# A novel pH-responsive supramolecular polymer constructed by pillar[5]arene-based host–guest interactions

Binyuan Xia,[a] Bo Zheng,[a] Chengyou Han,[a] Shengyi Dong,[a] Mingming Zhang,[a] Bingjie Hu,[b] Yihua Yu,[b] and Feihe Huang[a,]*

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China; Email address: fhuang@zju.edu.cn*

[b] *Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, P. R. China*

## Electronic Supplementary Information (28 pages)

1. *Materials and methods* S2
2. *Characterizations of compounds* S3
3. *Stoichiometry and association constant determination for the complexations between **10** and **1** and between **10** and **2*** S17
4. *Partial 2-D COSY spectrum of a chloroform-d solution of 40.0 mM **8*** S22
5. *Full 2-D NOESY spectrum of a chloroform-d solution of 40.0 mM **8*** S23
6. *Partial 2-D COSY spectrum of a chloroform-d solution of 40.0 mM **9*** S23
7. *Full 2-D NOESY spectrum of a chloroform-d solution of 40.0 mM **9*** S24
8. *Calculated values of maximum polymerization degree n at different concentrations of **8** and **9*** S25
9. *References* S28

## *1. Materials and methods*

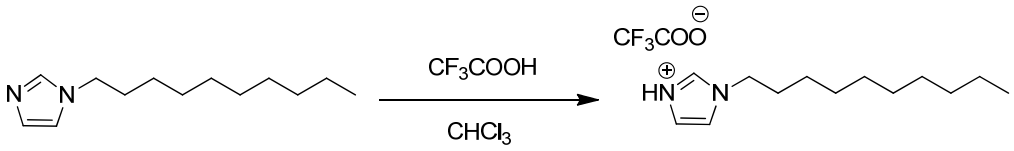
Hydroquinone, methyl chloroacetate, 1,4-dipropoxybenzene, trifluoroacetic acid, triethylamine, boron trifluoride diethyl etherate, paraformaldehyde, 1,2-dichloroethane, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), and 4-dimethylamiopyridine (DMAP) were reagent grade and used as received. 1-Decylimidazole (**1**),[S1] 4-propoxyphenol (**3**)[S2] and 1-hydroxydecyl-imidazole (**7**)[S3] were synthesized according to literature procedures. Solvents were employed as purchased or dried according to procedures described in the literature.

NMR spectra were collected on a Bruker AVANCE DMX-500 spectrometer or a Varian Unity INOVA-400 spectrometer with TMS as the internal standard. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

Viscosity measurements were carried out with Ubbelohde micro dilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 303 K in chloroform.

## 2. *Characterizations of compounds*

### *2.1. Compound **2***




**1** **2**

A solution of 1-decylimidazole (2.08 g, 10.0 mmol) (**1**) with excess trifluoroacetic acid in chloroform was stirred at room temperature for 10 seconds. Then the solvent was evaporated to yield **2** as a colorless oil (3.22 g, 100%). $^{1}$H NMR (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 8.80 (s, 1H), 7.42 (s, 1H), 7.17 (s, 1H), 4.17 (t, $J$ = 8.0 Hz, 2H), 1.95–1.82 (m, 2H), 1.33–1.26 (m, 14H), 0.88 (t, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 134.9, 120.8, 120.7, 49.5, 31.8, 30.2, 29.3, 29.2, 29.1, 28.8, 26.1, 22.6, 14.0. LRESIMS: *m*/*z* 209.2 $[M - CF_3COO]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M - CF_3COO]^+$ $C_{13}H_{25}N_2^+$, 209.20123; found 209.20118; error −0.2 ppm.

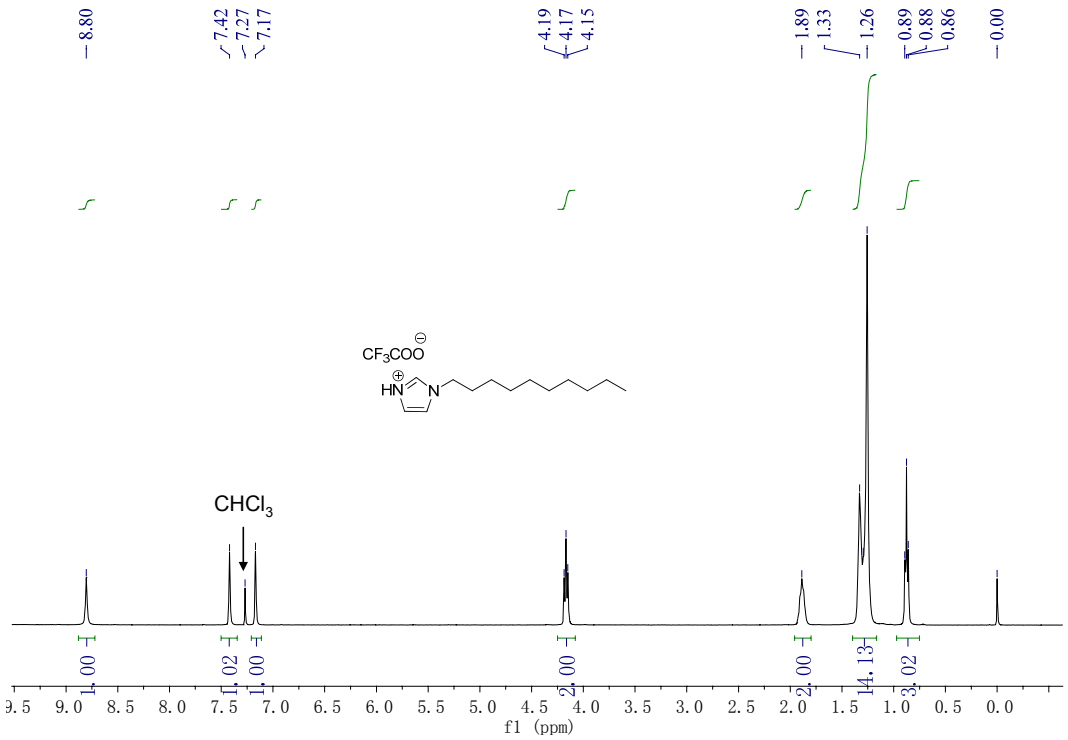



***Figure S1.*** $^{1}$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **2**.

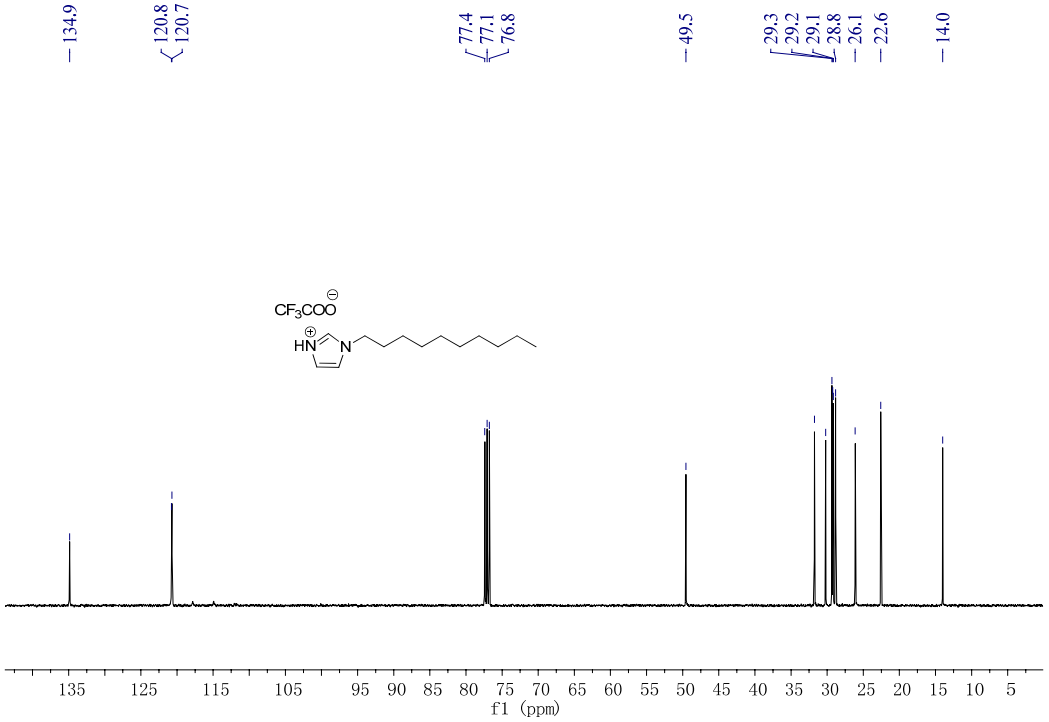



***Figure S2.*** $^{13}$C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of **2**.

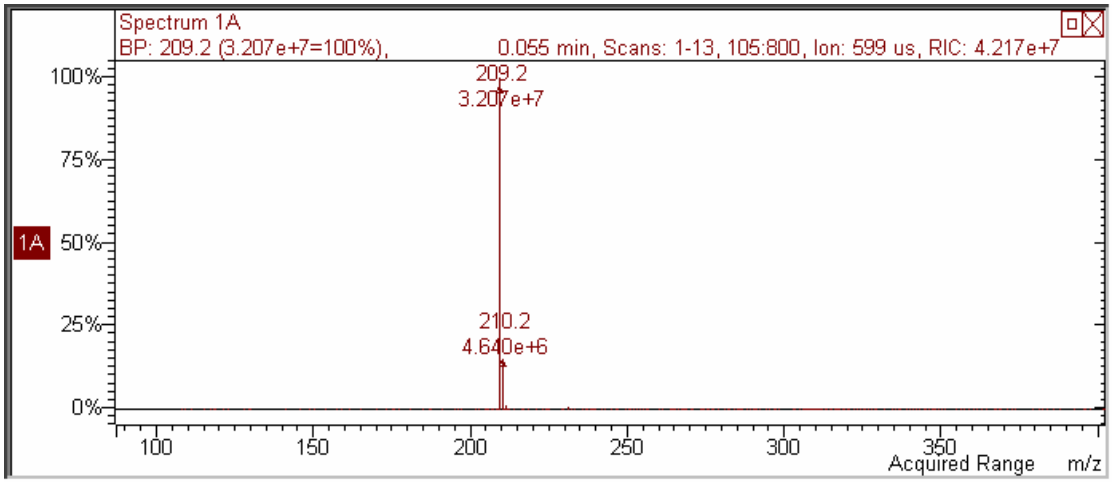
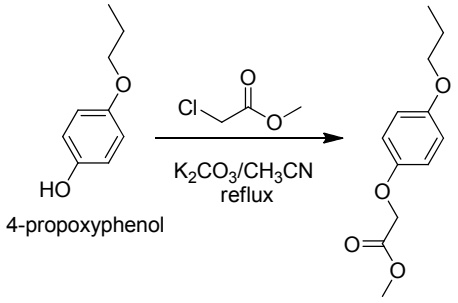



***Figure S3.*** Electrospray ionization mass spectrum of **2**. Assignment of main peak: *m*/*z* 209.2 $[M - CF_3COO]^+$ (100%).

*2.2. Compound* ***4***




**3** **4**

A mixture of **3** (24.0 g, 158 mmol), methyl chloroacetate (17.1 g, 158 mmol) and potassium carbonate (43.5 g, 315 mmol) in $CH_3CN$ (250 mL) was heated at reflux overnight under nitrogen atmosphere and then gradually cooled to room temperature. After filtration, the solvent was evaporated under vacuum. Then the residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate, 10:1) to give **4** (22.0 g, 63%) as a white solid. M.p. 46.6–47.2 °C. $^1$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 6.84–6.81 (m, 4H), 4.59 (s, 2H), 3.87 (t, $J$ = 8.0 Hz, 2H), 3.80 (s, 3H), 1.82–1.74 (m, 2H), 1.02 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 169.7, 154.1, 151.9, 115.8, 115.7, 115.5, 115.4, 70.0, 66.2, 52.1, 22.6, 10.5. LRESIMS: *m*/*z* 225.1 $[M + H]^+$ (100%), 242.1 $[M + NH_4]^+$ (9%), 247.0 $[M + Na]^+$ (20%). HRESIMS: *m*/*z* calcd for $[M + Na]^+$ $C_{12}H_{16}O_4Na$, 247.0946; found 247.0948; error 0.8 ppm.

