C_{44}H_{48}O_{10}$: C, 71.72; H, 6.57. Found: C, 72.15; H, 6.50. HR-MS (FAB) Calcd for C44H49O10 $[M]^+$: 737.33253, found 737.33271.



4. Under a nitrogen atmosphere **3** (300 mg, 0.41 mmol) was dissolved in DMF (5 mL). Sodium hydride (39.4 mg, 0.82 mmol) was added and the reaction mixture was stirred. Then, *N*-(8-bromooctyl)-trimetylammonium hexafluorophosphate (195 mg, 0.62 mmol) was added and the reaction mixture was heated at 80 °C for 48h. 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; dichloromethane : methanol = 18 : 1) afforded a white solid (**4**, 0.21 g, 0.20 mmol, Yield: 49%). ^{1}H NMR (acetone-d_6, 500 MHz, ppm): δ 6.90, 6.89, 6.87, 6.86, 6.84 (s, 10H, phenyl protons), 3.91 (t, 2H, methylene protons adjacent to O atom), 3.75, 3.74, 3.73, 3.72, 3.71 (m, 37H, methylene bridge and methoxy protons), 3.37, 3.35 (m, 10H, methylene protons adjacent to N atom and methyl protons), 1.83, 1.67, 1.58, 1.44, 1.36, 1.21 (br, 12H, methylene protons). ^{13}C NMR (acetone-d_6, 125 MHz, ppm): δ 151.4, 151.3, 150.6, 129.2, 129.0, 115.3, 114.8, 114.5, 114.3 (C of phenyl), 68.8, 67.6 (C of methylene linker), 56.0 (C of methoxy), 53.6 (C of methyl), 30.3, 30.2, 30.1, 30.0, 29.6, 26.7, 23.3 (C of methylene bridge and methylene linker). Anal. Calcd for C55H72O10NPF6 C, 62.79; H, 6.90; N, 1.33. Found: C, 62.43; H, 6.98; N, 1.40. HR-MS (FAB) Calcd for C55H73O10NPF6 $[M]^+$: 1052.4876, found 1052.4885.



Determination of Association Constant for the 3-OTMA Complex. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of **OTMA** (2 mM) and varying concentrations of **3** (1 to 20 mM). By the non-linear curve-fitting methods, the association constant (K) for **3-OTMA** complex is estimated to be about 780 ± 110 M^{-1} for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:[3]

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

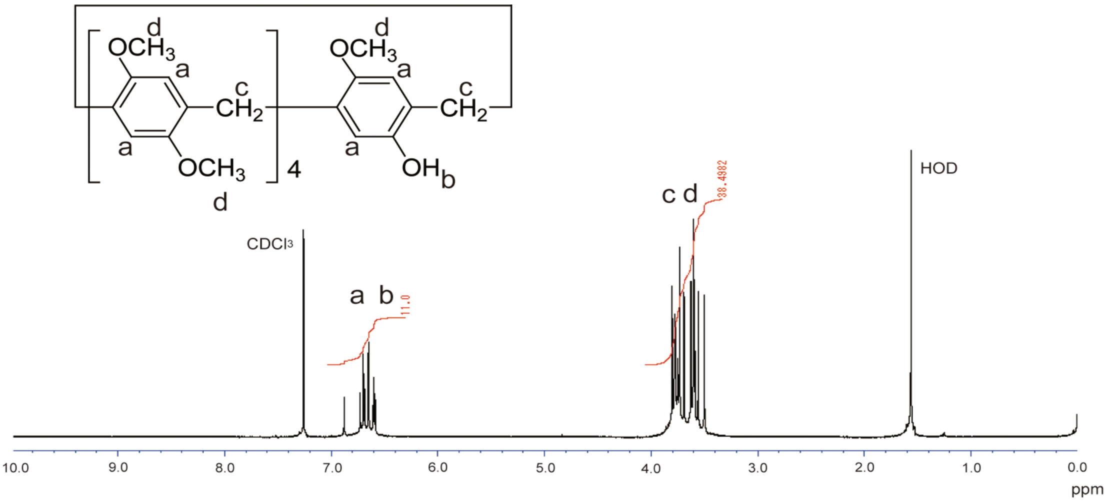
Where $\Delta\delta_{obs}$ is the chemical shift change of trimethyl group on **OTMA** at $[H]_0$, $\Delta\delta_{11}$ is the chemical shift change of the proton resonance for the trimethyl group when the guest **OTMA** is completely complexed, $[G]_0$ is the fixed initial concentration of the guest **OTMA**, and $[H]_0$ is the initial concentration of the host **3**.

References

1) A. Mary, D. Z. Renko, C. Guillou and C. Thal, *Bioorg. Med. Chem.,* 1998, **6**, 1835.
2) T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi and Y. Nakamoto, Y. *J. Org. Chem.,* 2011, **76**, 328.
2) 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 and ^{13}C NMR Spectra of 3

