Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Pillar[n]arenes (n = 8-10) with Two Cavities: Synthesis, Structures and Complexing Properties

Xiao-Bo Hu,[1] Zhenxia Chen,[1] Lei Chen,[1] Ling Zhang,[2] Jun-Li Hou,[*,1] and Zhan-Ting Li[1]

[1] Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China
[2] Honeywell Integrated Technology (China) Co. Ltd., 430 Li Bing Road, Shanghai, 201203, China

*To whom correspondence should be addressed: houjl@fudan.edu.cn

Contents:

1. General:

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz with a Mercury plus 400 spectrometer at 298 K. Chemical shifts were referenced to $CHCl_3$ residue (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR). Mass spectra were recorded with Bruker MicroTOF II spectrometer. 1,4-diethoxybenzene and paraformaldehyde were obtained from Alfa Aesar. For single crystal growing, PA[8], PA[9] and PA[10] (2-5 mg) were respectively dissolved in acetonitrile, DMF, and acetone (0.3 ml). The single crystals were obtained by slow evaporation the solutions under 20 ^{o}C for 2-4 weeks. For the all three crystals, the data sets were treated with the SQUEEZE program to remove highly disordered solvent molecules. The crystallographic formulae include the number of solvent molecules suggested by the SQUEEZE program.

2. Synthetic procedure for PA[n] (n = 5-10):

To the solution of 1,4-diethoxybenzene (6.00 g, 36 mmol) in chloroform (300 ml) was added paraformaldehyde (1.08 g, 36 mmol). The suspension was stirred at 25 ^{o}C for 20 min to crush the large paraformaldehyde particles. And then, boron trifluoride diethyl etherate (4.5 ml, 36 mmol) was added to the solution. After continuing stirred at 25 ^{o}C for 20 min, the reaction was quenched by addition of water. The organic phase was separated and washed with saturated aqueous $NaHCO_3$, H_2O, and brine. The crude product was purified by column chromatograph (CH_2Cl_2/petroleum ether) to yield PA[5] (CH_2Cl_2/petroleum ether = 1 : 1, R_f = 0.2, 1.28 g, 20%), PA[6] (CH_2Cl_2/petroleum ether = 4 : 1, R_f = 0.3, 0.96 g, 15%), PA[7] (CH_2Cl_2/petroleum ether = 10 : 1, R_f = 0.3, 192 mg, 3%), PA[8] (CH_2Cl_2/petroleum ether = 30 : 1, R_f = 0.3, 64 mg, 1%), PA[9] (CH_2Cl_2/petroleum ether = 50 : 1, R_f = 0.2, 126 mg, 2%), and PA[10] (CH_2Cl_2/petroleum ether = 100 : 0, R_f = 0.2, 130 mg, 2%) as white solids.

3. Characterization data and spectra for PA[n] (n = 5-10):

PA[5][1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.72 (s, 10 H), 3.83 (q, J = 6.4 Hz, 20 H), 3.76 (s, 10 H), 1.26 (t, J = 6.4 Hz, 30 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.8, 128.4, 115.0, 63.7, 29.8, 15.1.

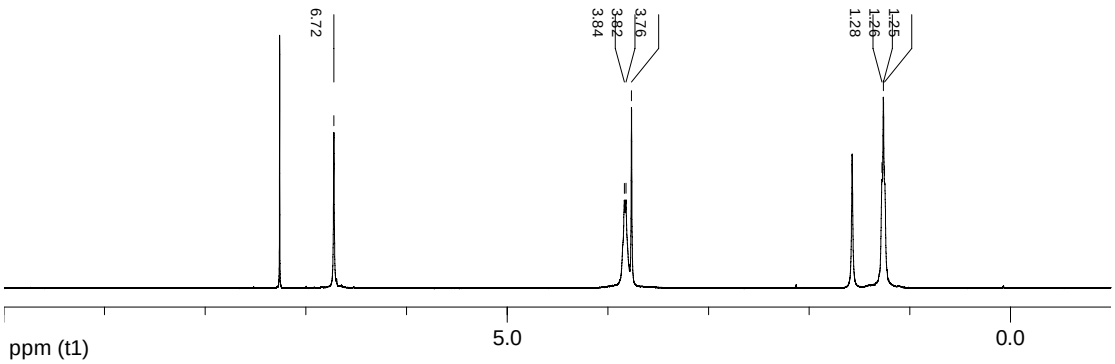

Figure S1. ^{1}H NMR spectrum of PA[5] in $CDCl_3$.