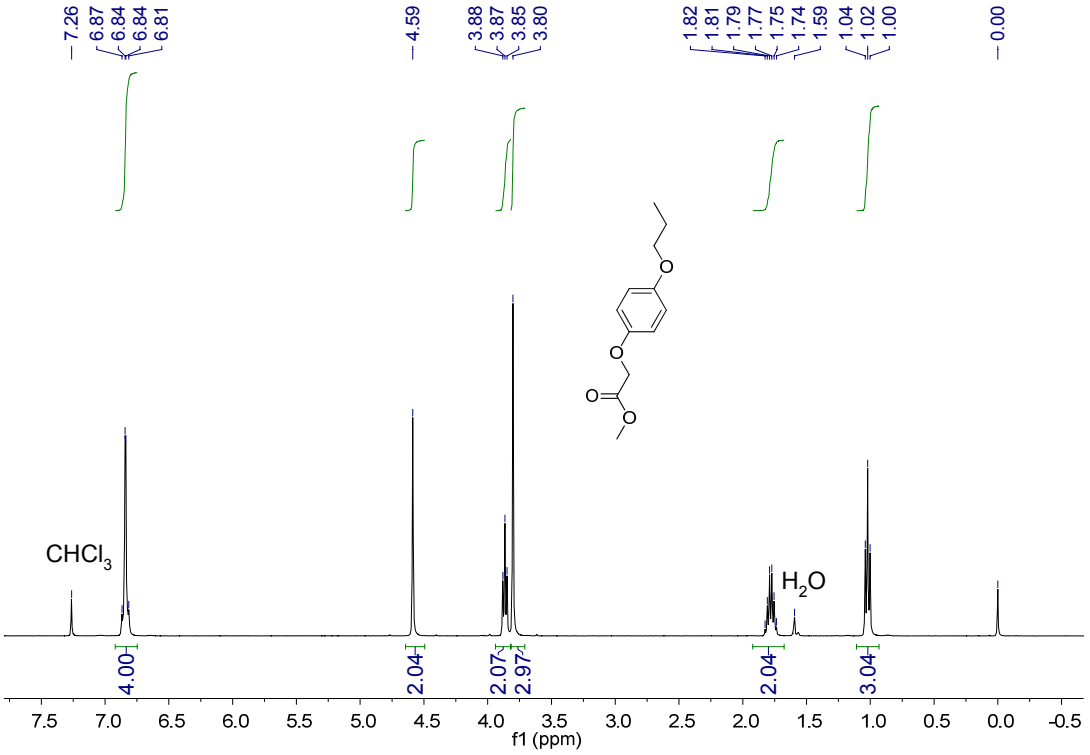



***Figure S4.*** [1]H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **4**.

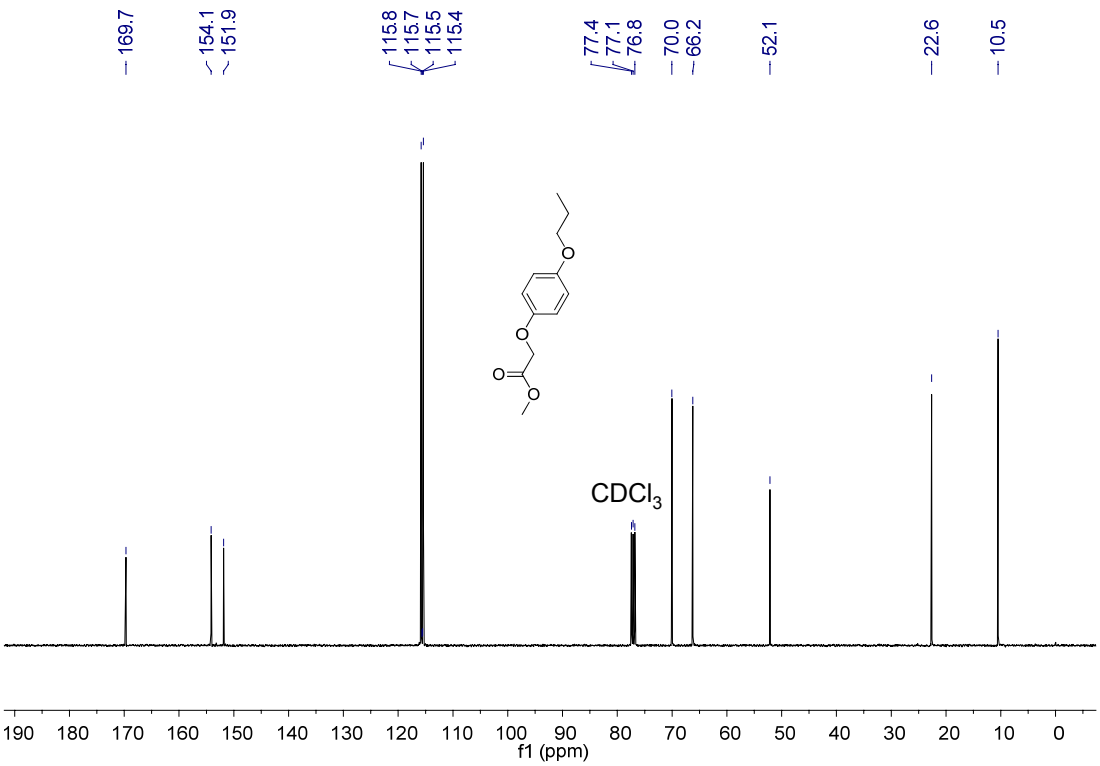



***Figure S5.*** [13]C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of **4**.

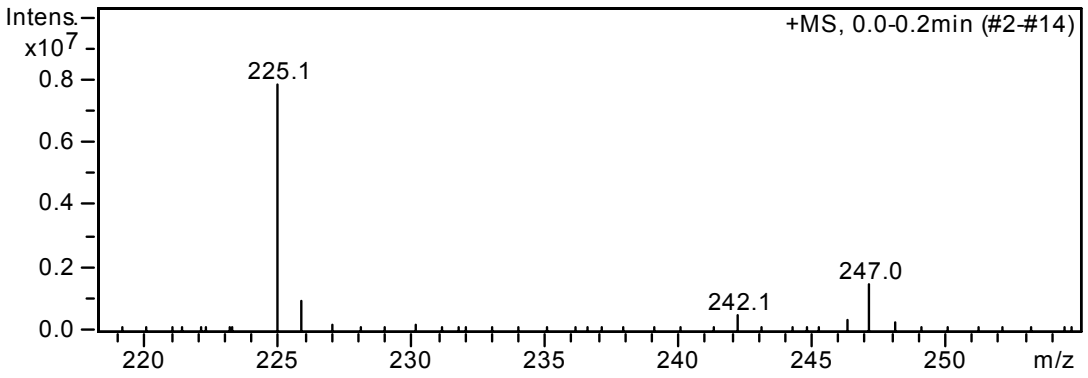
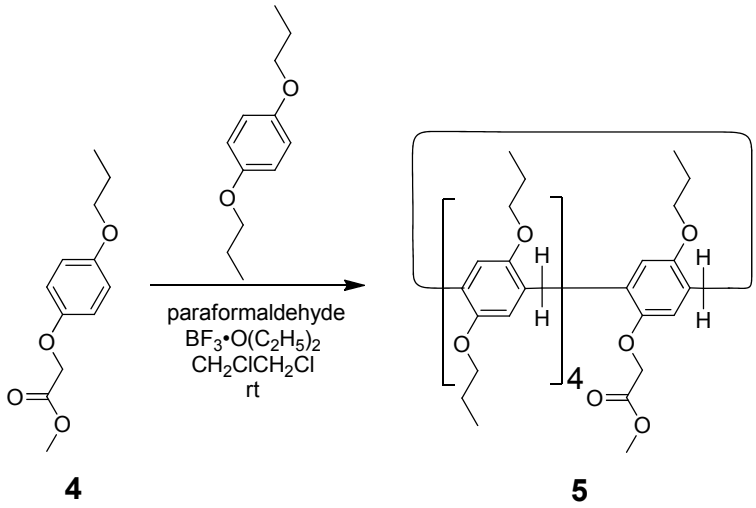



***Figure S6.*** Electrospray ionization mass spectrum of **4**. Assignment of main peaks: *m*/*z* 225.1 $[M + H]^+$ (100%), 242.1 $[M + NH_4]^+$ (9%), and 247.0 $[M + Na]^+$ (20%).

*2.3. Compound **5***




A mixture of 1,4-dipropoxybenzene (17.5 g, 90.0 mmol), **4** (2.30 g, 10.0 mmol), and paraformaldehyde (3.10 g, 100 mmol) in 1,2-dichloroethane (800 mL) was stirred at room temperature for 30 min. After the addition of $BF_3{\cdot}O(C_2H_5)_2$ (12.5 mL, 100 mmol), the mixture was stirred for 4 hours. The solvent was removed in vacuo. Then the resultant residue was dissolved in $CH_2Cl_2$ (100 mL) and washed with water (100 mL × 3). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated to afford the crude product, which was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate, 500:1 to 100:1) to give **5** (2.10 g, 20%) as a white solid.

M.p. 109.7–112.0 °C. $^{1}$H NMR (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 6.91–6.69 (m, 10H), 4.49 (s, 2H), 3.87–3.79 (m, 28H), 2.84 (s, 3H), 1.87–1.73 (m, 16H), 1.72–1.66 (m, 2H), 1.08–1.01 (m, 24H), 0.97 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 169.8, 151.1, 150.0, 149.8, 149.7, 149.6, 149.5, 148.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.4, 115.6, 115.4, 115.1, 115.0, 114.7, 114.4, 113.4, 70.1, 70.0, 69.9, 69.8, 65.3, 51.3, 30.9, 29.8, 29.5, 29.0, 28.4, 23.2, 23.1, 22.9, 10.9, 10.8, 10.7. LRESIMS: *m*/*z* 1079.1 $[M + H_3O]^+$ (100%), *m*/*z* 1084.0 $[M + Na]^+$ (26%), *m*/*z* 1100.0 $[M + K]^+$ (52%). HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{65}H_{88}O_{12}^+$, 1060.6276; found 1060.6270; error –0.6 ppm.