(a) ^{1}H NMR Spectrum



(b) ^{13}C NMR Spectrum

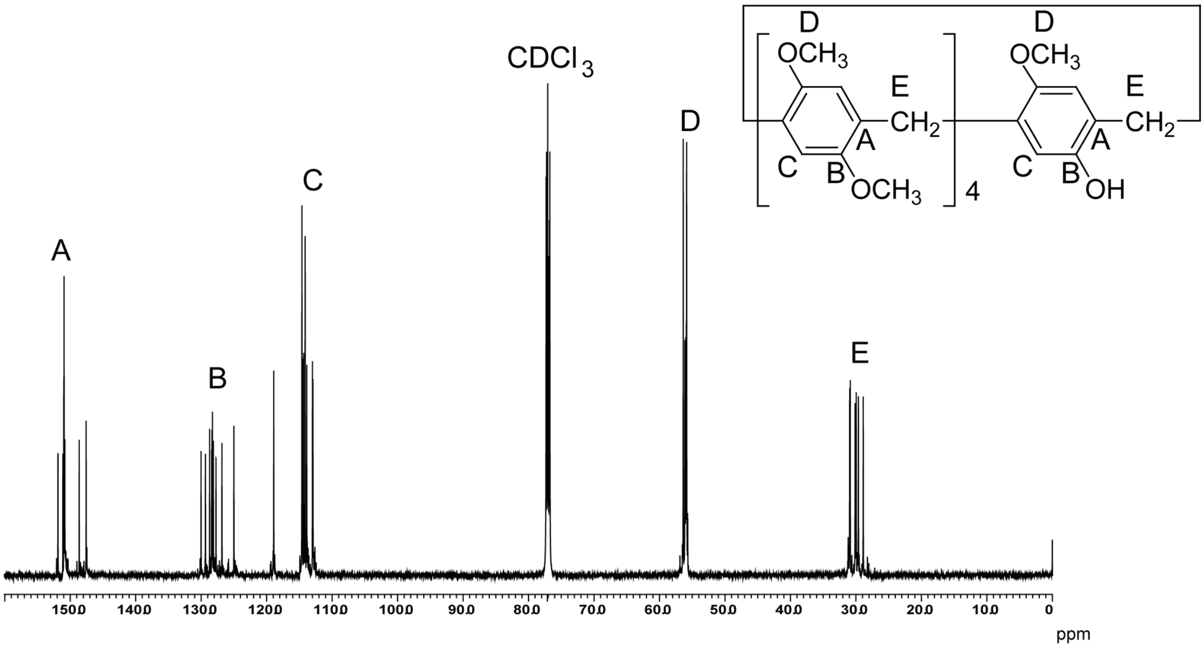


Figure 1S. (a) ^{1}H and (b) ^{13}C NMR spectra of **3** in $CDCl_3$ at 25 °C.

HSQC analysis of 3

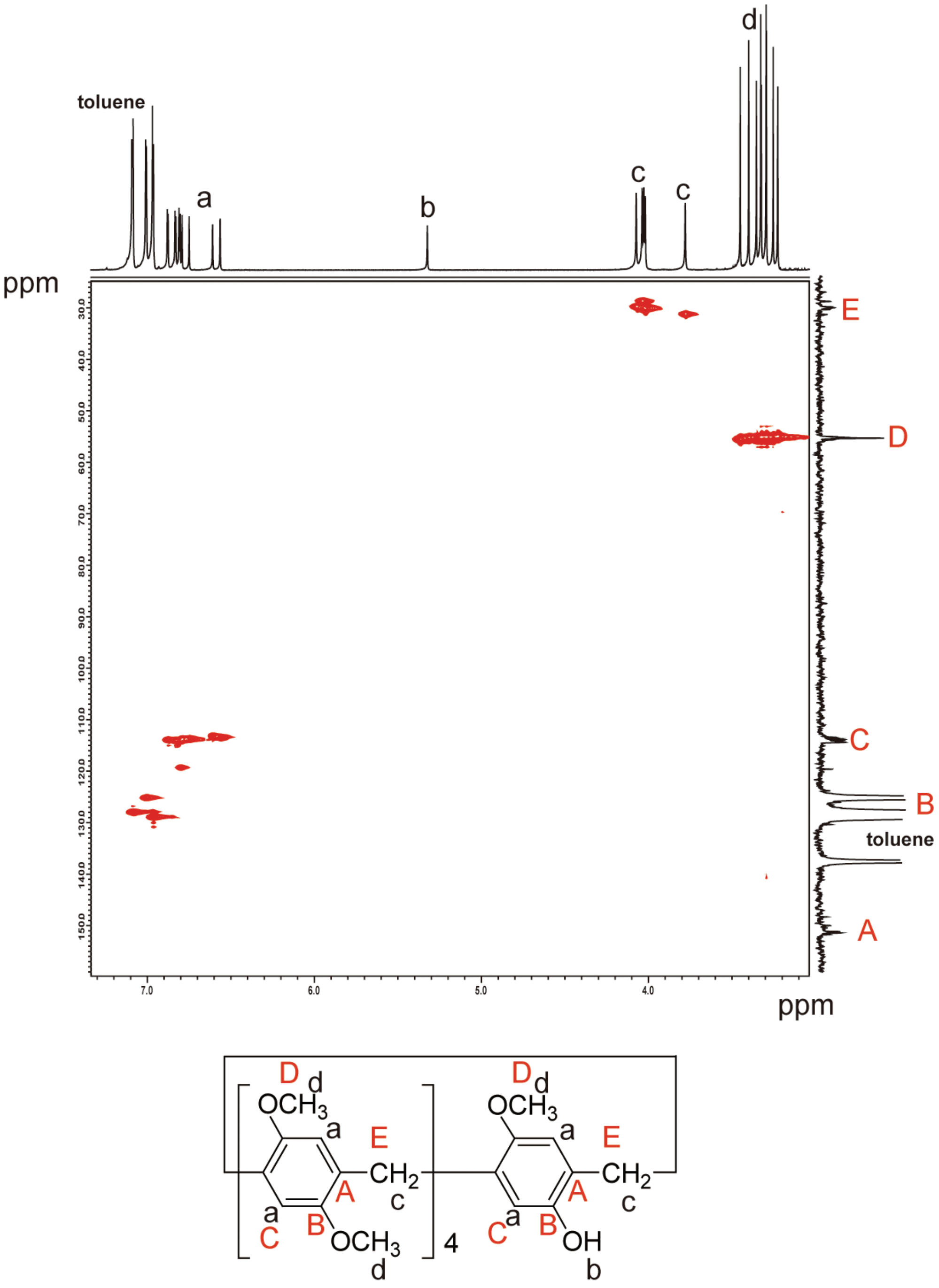


Figure 2S. (a) HSQC analysis of **3** in toluene-d_8 at 25 °C.