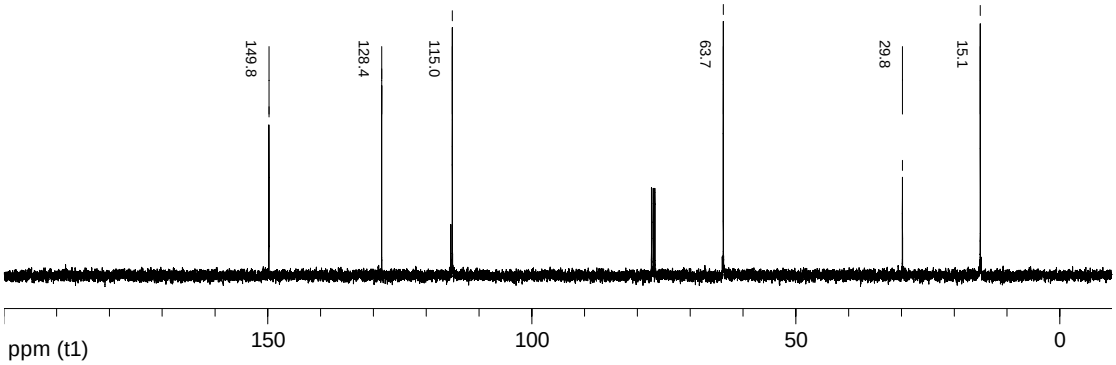

Figure S2. ^{13}C NMR spectrum of PA[5] in $CDCl_3$.

PA[6][1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.69 (s, 12 H), 3.83 (q, J = 6.4 Hz, 24 H), 3.79 (s, 12 H), 1.28 (t, J = 6.4 Hz, 36 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.4, 127.8, 115.2, 64.0, 30.9, 15.2.

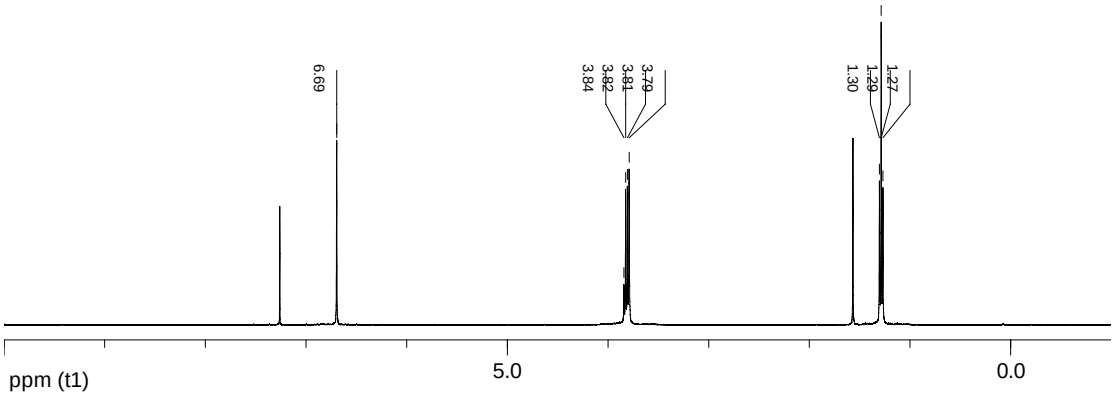

Figure S3. ^{1}H NMR spectrum of PA[6] in $CDCl_3$.

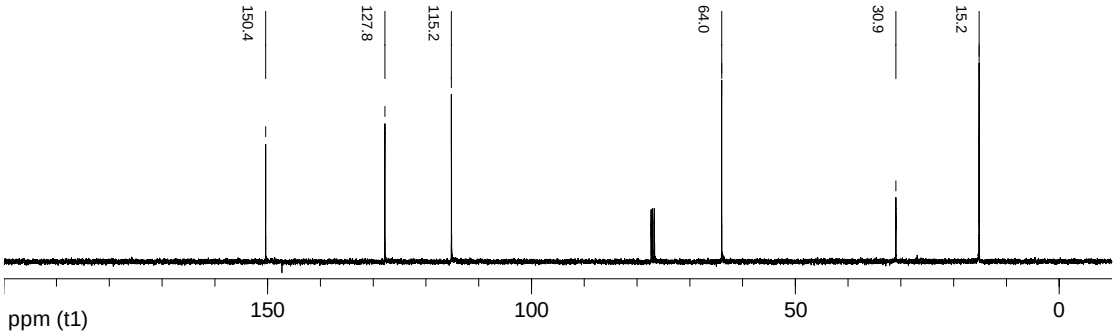

Figure S4. ^{13}C NMR spectrum of PA[6] in $CDCl_3$.

PA[7]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.63 (s, 14 H), 3.83 (s, 14 H), 3.79 (q, J = 6.4 Hz, 28 H), 1.22 (t, J = 6.4 Hz, 42 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.6, 127.9, 115.2, 64.2, 31.0, 15.1. MS (ESI): *m/z* 1269 $[M+Na]^+$, HR-MS (ESI-TOF): Calcd. for $C_{77}H_{98}O_{14}Na$: 1269.6854. Found: 1269.6822.