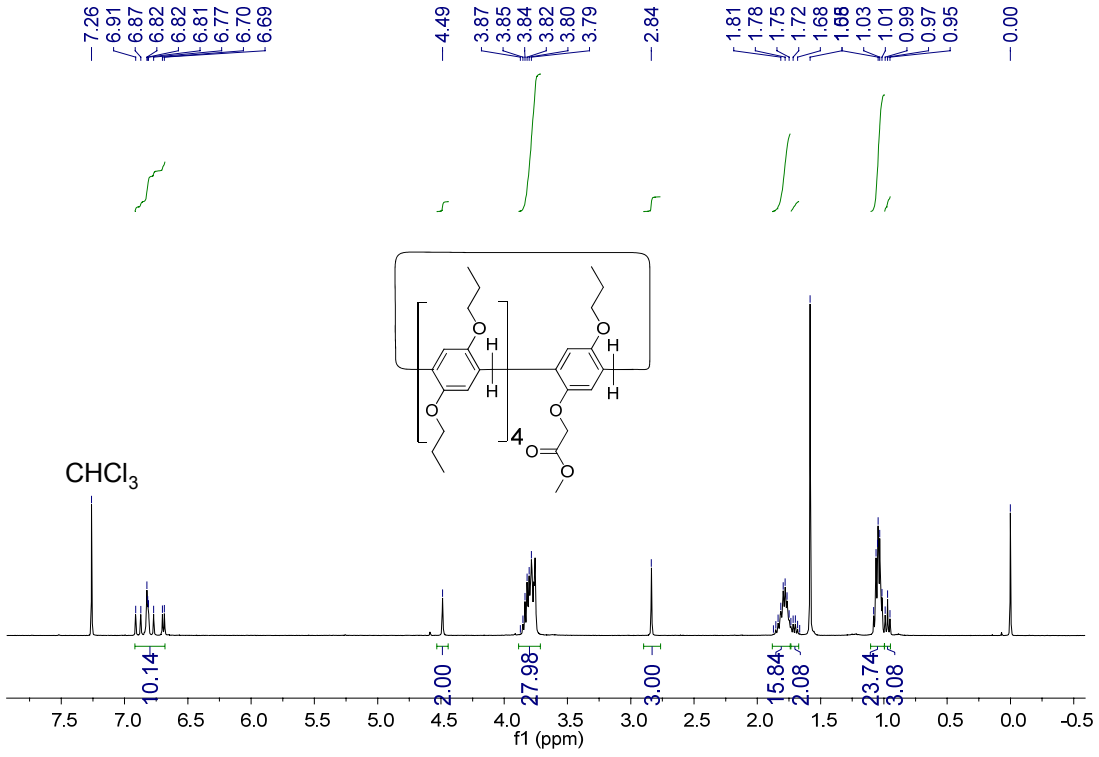



***Figure S7.*** $^{1}$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **5**.

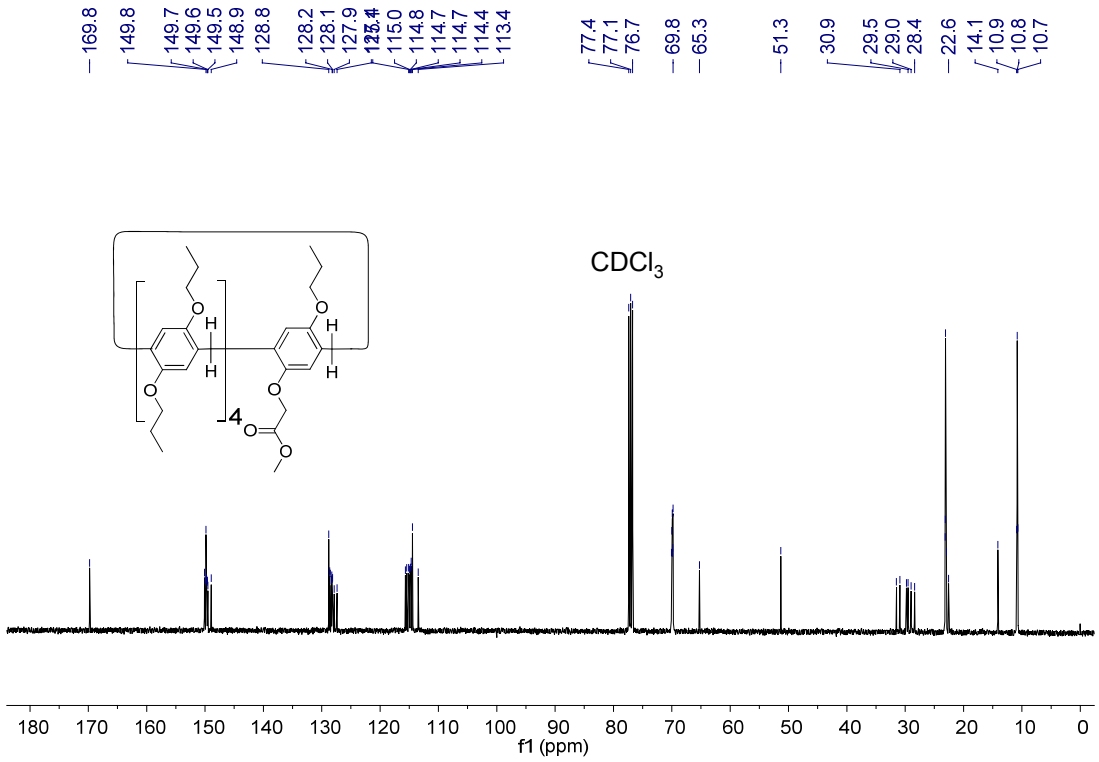



***Figure S8.*** $^{13}$C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of **5**.

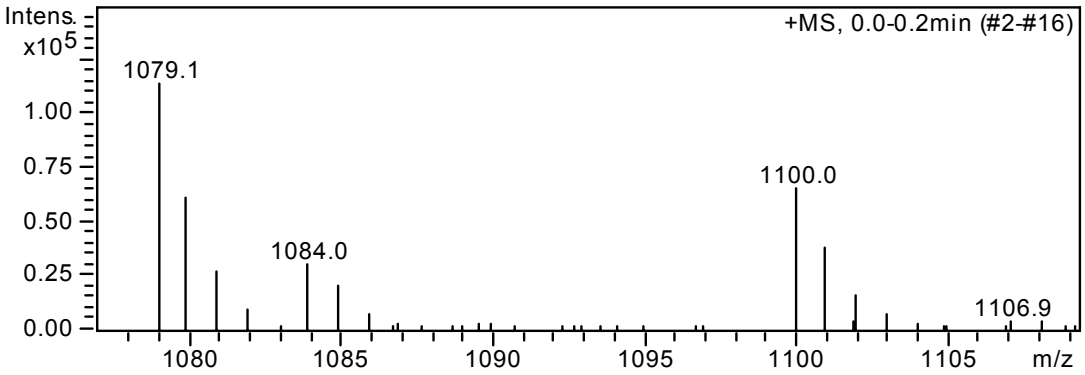
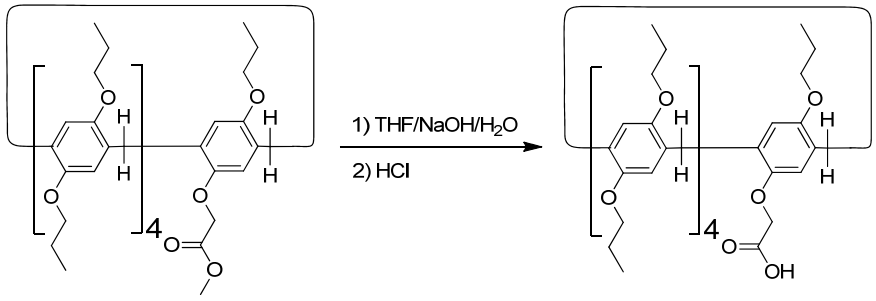



***Figure S9.*** Electrospray ionization mass spectrum of **5**. Assignment of main peaks: *m*/*z* 1079.1 $[M + H_3O]^+$ (100%), 1084.0 $[M + Na]^+$ (26%), and 1100.0 $[M + K]^+$ (52%).

*2.4. Compound* ***6***




**5** **6**

A solution of **5** (2.10 g, 2.00 mmol) and 20% aqueous NaOH (20.0 mL) in THF (100 mL) was stirred at 65 °C for 4 hours. After cooling, the solution was treated with 30 mL of 4 M HCl (aqueous). The mixture was concentrated, washed with water and air dried to give **6** as a white solid (2.04 g, 99%). M.p. 124.3–125.7 °C. $^{1}$H NMR (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 6.84–6.62 (m, 10H), 4.35 (s, 2H), 3.88–3.69 (m, 28H), 1.86–1.66 (m, 16H), 1.61–1.55 (m, 2H), 1.08–0.93 (m, 24H), 0.88–0.84 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 150.9, 150.0, 149.9, 149.8, 149.8, 148.1, 129.0, 128.7, 128.4, 128.2, 128.1, 127.9, 115.2, 115.1, 114.9, 114.8, 114.5, 70.2, 70.1, 70.0, 69.9, 69.8, 65.7, 30.3, 30.1, 29.6, 29.3, 23.1, 23.0, 22.8, 10.8, 10.7, 10.6. LRESIMS: $m/z$ 1046.0 $[M - H]^-$ (100%). HRESIMS: $m/z$ calcd for $[M + Na]^+$ $C_{64}H_{86}NaO_{12}^+$, 1069.6017; found 1069.5976; error −3.8 ppm.