HMBC Analysis of 3

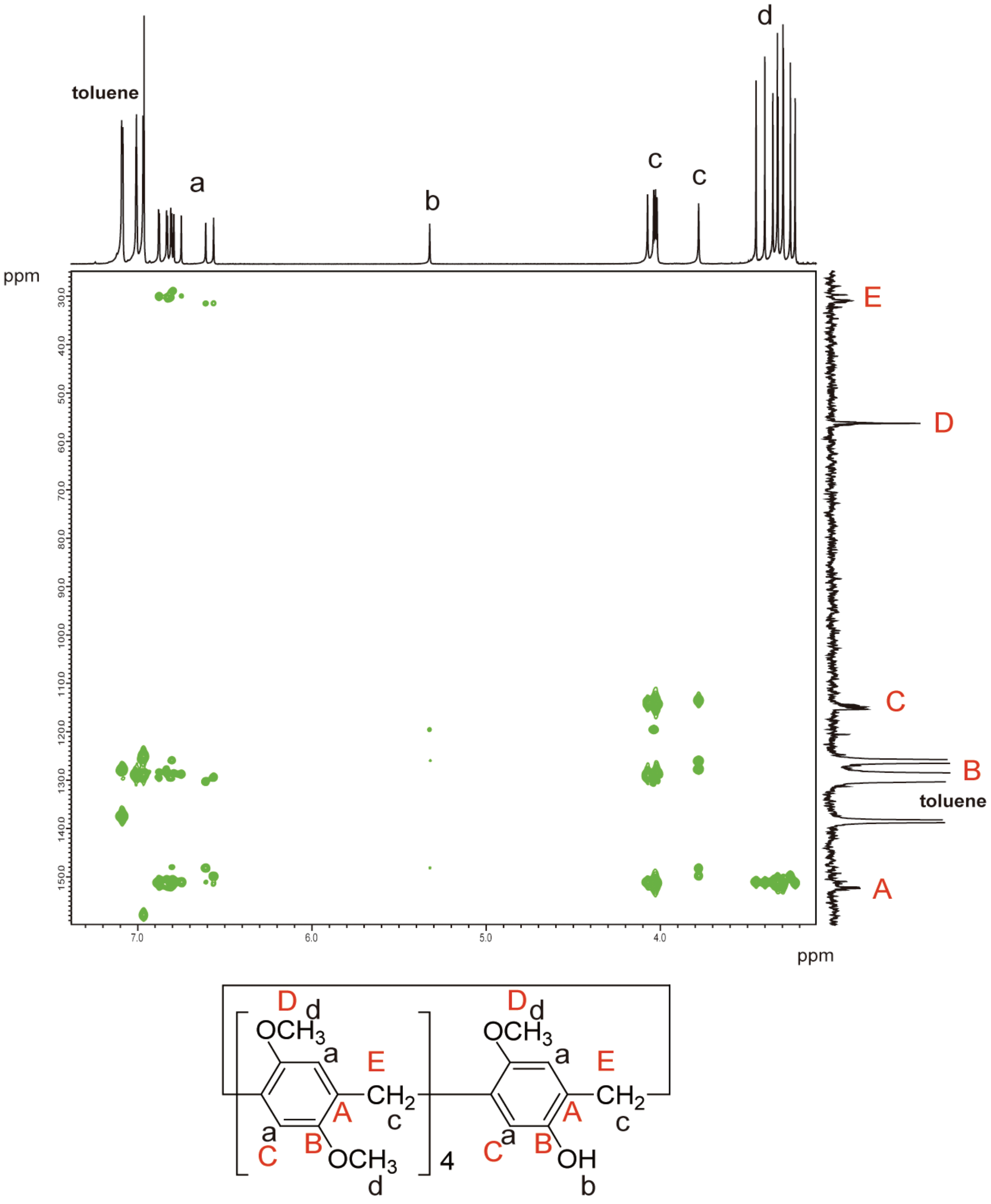


Figure 3S. (a) HMBC analysis of **3** in toluene-d_8 at 25 °C.