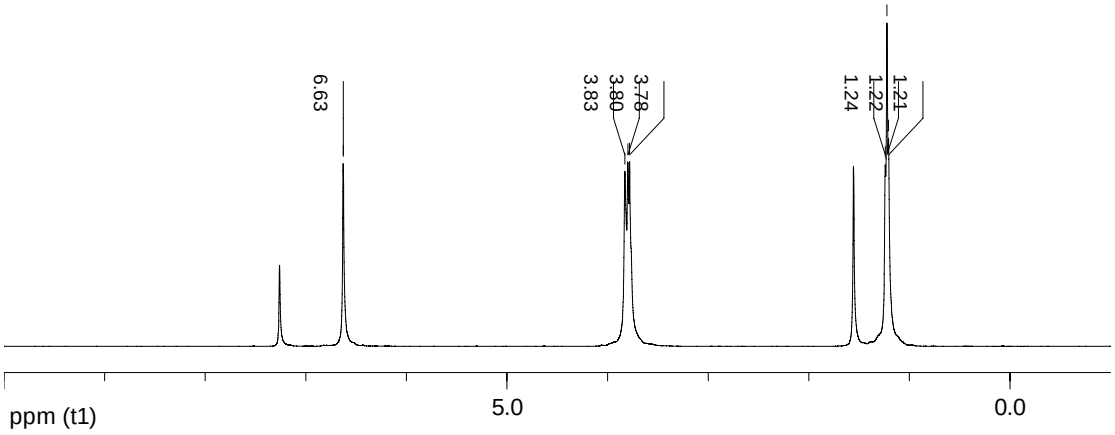

Figure S5. ^{1}H NMR spectrum of PA[7] in $CDCl_3$.

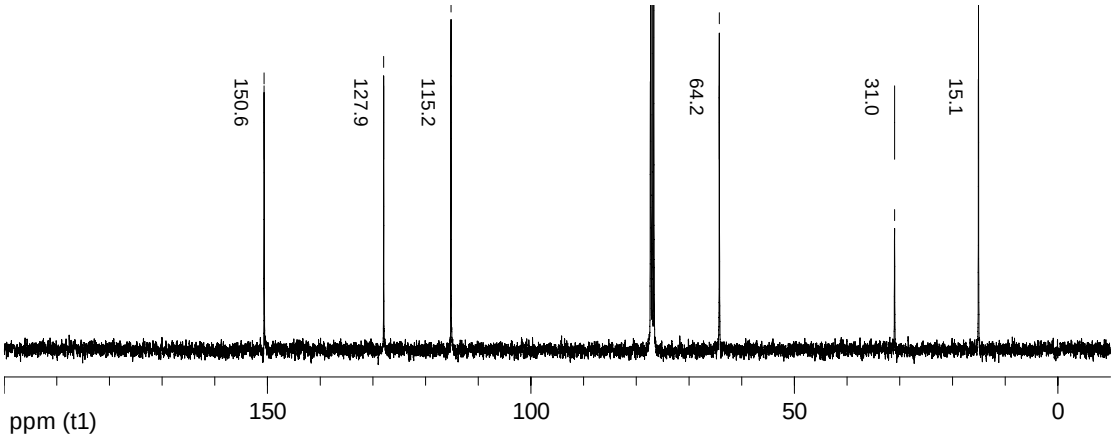

Figure S6. ^{13}C NMR spectrum of PA[7] in $CDCl_3$.

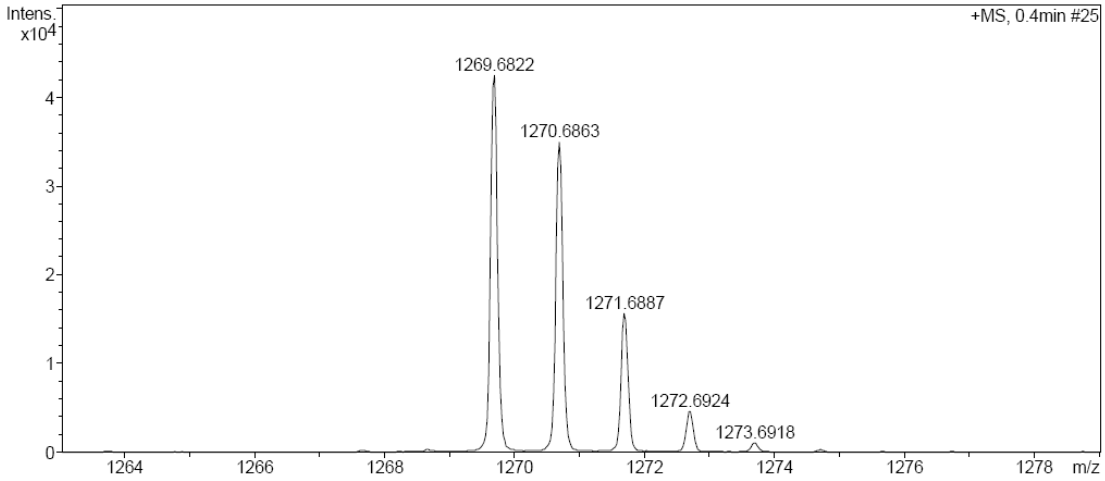

Figure S7. HR ESI-MS of PA[7].

PA[8]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.61 (s, 16 H), 3.84 (s, 16 H), 3.80 (q, J = 6.8 Hz, 32 H), 1.23 (t, J = 6.8 Hz, 48 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.6, 127.8, 114.9, 64.2, 30.4, 15.0. MS (ESI): *m/z* 1448 $[M+Na]^+$, HR-MS (ESI-TOF): Calcd. for $C_{88}H_{112}O_{16}Na$: 1447.7848. Found: 1447.7841.