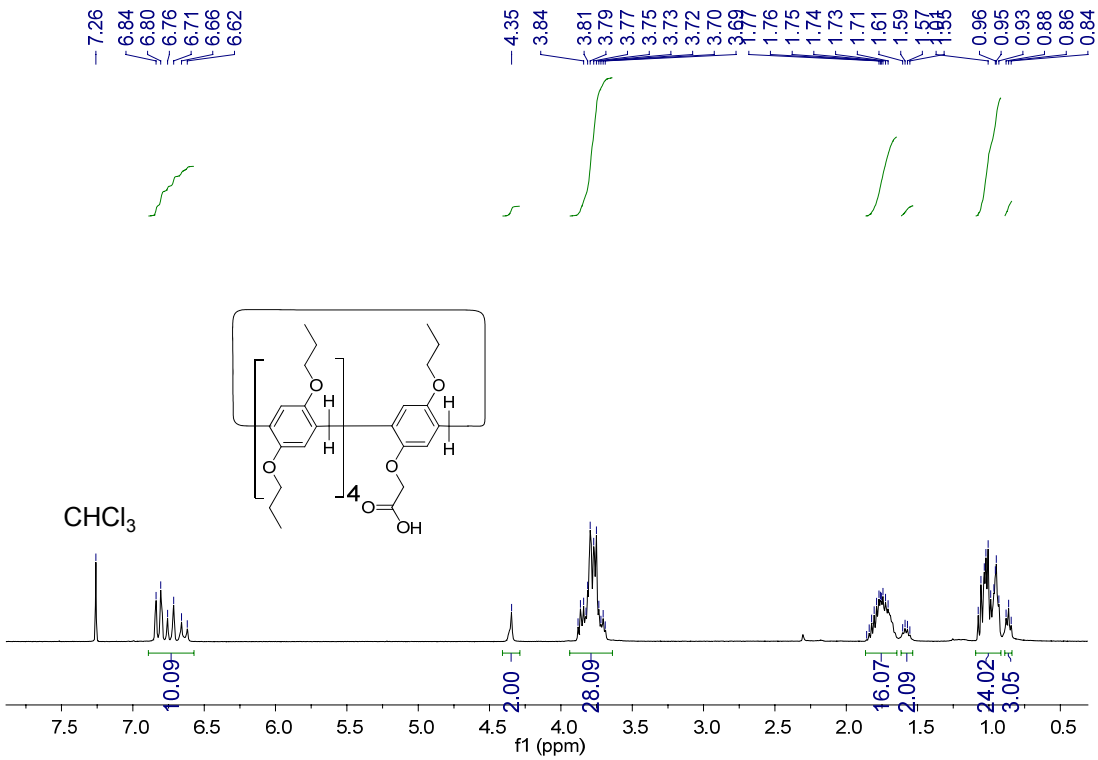



***Figure S10.*** $^{1}$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **6**.

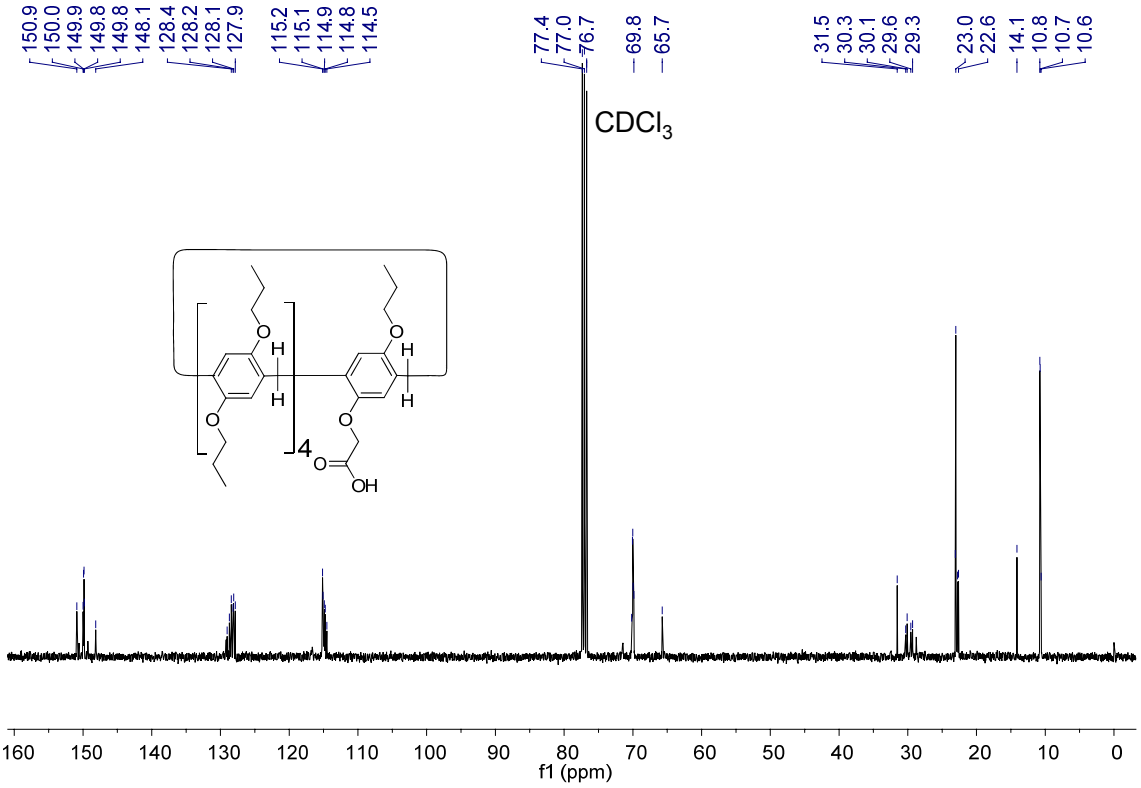



***Figure S11.*** $^{13}$C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of **6**.

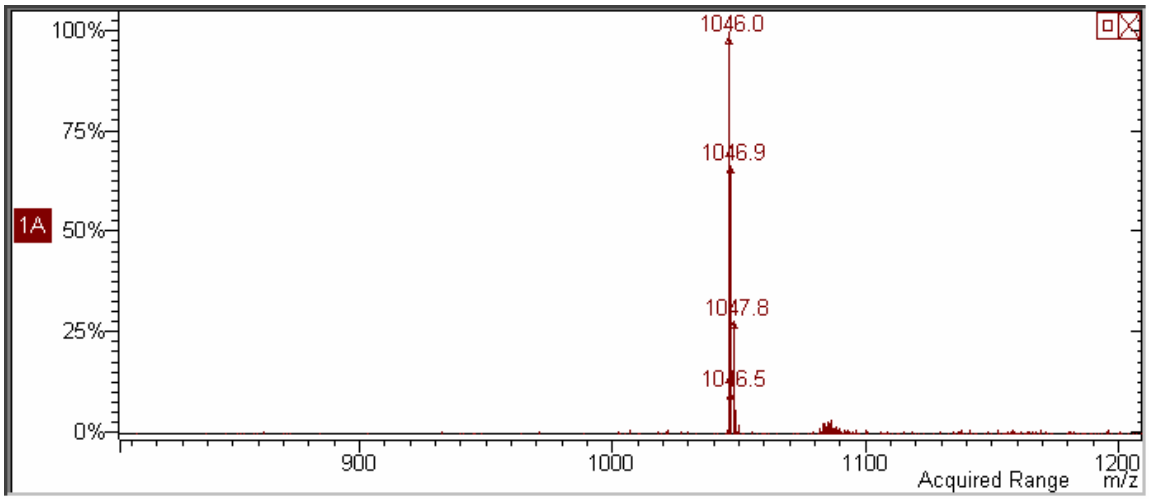
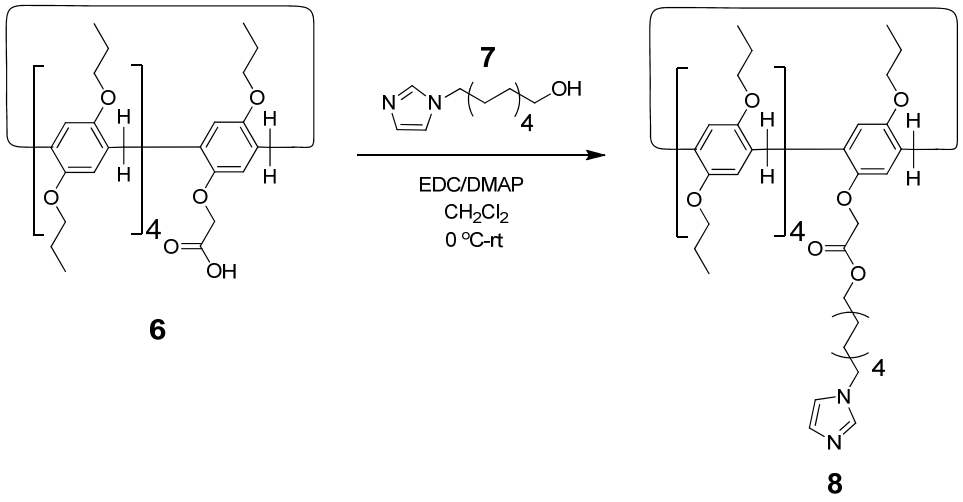



***Figure S12.*** Electrospray ionization mass spectrum of **6**. Assignment of main peak: *m*/*z* 1046.0 $[M - H]^-$ (100%).

*2.5. Compound **8***




A solution of **6** (1.58 g, 1.51 mmol), **7** (0.339 g, 1.51 mmol), EDC (0.579 g, 3.02 mmol) and DMAP (catalytic amount) in dry dichloromethane (20 mL) was stirred at 0 °C overnight. The solvent was removed in vacuo. The residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate, 10:1 to 3:1) to give **8** (1.59 g, 84%) as a white solid. M.p. 201.7–202.7 °C. $^1$H NMR (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 7.12 (s, 1H), 7.08 (s, 1H), 6.93–6.73 (m, 10H), 6.48 (s, 1H),

4.56 (s, 2H), 3.94–3.66 (m, 30H), 3.32 (b, 1H), 2.40 (b, 2H), 1.91–1.67 (m, 18H), 1.15–1.08 (m, 27H), 0.75 (b, 4H), 0.48 (b, 2H), 0.37 (b, 2H), 0.24 (b, 2H), –0.15 (b, 3H), –0.55 (b, 2H), –0.72 (b, 2H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 169.2, 149.9, 149.8, 149.7, 149.6, 148.5, 136.7, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 118.7, 115.6, 114.8, 114.4, 114.2, 70.0, 69.8, 69.7, 65.7, 64.8, 46.3, 29.9, 29.8, 29.5, 29.2, 29.0, 28.6, 27.9, 23.4, 23.3, 11.1, 10.9, 10.8. LRESIMS: *m*/*z* 1254.3 $[M + H]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M + H]^+$ $C_{77}H_{109}N_2O_{12}^+$, 1253.7975; found 1253.7946; error −2.3 ppm.