NOESY Analysis of 3

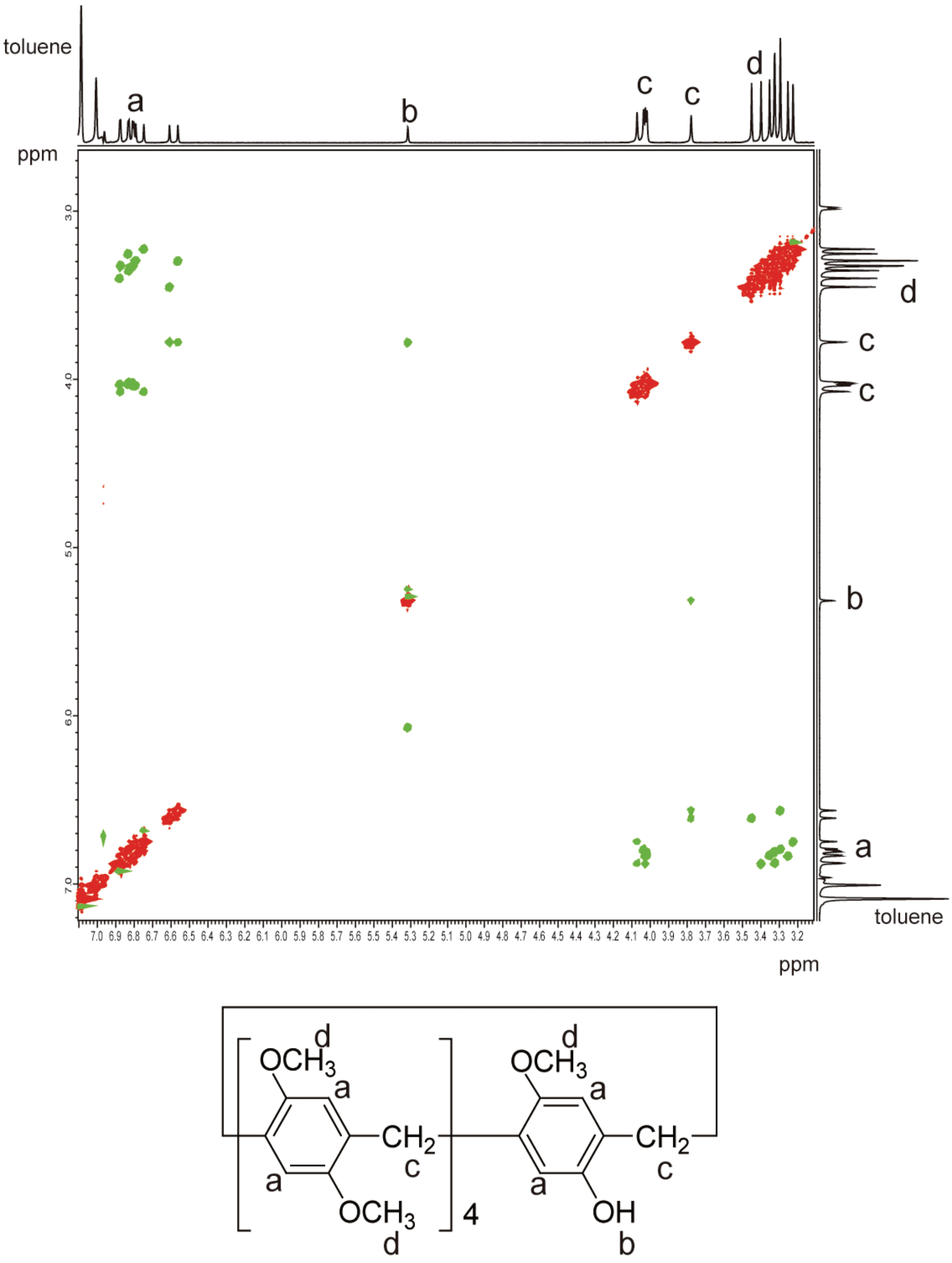
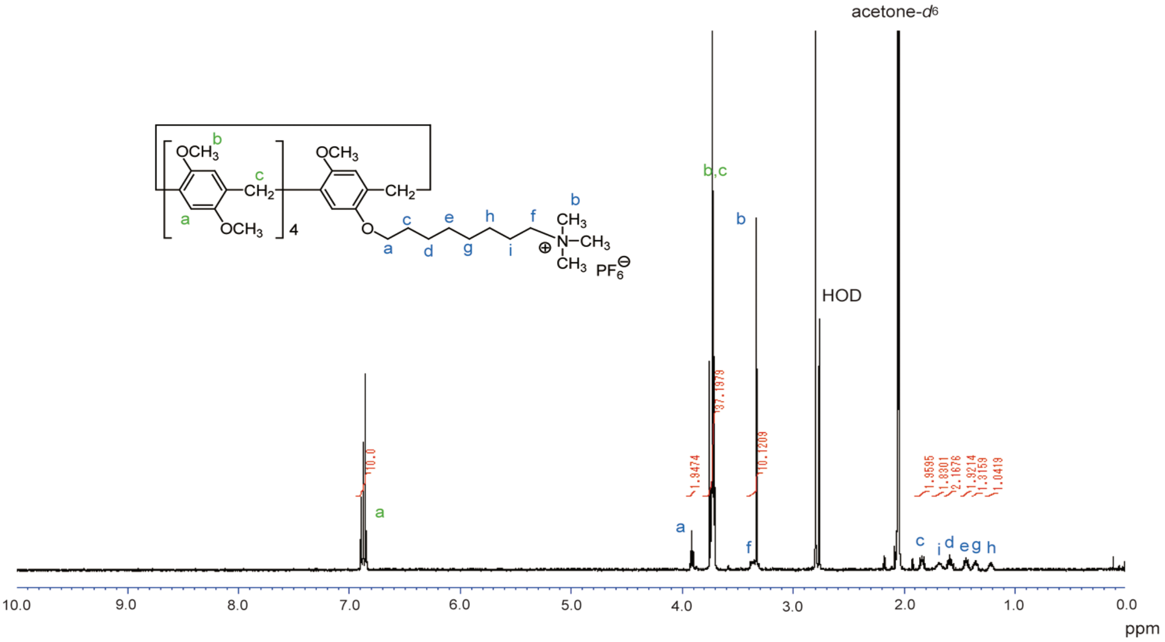


Figure 4S. (a) NOESY study of **3** in toluene-d_8 at 25 ^{o}C (mixing time = 500 ms).

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

(a) ^{1}H NMR Spectrum



(b) ^{13}C NMR Spectrum

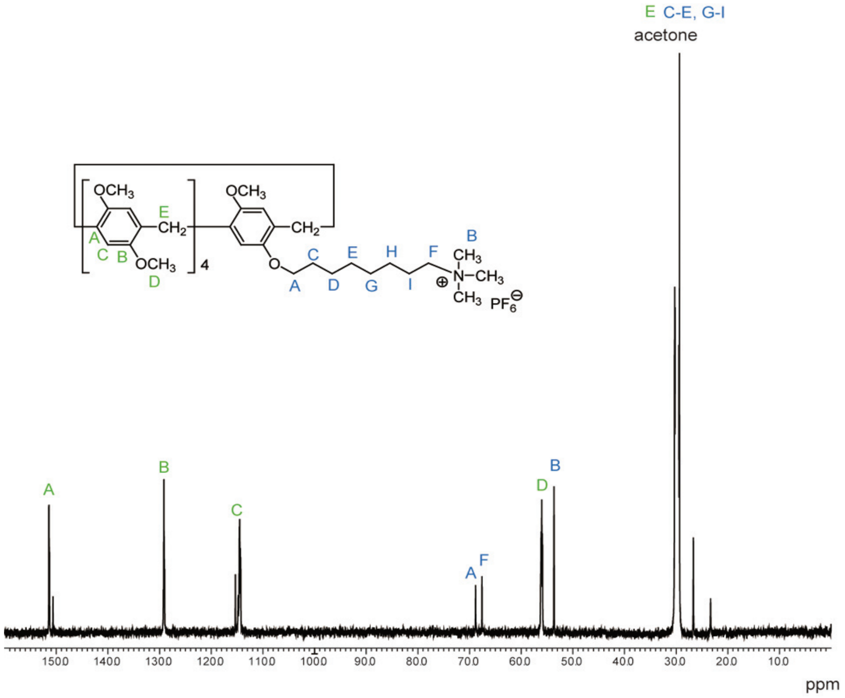


Figure 5S. (a) ^{1}H and (b) ^{13}C NMR spectra of **4** in acetone-d_6 at 25 °C.