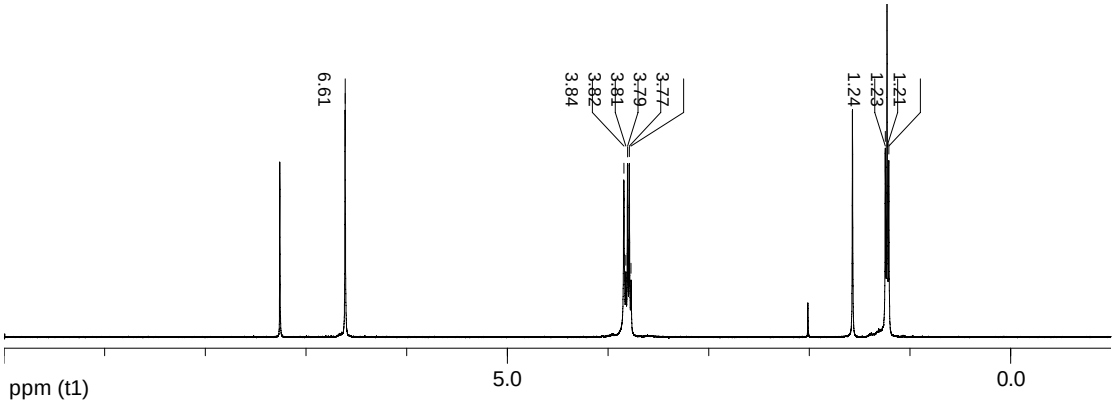

Figure S8. ^{1}H NMR spectrum of PA[8] in $CDCl_3$.

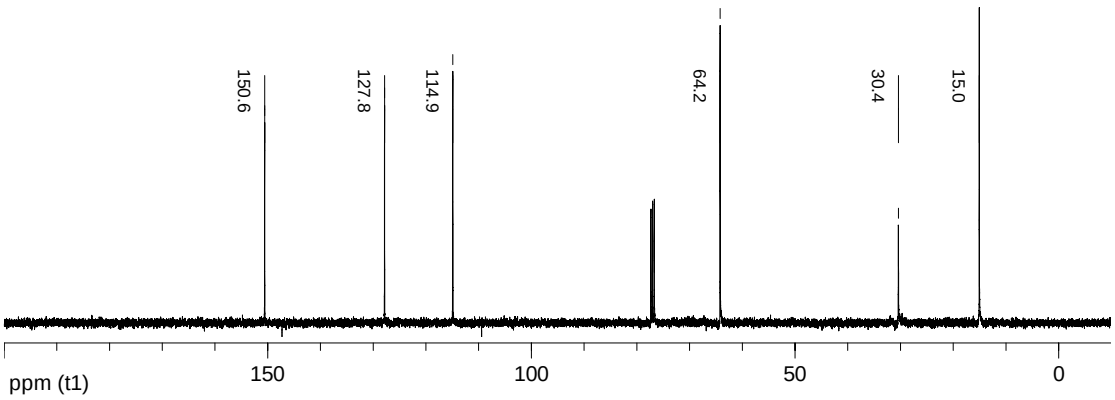

Figure S9. ^{13}C NMR spectrum of PA[8] in $CDCl_3$.

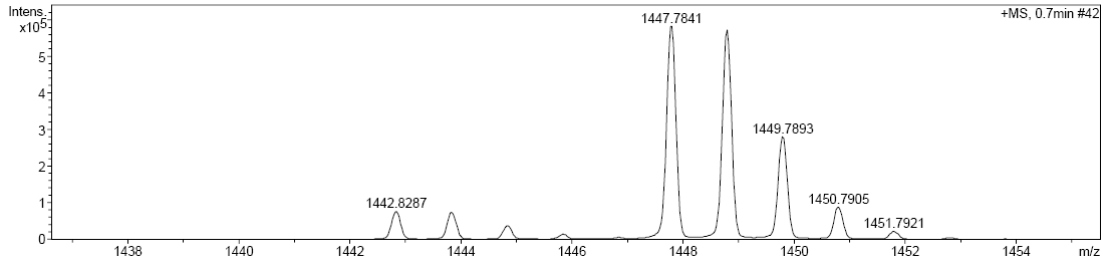

Figure S10. HR ESI-MS of PA[8].

PA[9]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.64 (s, 18 H), 3.83 (s, 18 H), 3.82 (q, J = 6.8 Hz, 36 H), 1.26 (t, J = 6.8 Hz, 54 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.4, 127.9, 114.9, 64.1, 30.0, 15.1. MS (ESI): *m/z* 1627 $[M+Na]^+$, HR-MS (ESI-TOF): Calcd. for $C_{99}H_{126}O_{18}Na$: 1626.8875. Found: 1626.8860.