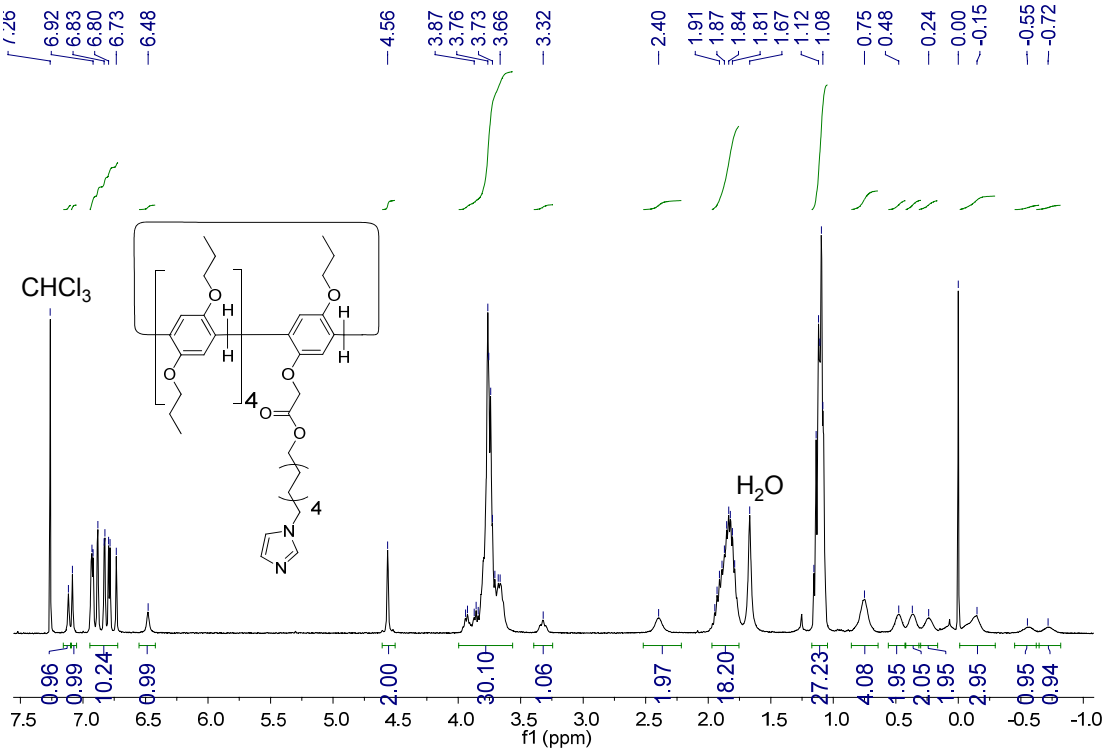



***Figure S13.*** $^1$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of 8.00 mM **8**.

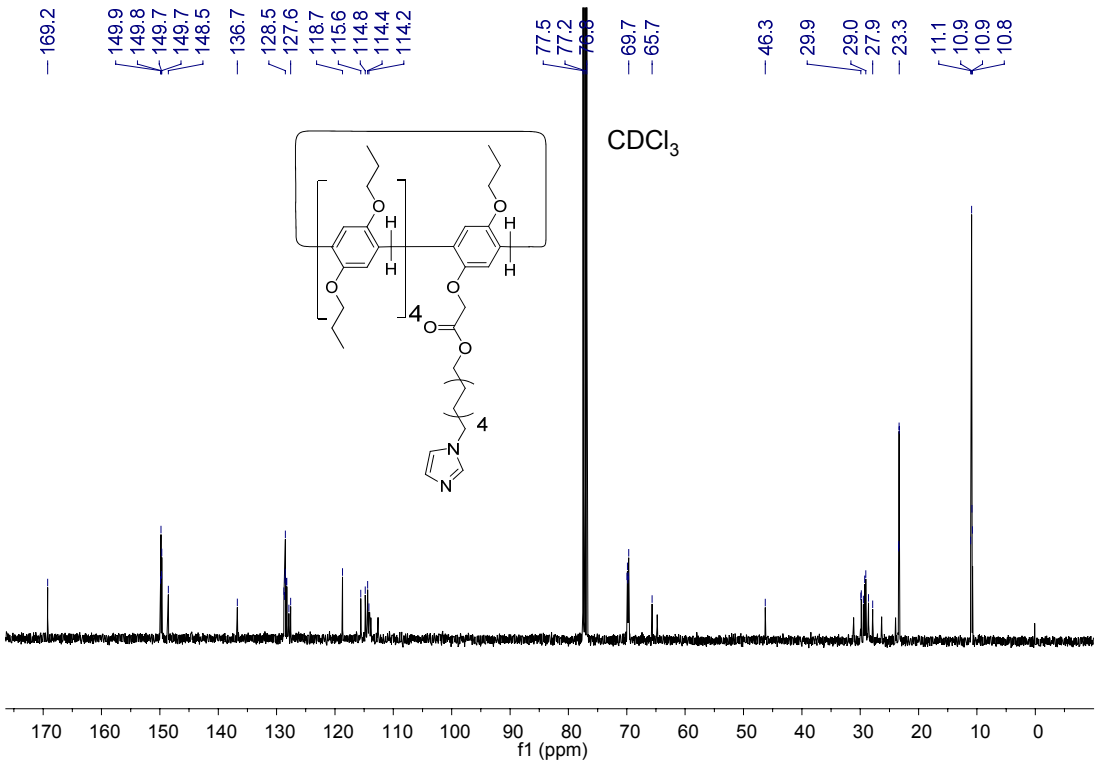



***Figure S14.*** $^{13}$C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of 20.0 mM **8**.

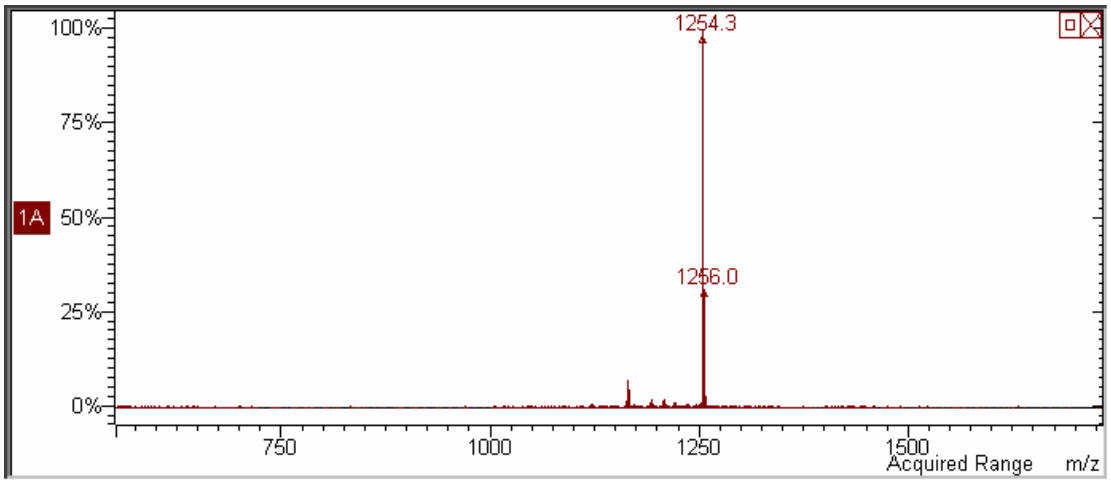
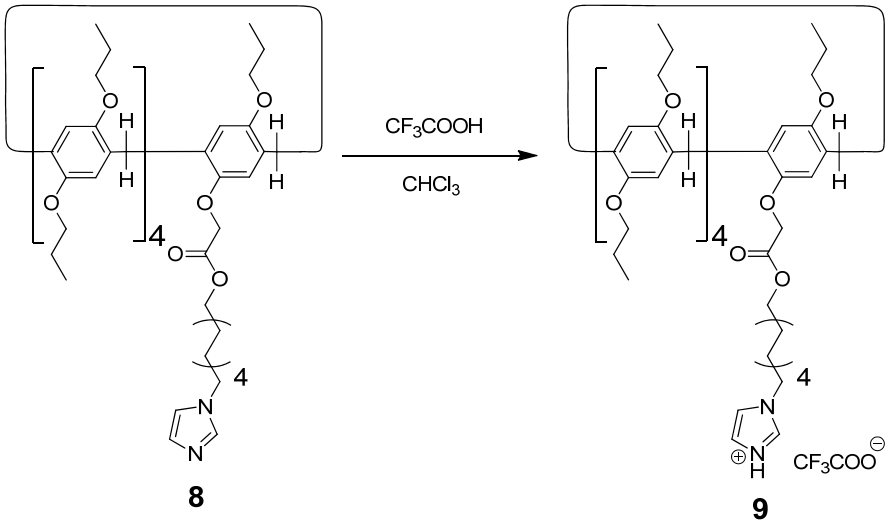



***Figure S15.*** Electrospray ionization mass spectrum of **8**. Assignment of main peak: *m*/*z* 1254.3 $[M + H]^+$ (100%).

*2.6. Compound* ***9***




**8** **9**

A solution **8** (2.00 g, 1.60 mmol) in chloroform with excess trifluoroacetic acid was stirred at room temperature for 10 seconds. The solvent was evaporated to give **9** as a white soild (2.18 g, 99%). M.p. 210.5–211.6 °C. $^{1}$H NMR (400 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 7.31 (s, 1H), 7.22 (s, 1H), 7.00–6.75 (m, 10H), 5.48 (s, 1H), 4.89 (b, 1H), 4.50–4.41 (m, 2H), 4.03 (b, 1H), 3.93–3.66 (m, 32H), 2.02–1.77 (m, 18H), 1.71 (b, 2H), 1.52–1.40 (m, 4H), 1.18–1.04 (m, 27H), 0.57 (b, 2H), 0.28–0.24 (m, 2H), –0.28 (b, 2H), –1.48 (b, 2H). $^{13}$C NMR (100 MHz, chloroform-*d*, room temperature) $\delta$ (ppm): 168.2, 150.3, 150.2, 149.9, 149.6, 148.1, 131.9, 129.5, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 120.5, 118.6, 115.4, 115.3, 115.0, 114.8, 114.7, 114.6, 113.6, 70.9, 70.8, 70.7, 70.6, 70.2, 70.0, 69.9, 65.2, 65.1, 46.4, 30.0, 29.3, 29.1, 28.9, 28.4, 27.8, 27.4, 27.3, 26.4, 25.7, 24.0, 23.4, 23.3, 23.0, 22.9, 11.0, 10.7, 10.6, 10.6. LRESIMS: *m*/*z* 1254.0 $[M - CF_3COO]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M - CF_3COO]^+$ $C_{77}H_{109}N_2O_{12}^+$, 1253.7975; found 1253.7927; error −3.8 ppm.

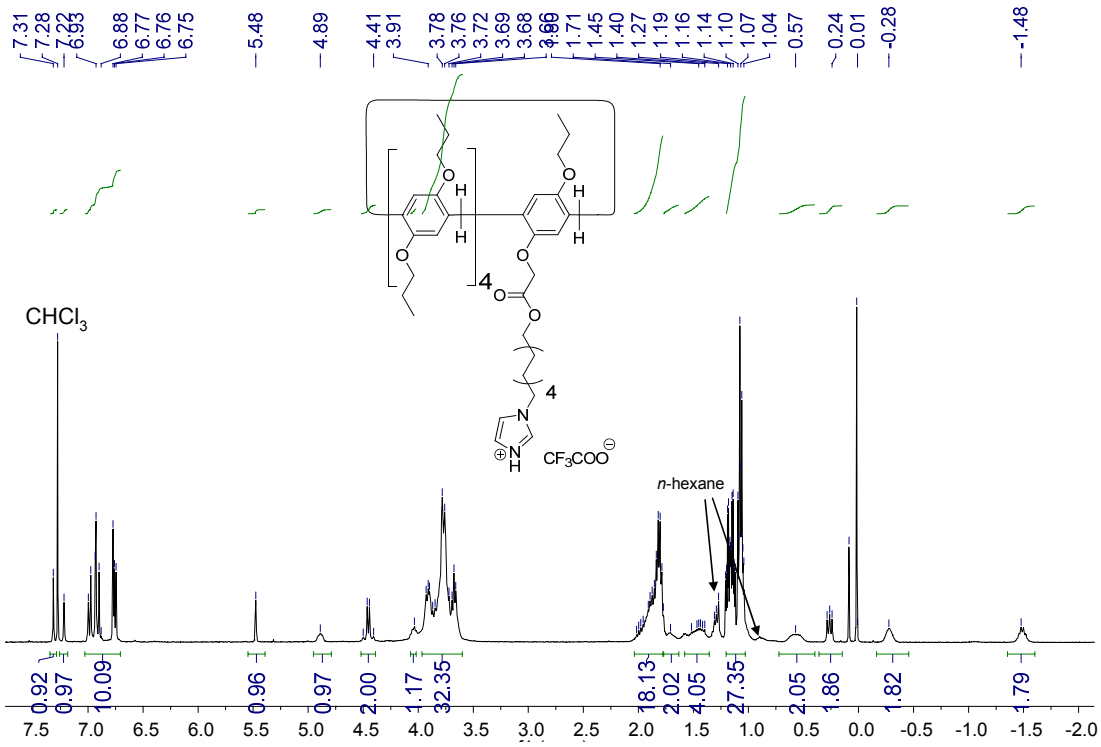



***Figure S16.*** $^{1}$H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of 8.00 mM **9**.

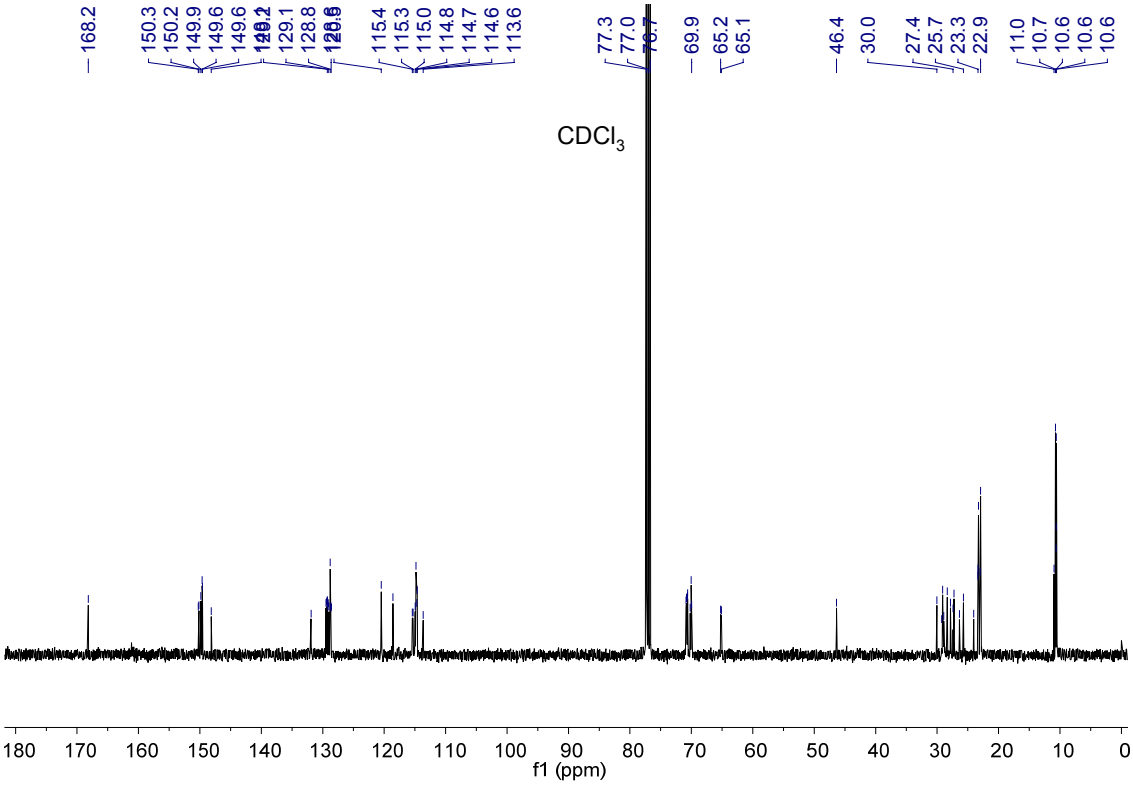



***Figure S17.*** $^{13}$C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of 20.0 mM **9**.

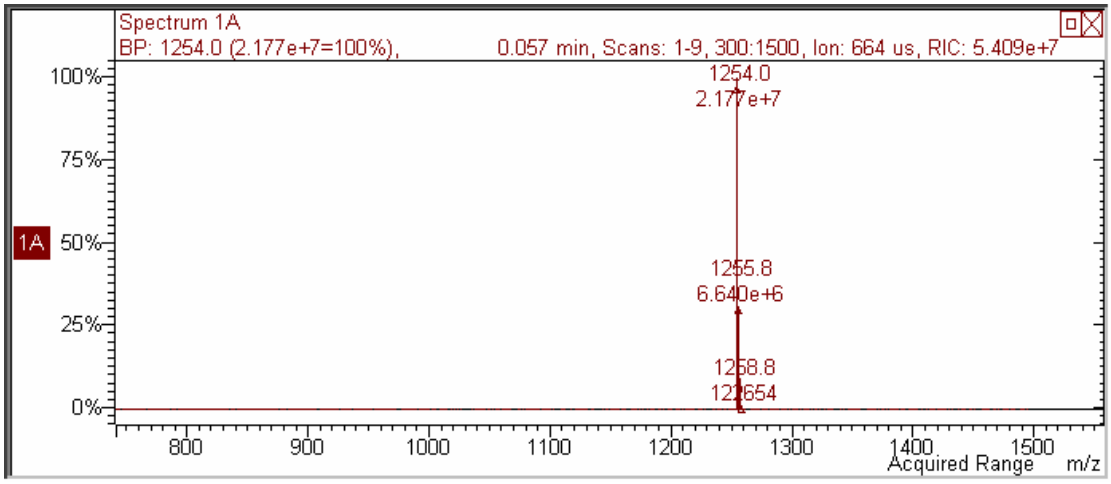



***Figure S18.*** Electrospray ionization mass spectrum of **9**. Assignment of main peak: *m*/*z* 1254.0 $[M - CF_3COO]^+$ (100%).