HSQC Analysis of 4

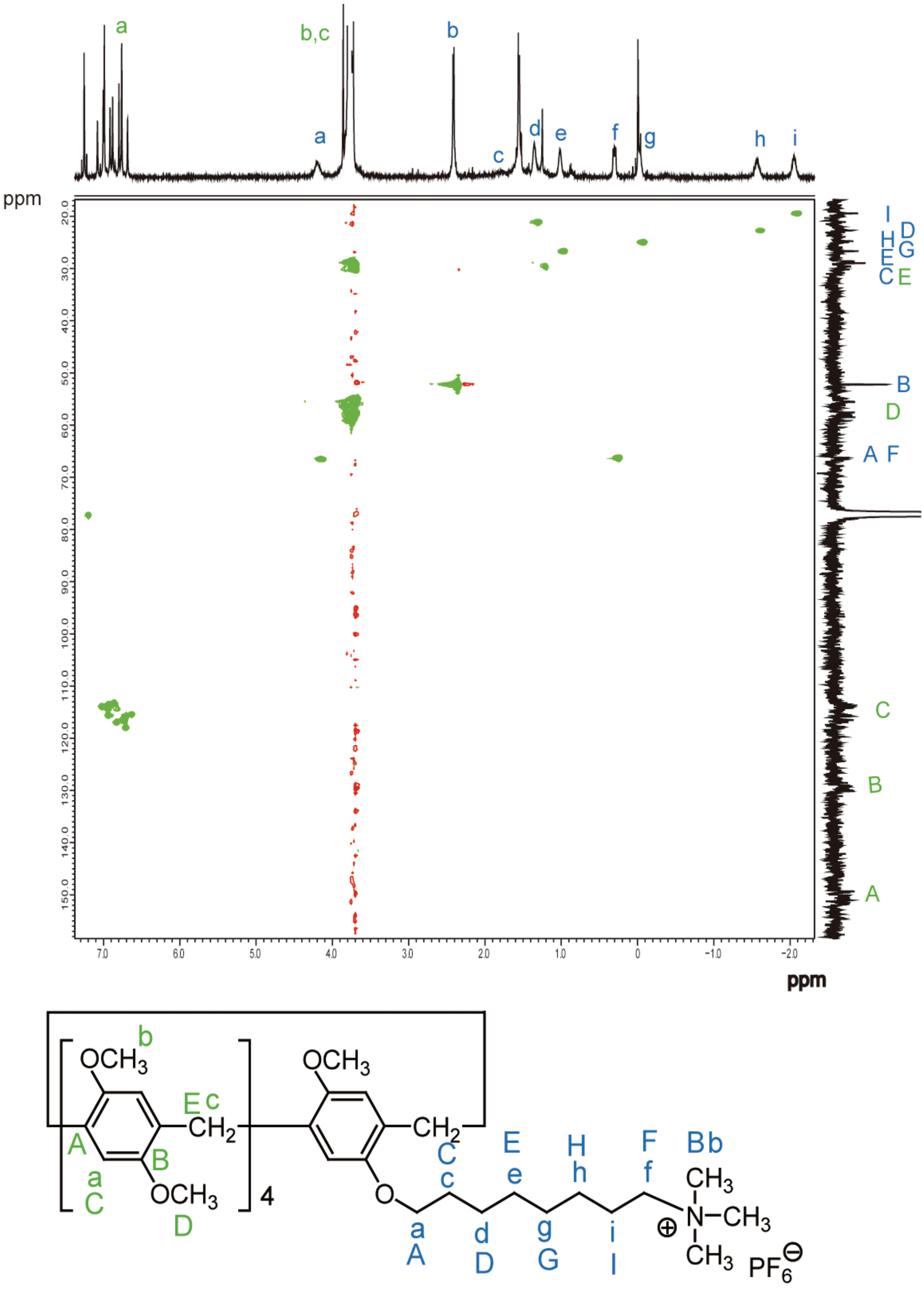


Figure 6S. HSQC analysis of **4** in $CDCl_3$.