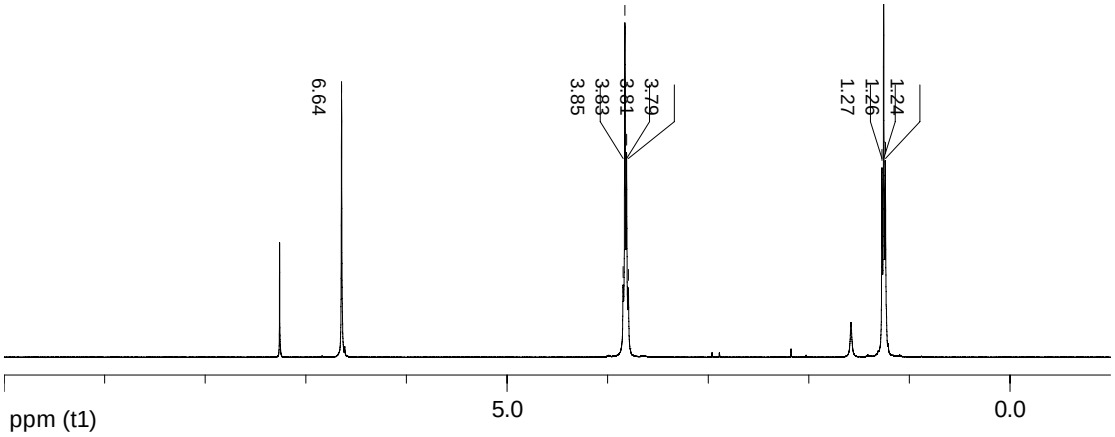

Figure S11. ^{1}H NMR spectrum of PA[9] in $CDCl_3$.

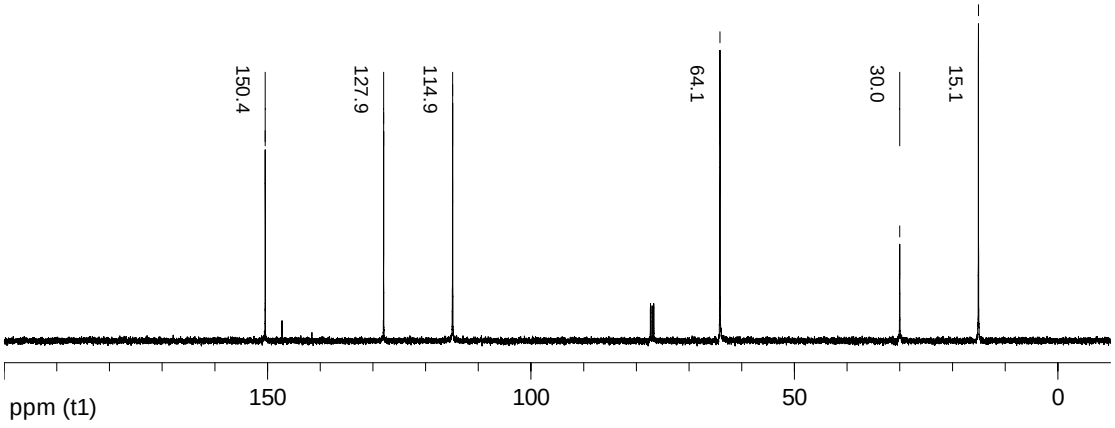

Figure S12. ^{13}C NMR spectrum of PA[9] in $CDCl_3$.

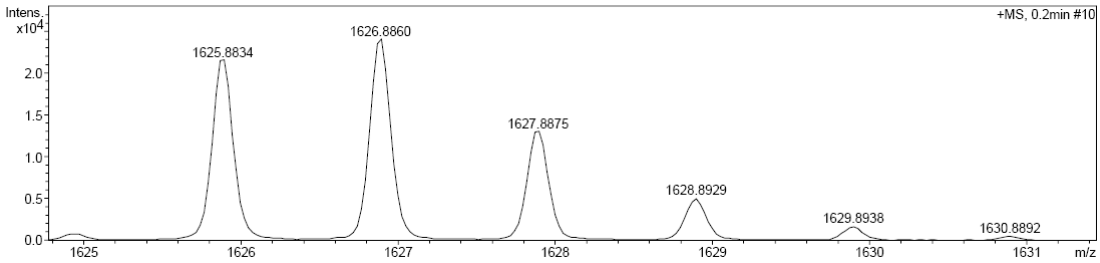

Figure S13. HR ESI-MS of PA[9].

PA[10]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.65 (s, 20 H), 3.83 (s, 20 H), 3.82 (q, J = 6.6 Hz, 40 H), 1.26 (t, J = 6.6 Hz, 60 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.5, 127.9, 114.9, 64.2, 30.0, 15.1. MS (ESI): *m/z* 1805 $[M+Na]^+$, HR-MS (ESI-TOF): Calcd. for $C_{110}H_{140}O_{20}Na$: 1804.9869. Found: 1804.9894.