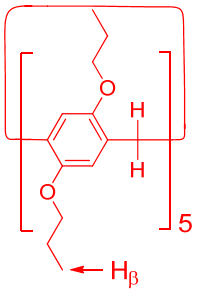
*3. Stoichiometry and association constant determination for the complexations between **10** and **1** and between **10** and **2***

To determine the stoichiometry and association constant between **10** and **1** (or **2**), proton NMR titrations were done with solutions which had a constant concentration of dipropylpillar[5]arene (**10**, 2.00 mM) and varying concentrations of **1** (or **2**). By a non-linear curve-fitting method, the association constant of **1**⊃**10** was determined to be $(2.3 \pm 0.2) \times 10^2$ $M^{-1}$, which is about 50 times lower than the association constant of **2**⊃**10** $(1.0 \pm 0.3) \times 10^4$ in chloroform. By mole ratio plots, 1:1 stoichiometry was obtained for both **1**⊃**10** and **2**⊃**10**.

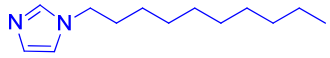
The non-linear curve-fitting was based on the equation:[S4]

$$\Delta\delta = (\Delta\delta_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of $H_\beta$ on **10** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of $H_\beta$ when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **1** (or **2**). The errors were obtained from the non-linear curve-fitting.




**10**




**1**

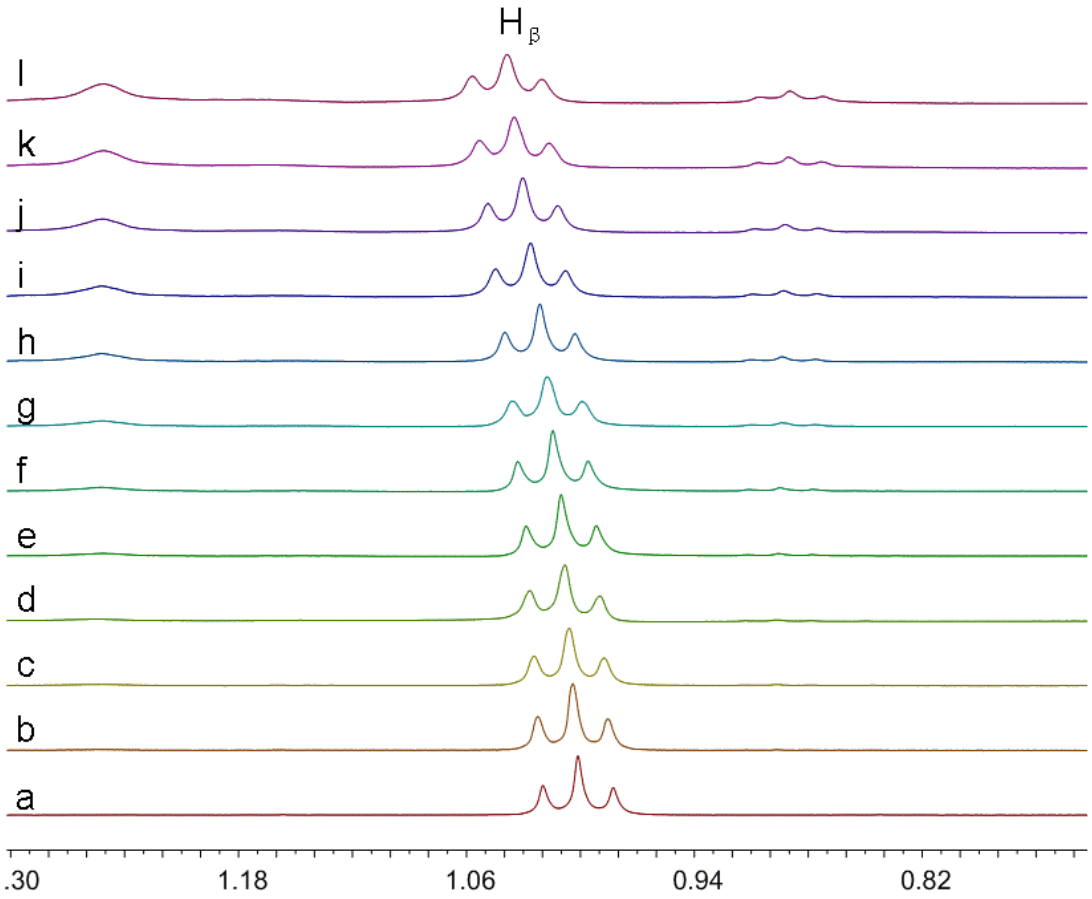



***Figure S19***. Partial $^{1}$H NMR spectra (400 MHz, chloroform-*d*, room temperature) of **10** at a concentration of 2.00 mM upon addition of **1** (10.0 mM): (a) 0.00 mM; (b) 0.196 mM; (c) 0.385 mM; (d) 0.566 mM; (e) 0.741 mM; (f) 1.15 mM; (g) 1.53 mM; (h) 1.87 mM; (i) 2.48 mM; (j) 3.01 mM; (k) 3.87 mM; (l) 4.54 mM.

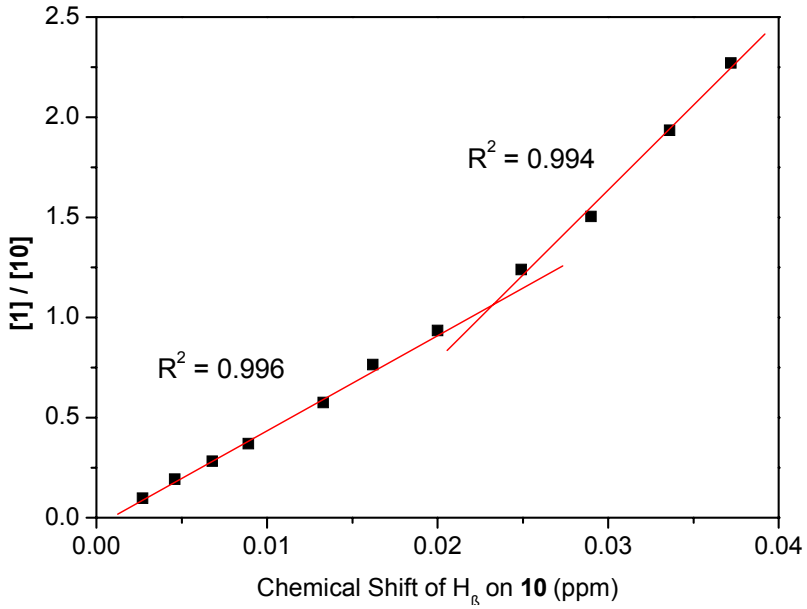



***Figure S20***. Mole ratio plot for **10** and **1**, indicating a 1:1 stoichiometry. The concentration of **10** is 2.00 mM. The concentrations of **1** (from left to right) are 0.196 mM, 0.385 mM, 0.566 mM, 0.741 mM, 1.15 mM, 1.53 mM, 1.87 mM, 2.48 mM, 3.01 mM, 3.87 mM, and 4.54 mM, respectively.

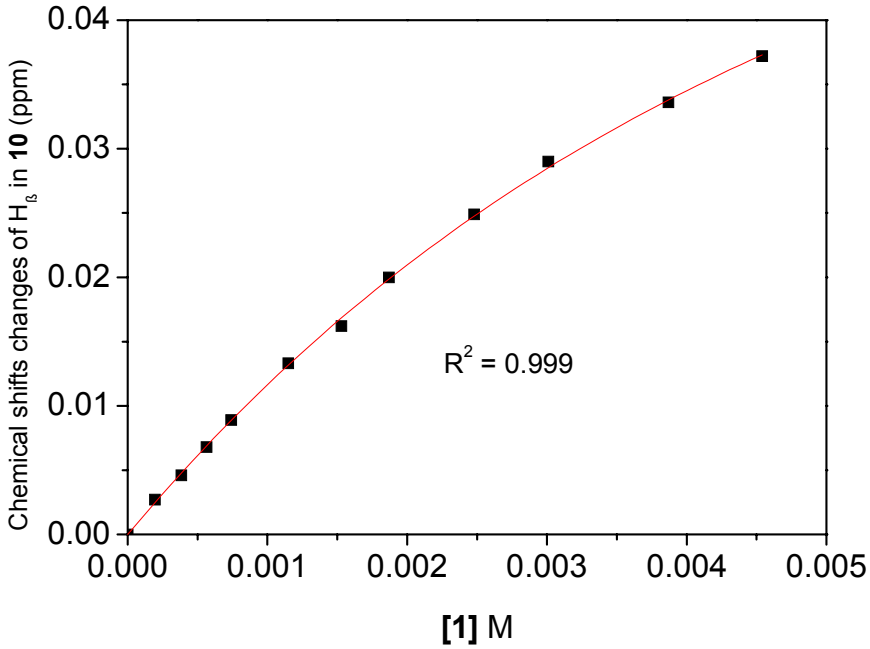
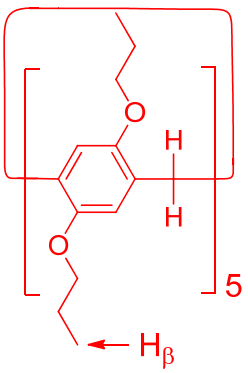



***Figure S21***. The chemical shift changes of $H_\beta$ on **10** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The association constant ($K_a$) of **10**⊃**1** was estimated to be about $(2.3 \pm 0.2) \times 10^2\ M^{-1}$. $[\mathbf{10}]_0 = 2.00$ mM.




**10**


**2**

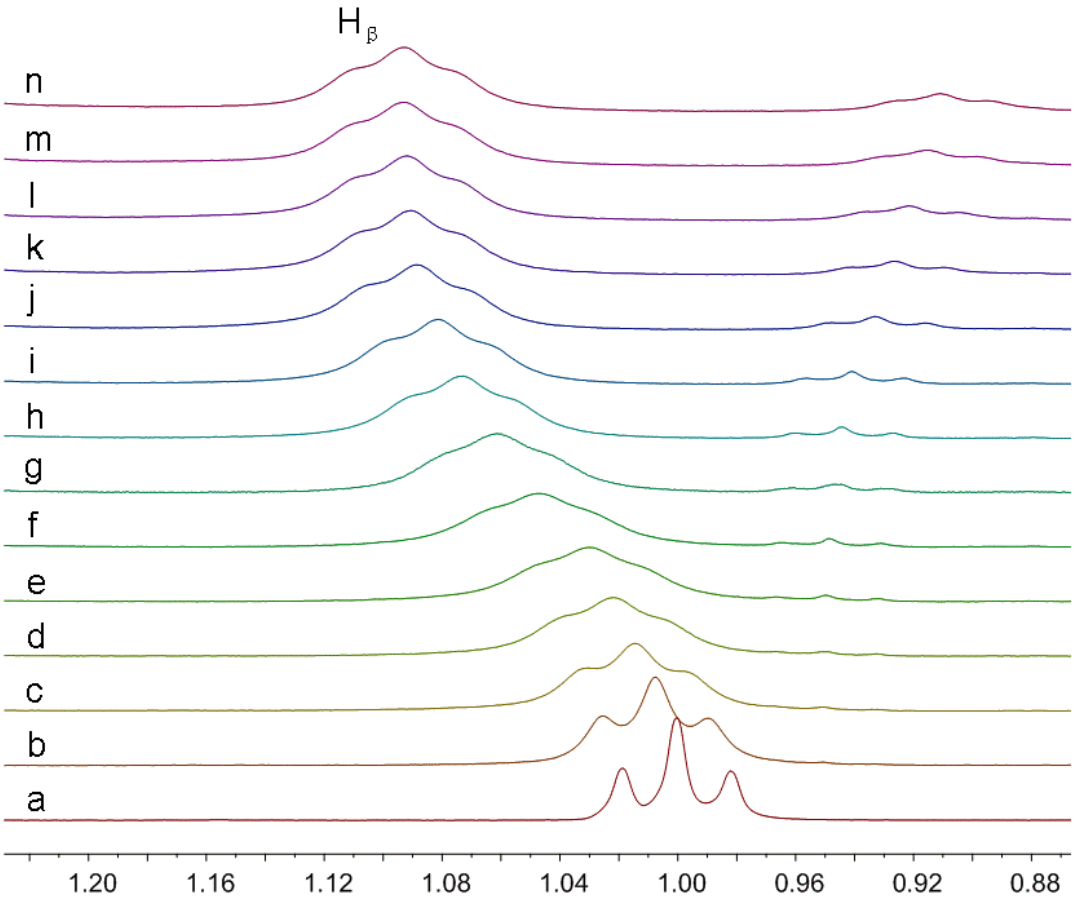



***Figure S22***. Partial $^{1}$H NMR spectra (400 MHz, chloroform-*d*, room temperature) of **10** at a concentration of 2.00 mM upon addition of **2** (10.0 mM): (a) 0.00 mM; (b) 0.196 mM; (c) 0.385 mM; (d) 0.566 mM; (e) 0.741 mM; (f) 1.15 mM; (g) 1.53 mM; (h) 1.87 mM; (i) 2.19 mM; (j) 2.75 mM; (k) 3.24 mM; (l) 3.67 mM; (m) 4.38 mM; (n) 4.95 mM.