HMBC Analysis of 4

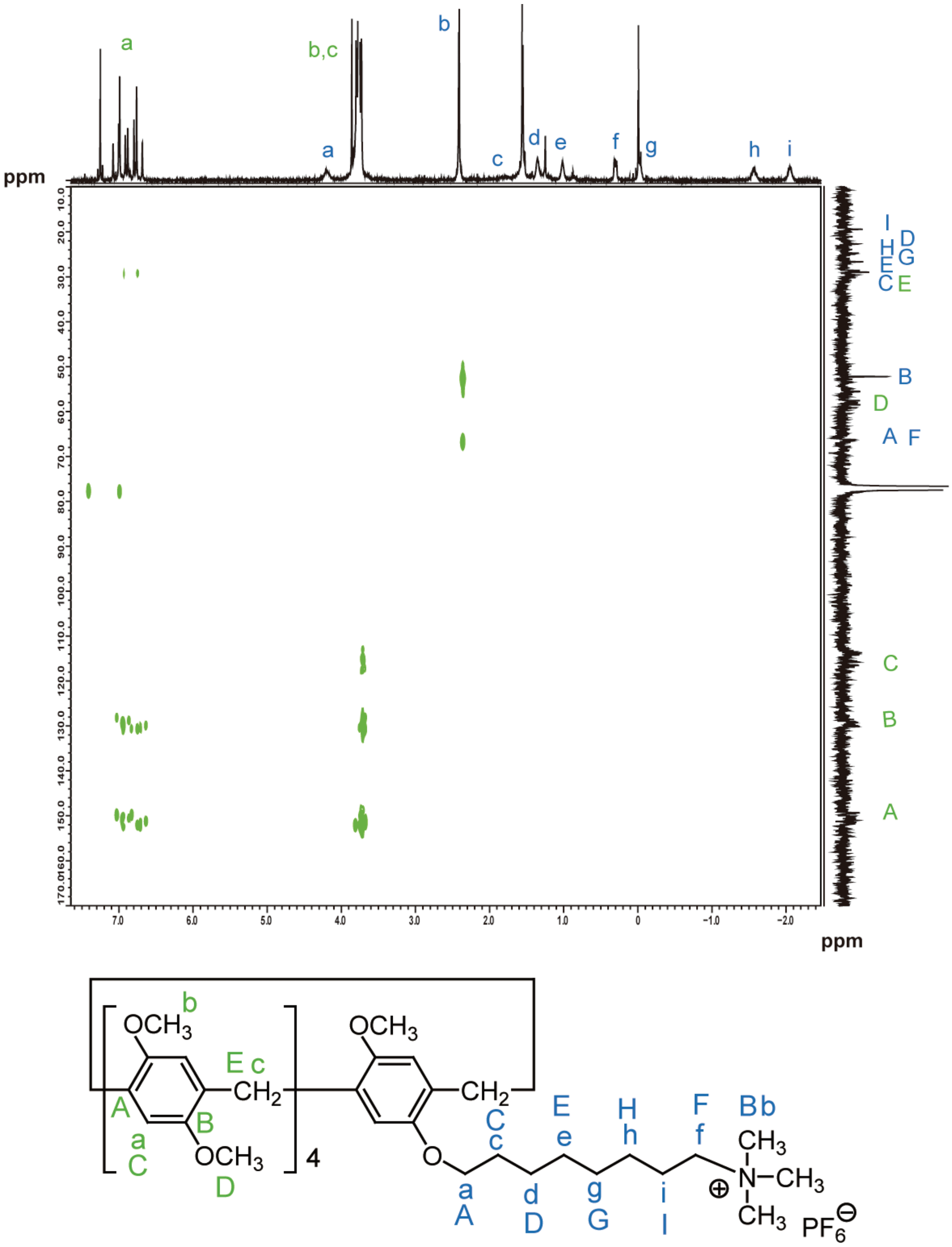


Figure 7S. HMBC analysis of **4** in $CDCl_3$.

^{1}H NMR Spectrum of 2

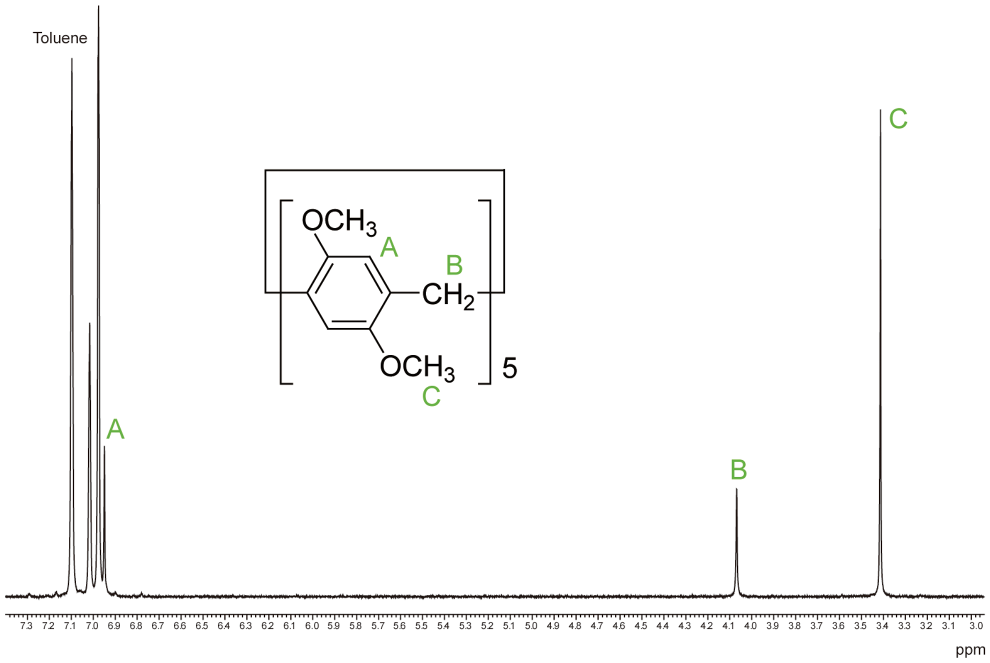


Figure 8S. (a) ^{1}H NMR spectrum of **2** in toluene-d_8 at 25 °C. Due to the high symmetrical structure of **2**, singlet proton resonances from phenyl, methylene and methoxy protons were observed.

Job Plot

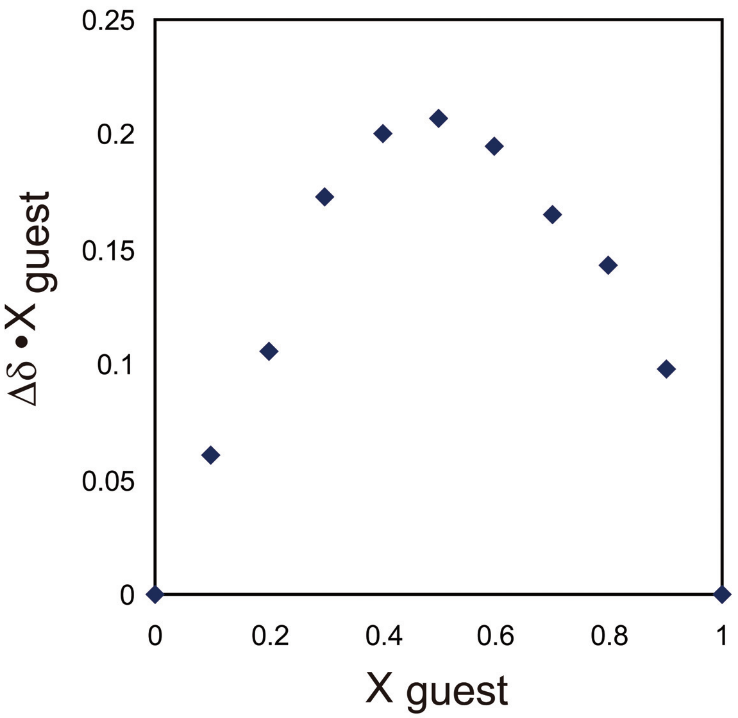


Figure 9S. Job plot of the complex between **3** and **OTMA**. The Job plot was conducted by varying the mole fractions of guest **OTMA** and host **3**. Peak shifts of trimethyl protons for **OTMA** were utilized. Concentration: [**OTMA**]+[**3**] = 10 mM.