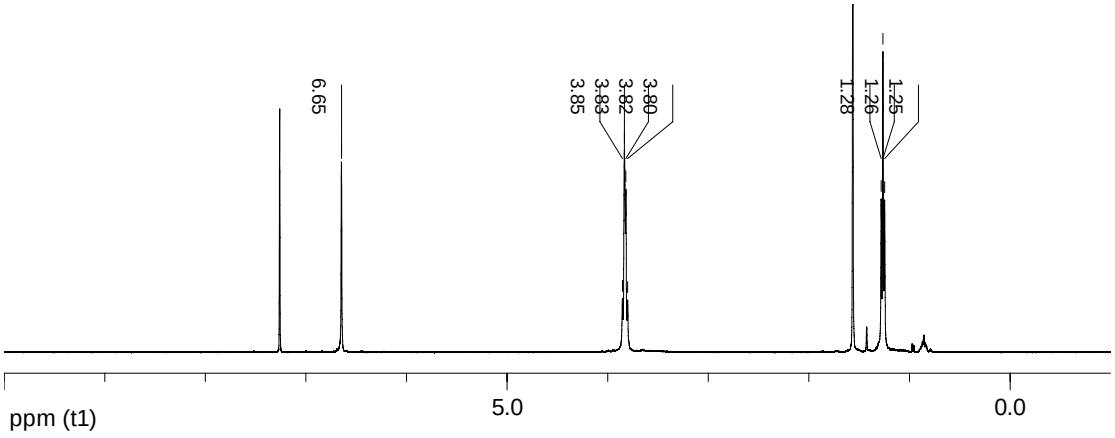

Figure S14. ^{1}H NMR spectrum of PA[10] in $CDCl_3$.

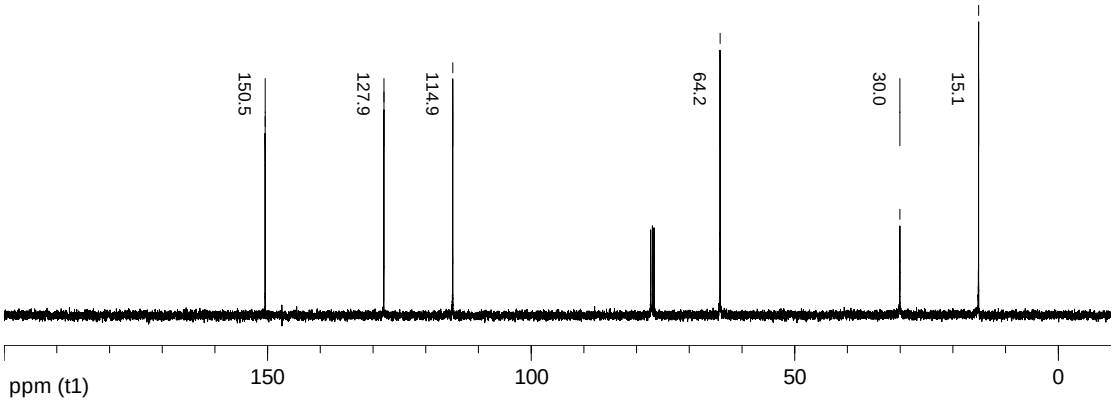

Figure S15. ^{13}C NMR spectrum of PA[10] in $CDCl_3$.

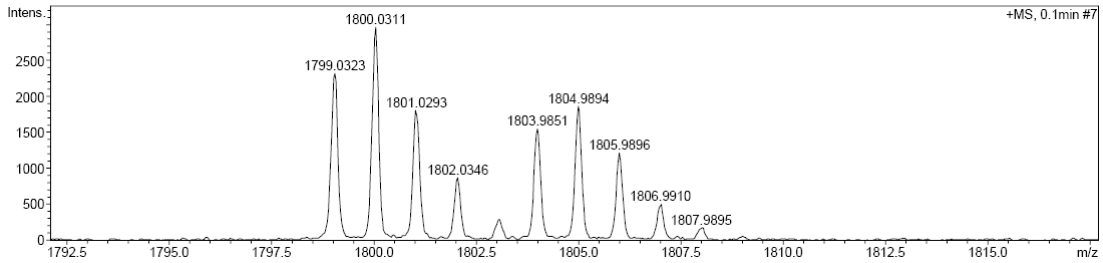

Figure S16. HR ESI-MS of PA[10].