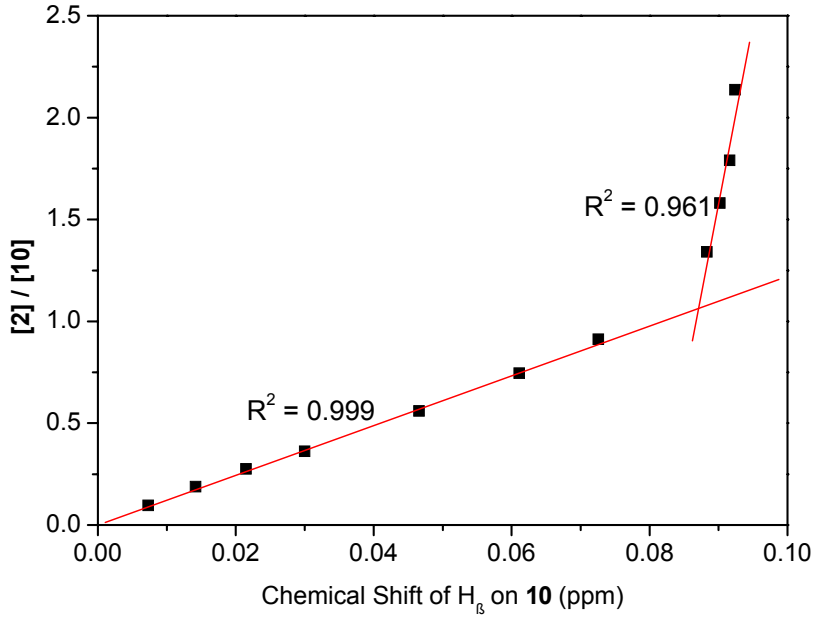



***Figure S23***. Mole ratio plot for **10** and **2**, indicating a 1:1 stoichiometry. The concentration of **10** is 2.00 mM. The concentrations of **2** (from left to right) are 0.196 mM, 0.385 mM, 0.566 mM, 0.741 mM, 1.15 mM, 1.53 mM, 1.87 mM, 2.19 mM, 2.75 mM, 3.24 mM, and 3.67 mM, respectively.

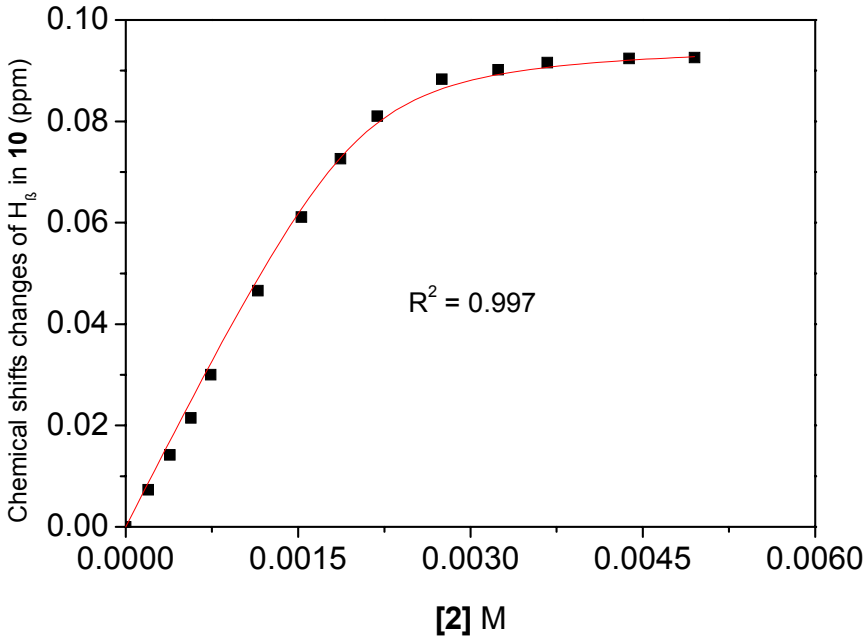



***Figure S24***. The chemical shift changes of $H_\beta$ on **10** upon addition of **2**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The association constant ($K$) of **10**⊃**2** was estimated to be about $(1.0 \pm 0.3) \times 10^4$ $M^{-1}$. $[\mathbf{10}]_0$ = 2.00 mM.