Association Constant of the Complex between 3 and OTMA

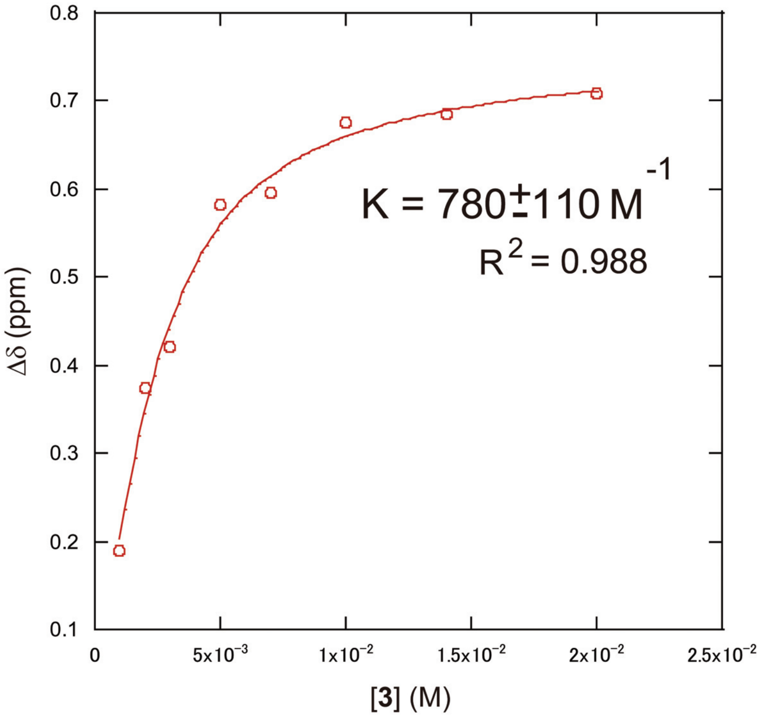


Figure 10S. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of **OTMA** (2 mM) and varying concentrations of **3** (1 to 20 mM). By the non-linear curve-fitting methods, the association constant (K_1) for **3-OTMA** complex is estimated to be about 780 ± 110 M^{-1} for 1:1 stoichiometry.

^{1}H NMR Spectrum of the Mixture of 3 and OTMA in Acetone-d_6

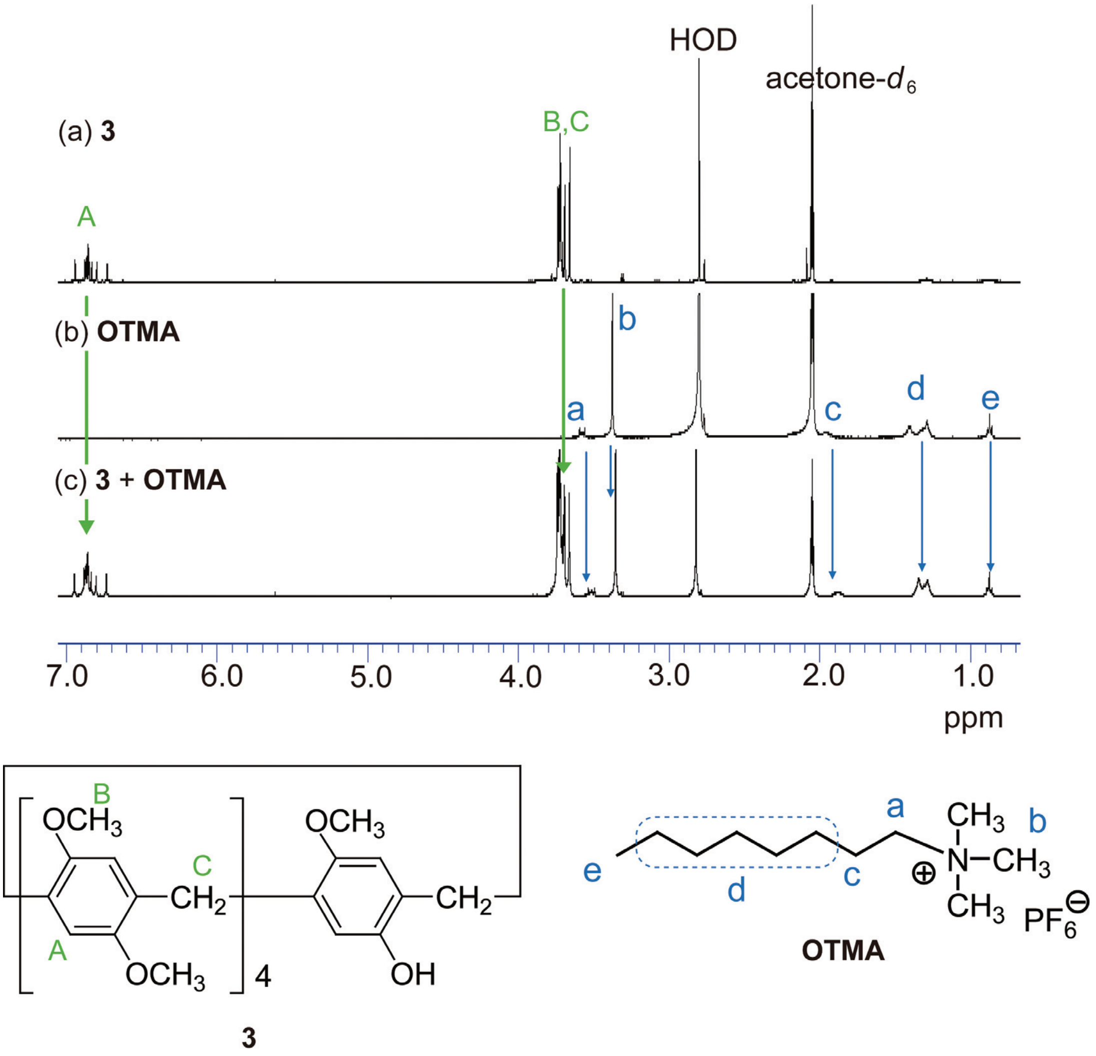


Figure 11S. ^{1}H NMR spectra of (a) **3**, (b) **OTMA** and (c) the 1:1 mixture of **3** (2.0 mM) and **OTMA** (2.0 mM) in acetone-d_6 at 25 °C. Proton peaks from **3** and **OTMA** did not change by mixing, indicating no complex formation between **3** and **OTMA** in acetone-d_6.