4. Comparing the ^{1}H NMR and ^{13}C NMR spectra of PA[n] (n = 5-10):

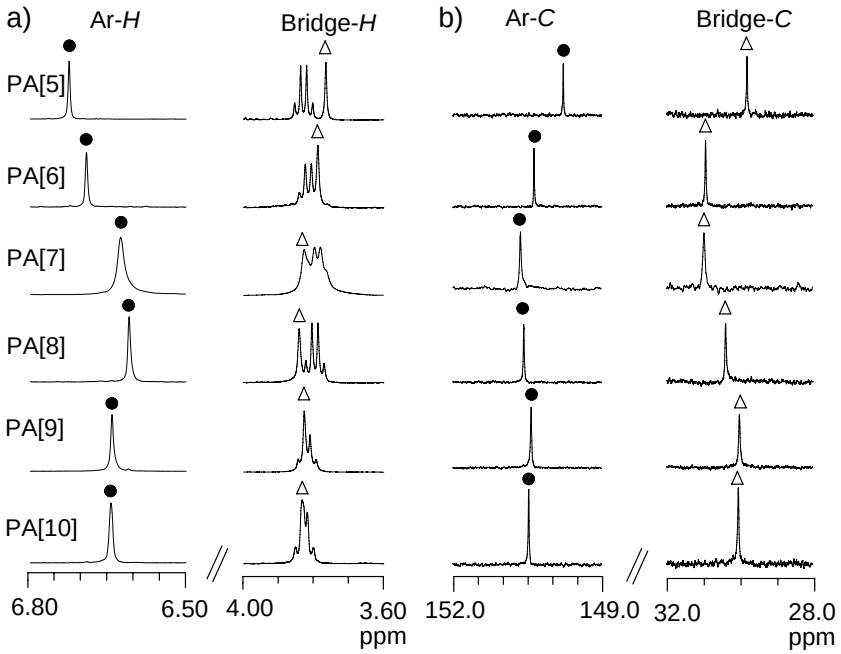

Figure S17. Partial (a) ^{1}H NMR (400 MHz, 2.0 mM) and (b) ^{13}C NMR (100 MHz, 10.0 mM) spectra of PA[n]s (n = 5-10) in $CDCl_3$ at 25 ^{o}C.

5. Variable temperature ^{1}H NMR experiments:

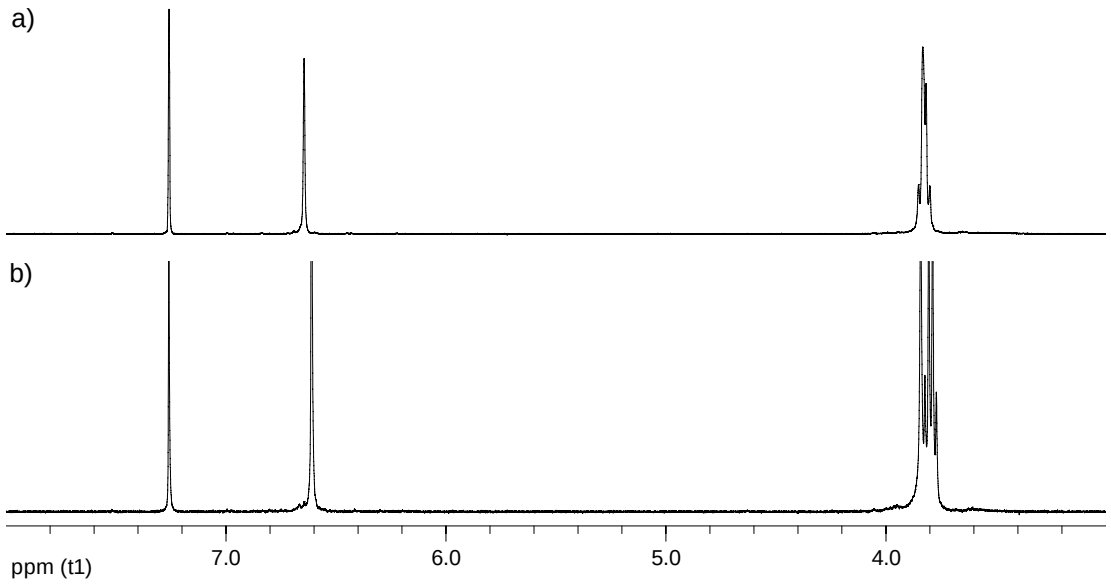

Figure S18. ^{1}H NMR spectra of PA[10] at (a) 25 °C and (b) -50 °C, indicating no signal splitting or broadening.

6. ^{1}H NMR titration experiments:

To determine the association constants (K_a) for PA[n]s (n = 5, 6, 9, 10) binding with OTA, ^{1}H NMR titration experiments were done with $CDCl_3$ solutions which had a constant concentration of PA[n] (1.0 mM) and varying concentration of OTA.

From the molar ratio plot, a 1:1 stoichiometry was obtained for PA[5], PA[6] and PA[9] binding with OTA. The association constants (K_a) of them were estimated by a non-linear curve-fitting method with the equation:[2]

$$\Delta\delta = (\Delta\delta_\infty/[H])\{0.5([G] + [H] + 1/K_a) - (([G] + [H] + 1/K_a)2 + 4[H][G])^{0.5}\} \quad \text{Eq. 1}$$

Where $\Delta\delta$ is the chemical shift change of Ar*H* on PA[n]s (n = 5, 6, 9) at [G], $\Delta\delta_\infty$ is the chemical shift change of Ar*H* when PA[n]s is completely complexed, [H] is the fixed initial concentration of the host, and [G] is the concentration of OTA.

From the molar ratio plot, a 1:2 stoichiometry was obtained for PA[10] binding with OTA. The association constant (K_a) was estimated by a non-linear curve-fitting method with the equation:[2]

$$\Delta\delta = (\Delta\delta_{HG}K_1[G] + \Delta\delta_{HG2}K_1K_2[G]^2) / (1 + K_1[G] + K_1K_2[G]^2) \quad \text{Eq. 2}$$

Where $\Delta\delta$ is the chemical shift change of Ar*H* on PA[10] at [G], $\Delta\delta_{HG}$ is the chemical shift change of Ar*H* when PA[10] is completely complexed by the first OTA, $\Delta\delta_{HG2}$ is the chemical shift change of Ar*H* when PA[10] is completely complexed by the second OTA, [H] is the fixed initial concentration of the host, and [G] is the

concentration of OTA.