*4. Partial 2-D COSY spectrum of a chloroform-d solution of 40.0 mM* ***8***

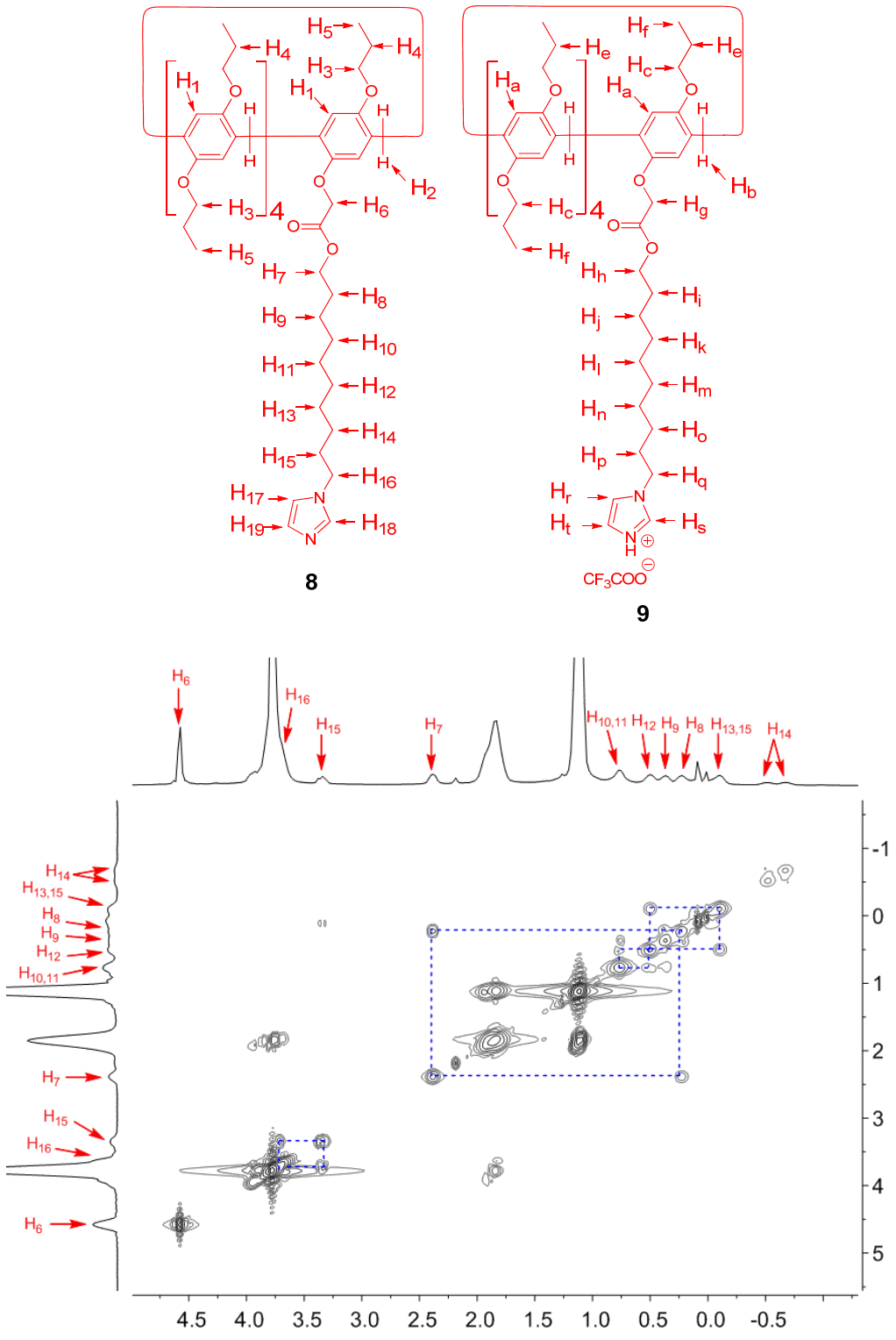



***Figure S25***. Partial 2-D COSY spectrum of a chloroform-*d* solution of 40.0 mM **8**.

*5. Full 2-D NOESY spectrum of a chloroform-d solution of 40.0 mM* ***8***

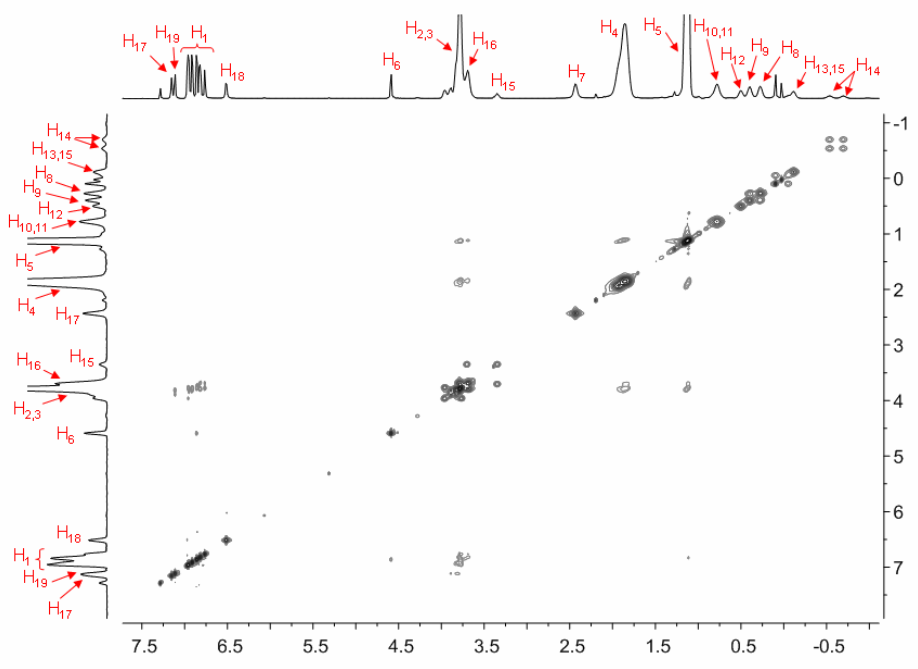



***Figure S26***. Full 2-D NOESY spectrum of a chloroform-*d* solution of 40.0 mM **8**.

*6. Partial 2-D COSY spectrum of a chloroform-d solution of 40.0 mM* ***9***

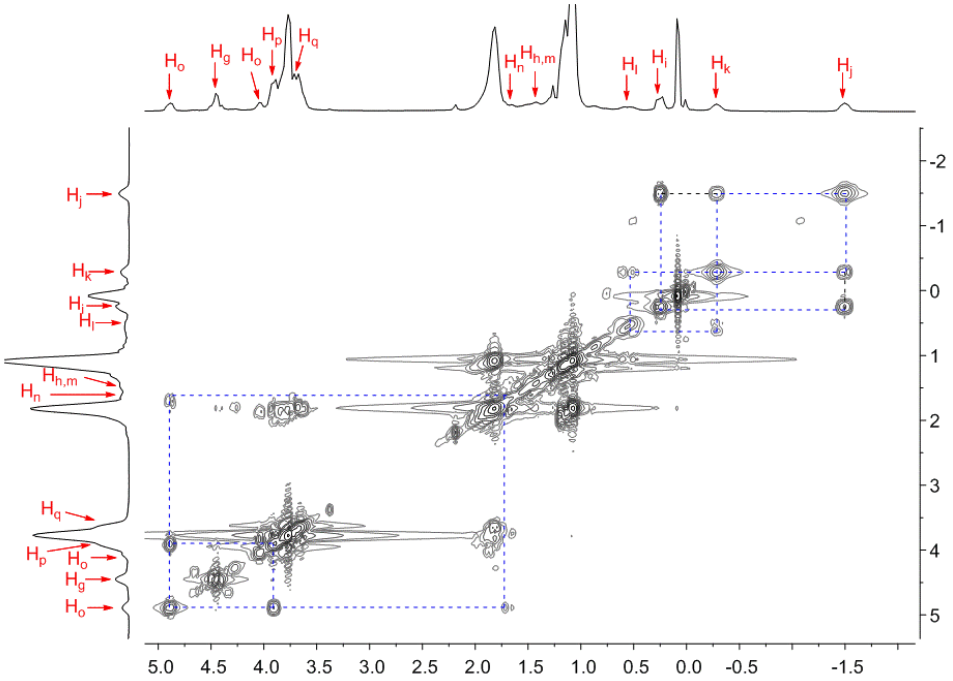



***Figure S27***. Partial 2-D COSY spectrum of a chloroform-*d* solution of 40.0 mM **9**.

*7. Full 2-D NOESY spectrum of a chloroform-d solution of 40.0 mM* ***9***

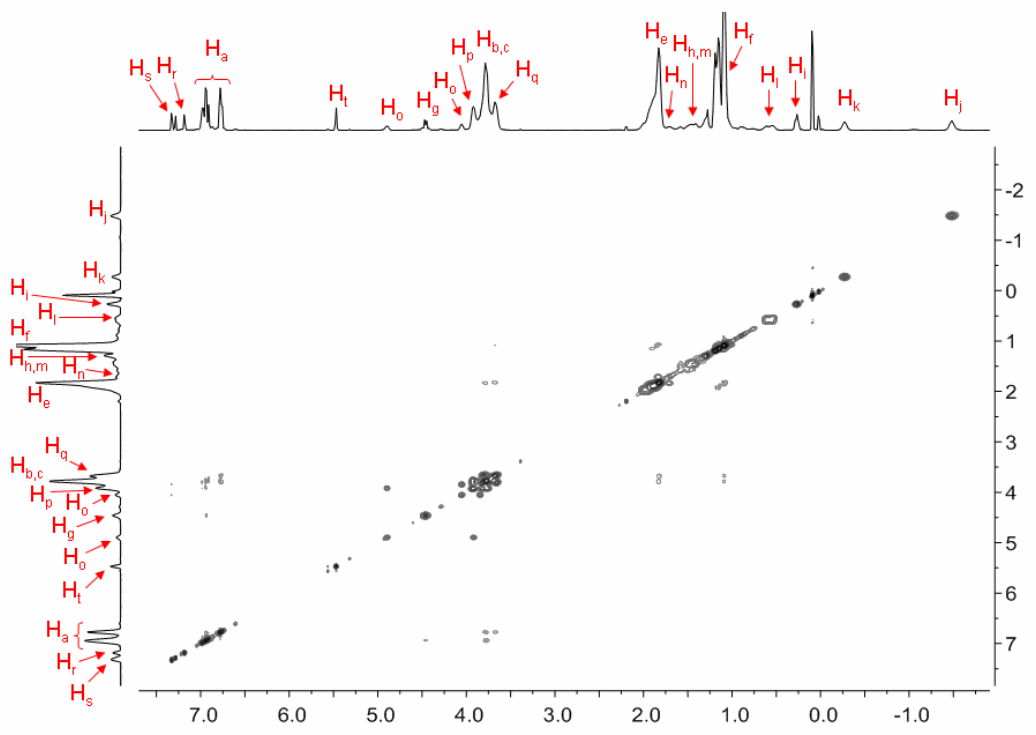



***Figure S28***. Full 2-D NOESY spectrum of a chloroform-d solution of 40.0 mM **9**.

*8. Calculated values of maximum polymerization degree n at different concentrations of **8** and **9***

Using the Carothers equation[S5] and assuming that the same average association constant holds for each successive step (isodesmic) and that cyclic species can either be ignored or taken into account, the average degree of polymerization, $n$, is easily derived as being related to the equilibrium constant $K_a$ and the initial monomer concentration as follows:[S6]

$n = 1/(1 - p)$ (1)

If we now define $p$ = extent of complexation,

$K_a = p[H]_0/(1 - p)^2[H]_0^2$.

Solving this quadratic equation leads to

$1 - p = \{(1 + 4K_a[H]_0)^{1/2} - 1\} / 2K_a[H]_0$

$n = 1/(1 - p) = 2K_a[H]_0/\{(1 + 4K_a[H]_0)^{1/2} - 1\}$ (2)

if $4K_a[H]_0 \gg 1$, $n = 2K_a[H]_0/\{(4K_a[H]_0)^{1/2} - 1\}$ and

if $(4K_a[H]_0)^{1/2} \gg 1$, $n = (K_a[H]_0)^{1/2}$ (3)

In this system $p$ is the extent of complexation and $[H]_0 = [\mathbf{8}]_0$ (or $[H]_0 = [\mathbf{9}]_0$). Therefore, degrees of polymerization calculated in this way represent maximum values that in practice will be reduced by formation of cyclics and possibly by reduction in the association constant as the suprapolymer grows ("attenuation"). As the concentration increases, the calculated size of aggregates increases to large values. For example, at $[\mathbf{9}]_0 = 400$ mM, $p = 98.2\%$ and $n_{max} = 1 / (1 - p) = 56$, indicating the formation of aggregates of increasing size. Here the association constant values of model systems **1**⊃**10** and **2**⊃**10** were used in the calculations with Eqs. 2 and 3.

*Table S1*. Calculated values of $p$ and $n$ at different concentrations of monomer **9**.

| [monomer **9**]$_0$ (mM) | $p$[a] | $n_{max}$ (Eq. 1)[b] | $n_{max}$ (Eq. 2) | $n_{max}$ (Eq. 3) |
|---|---|---|---|---|
| 2.00 | 0.779 ± 0.002 | 4.52 ± 0.05 | 5.00 ± 0.67 | 4.47 ± 0.68 |
| 8.00 | 0.879 ± 0.002 | 8.26 ± 0.16 | 9.46 ± 1.36 | 8.94 ± 1.36 |
| 33.0 | 0.951 ± 0.002 | 20 ± 1 | 18.7 ± 2.8 | 18.2 ± 2.8 |
| 133.0 | 0.960 ± 0.002 | 25 ± 1 | 37.0 ± 5.5 | 36.5 ± 5.5 |
| 200 | 0.974 ± 0.002 | 38 ± 3 | 45.2 ± 6.8 | 44.7 ± 6.8 |
| 400 | 0.982 ± 0.002 | 56 ± 6 | 63.7 ± 9.6 | 63.2 ± 9.6 |

[a] Calculated from $p = \Delta/\Delta_0$; error bars reflect a potential error of 0.0003 ppm in $\Delta$; the maximum chemical shift change of $H_f$ was estimated to be 0.0628 ppm (Fig. S29) using a chloroform-*d* solution with 0.200 mM of **9** and 40.0 mM of **2**.[S7] [b] Calculated from $n = 1/(1 - p)$.

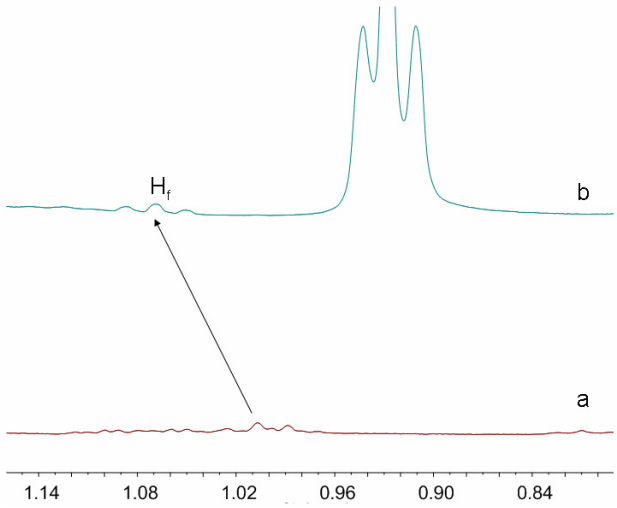



***Figure S29***. Partial $^1$H NMR spectra (400 MHz, chloroform-*d*, room temperature): (a) 0.200 mM **9**; (b) 0.200 mM **9** and 40.0 mM **2**.

*Table S2.* Calculated values of $p$ and $n$ at different concentrations of monomer **8**.

| [monomer **8**]$_0$ (mM) | $p$[a] | $n_{max}$ (Eq. 1)[b] | $n_{max}$ (Eq. 2) | $n_{max}$ (Eq. 3) |
|---|---|---|---|---|
| 2.00 | 0.346 ± 0.005 | 1.53 ± 0.01 | 1.34 ± 0.02 | 0.678 ± 0.030 |
| 8.00 | 0.441 ± 0.005 | 1.79 ± 0.02 | 1.94 ± 0.06 | 1.36 ± 0.06 |
| 33.0 | 0.572 ± 0.005 | 2.34 ± 0.03 | 3.30 ± 0.12 | 2.75 ± 0.12 |
| 133.0 | 0.765 ± 0.005 | 4.26 ± 0.10 | 6.05 ± 0.24 | 5.53 ± 0.24 |
| 200 | 0.894 ± 0.005 | 9.43 ± 0.49 | 7.30 ± 0.29 | 6.78 ± 0.30 |
| 400 | 0.933 ± 0.005 | 15 ± 1 | 10.1 ± 0.4 | 9.59 ± 0.42 |

[a] Calculated from $p = \Delta/\Delta_0$; error bars reflect a potential error of 0.0003 ppm in $\Delta$; the maximum chemical shift change of $H_5$ was estimated to be 0.0549 ppm (Fig. S30) using a chloroform-*d* solution with 0.200 mM of **8** and 40.0 mM of **1**.[S7] [b] Calculated from $n = 1/(1 - p)$.

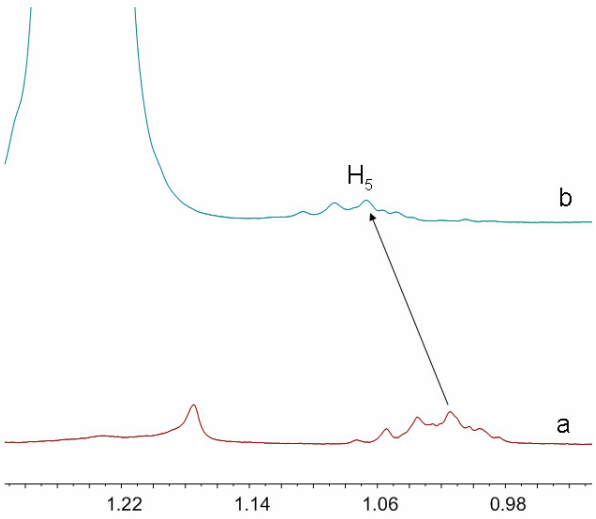



***Figure S30***. Partial $^1$H NMR spectra (400 MHz, chloroform-*d*, room temperature): (a) 0.200 mM **8**; (b) 0.200 mM **8** and 40.0 mM **1**.

9. *References*:

S1. M. Lee, U. H. Choi, S. Wi, C. Slebodnick, R. H. Colby and H. W. Gibson, *J. Mater. Chem.*, 2011, **21**, 12280.

S2. T. Eliseeva, M. J. Panzner, W. J. Youngs and C. A. Tessier, *J. Organomet. Chem.*, 2010, **695**, 1057.

S3. S. De, V. K. Aswal and S. Ramakrishnan, *Langmuir*, 2010, **26**, 17882.

S4. K. A. Connors, Binding Constants; Wiley: New York, 1987. P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999. 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; Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang and H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*., 1998, 1807.

S5. C. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 39.

S6. (a) H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522; (b) F. Huang, D. S. Nagvekar, X. Zhou and H. W. Gibson, *Macromolecules*, 2007, **40**, 3561.

S7. N. Yamaguchi, D. S. Nagvekar and H. W. Gibson, *Angew. Chem., Int. Ed.*, 1998, **37**, 2361.