Variable-Concentration ^{1}H NMR Spectra of 4 in $CDCl_3$

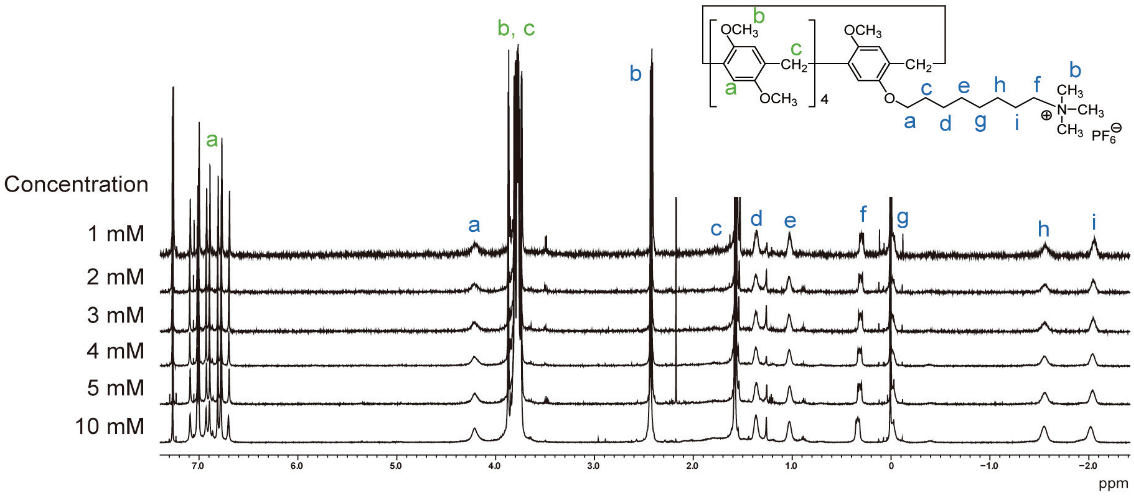
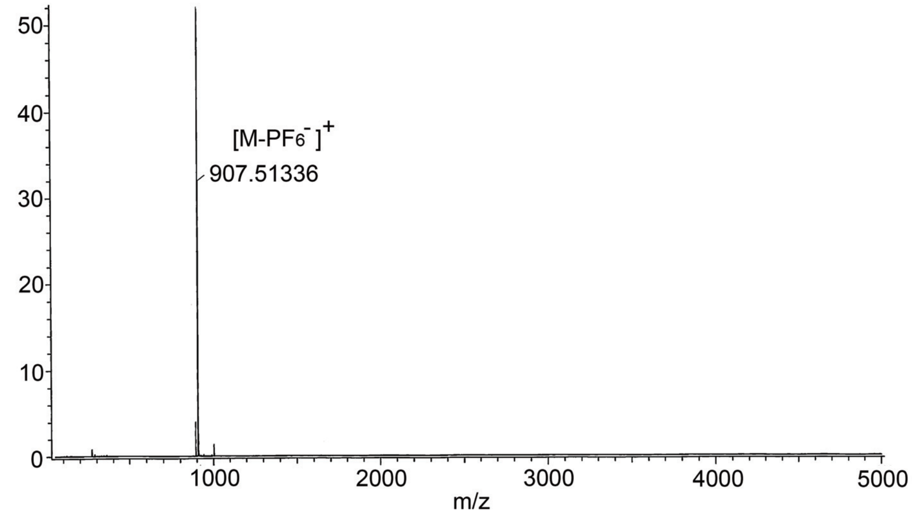


Figure 12S. Variable-concentration ^{1}H NMR spectra of (a) **4** in $CDCl_3$ at 25 °C. Proton resonances of **4** in $CDCl_3$ did not change upon diluting concentration, indicating that the supramolecular structure of **4** was independent of the concentration.

ESI-Mass Spectra of 4

(a) in acetone



(b) in $CHCl_3$

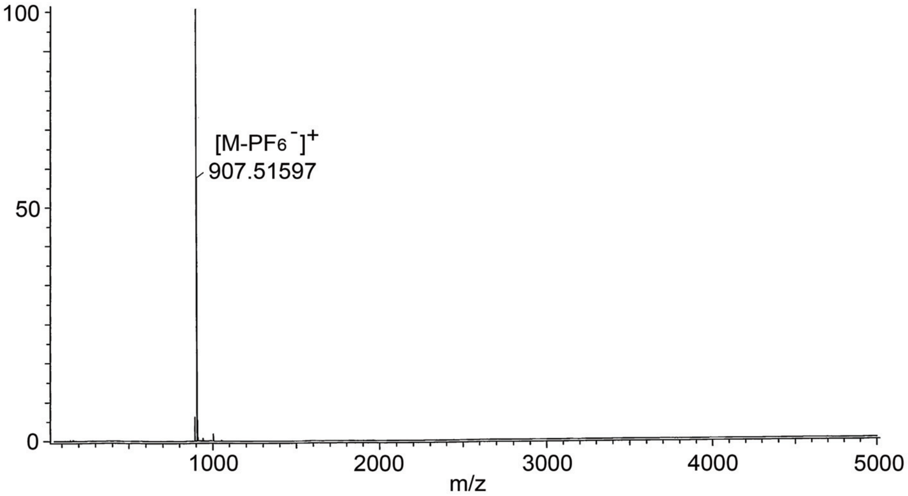


Figure 13S. ESI-mass spectra of **4** in (a) acetone and (b) $CHCl_3$ (1mg/mL). In both spectra, the monomer peak of **4** was detected but the other peaks from the supramolecular polymer were hardly observed.