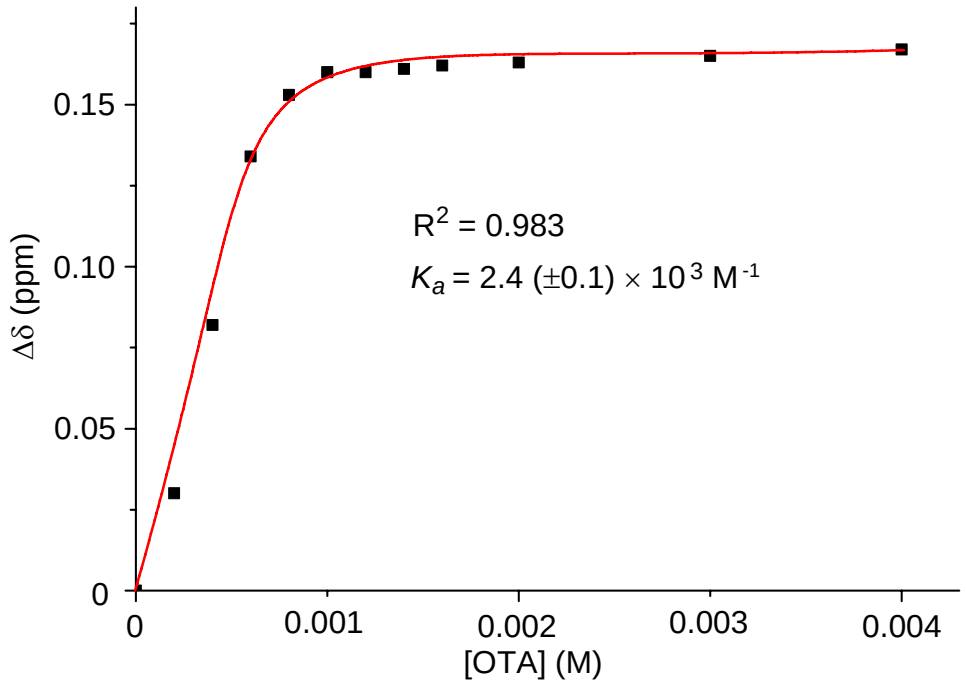

Figure S19. Changes of the chemical shift changes of Ar*H* on PA[5] with addition of OTA. The red solid line was obtained from the non-linear curve-fitting with Eq. 1.

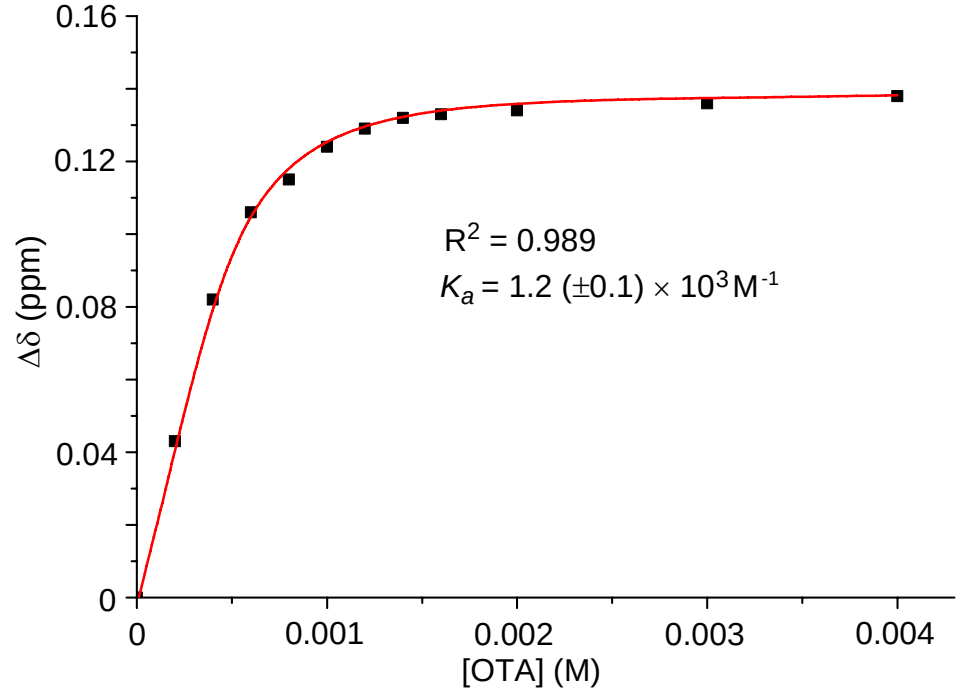

Figure S20. Changes of the chemical shift changes of Ar*H* on PA[6] with addition of OTA. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

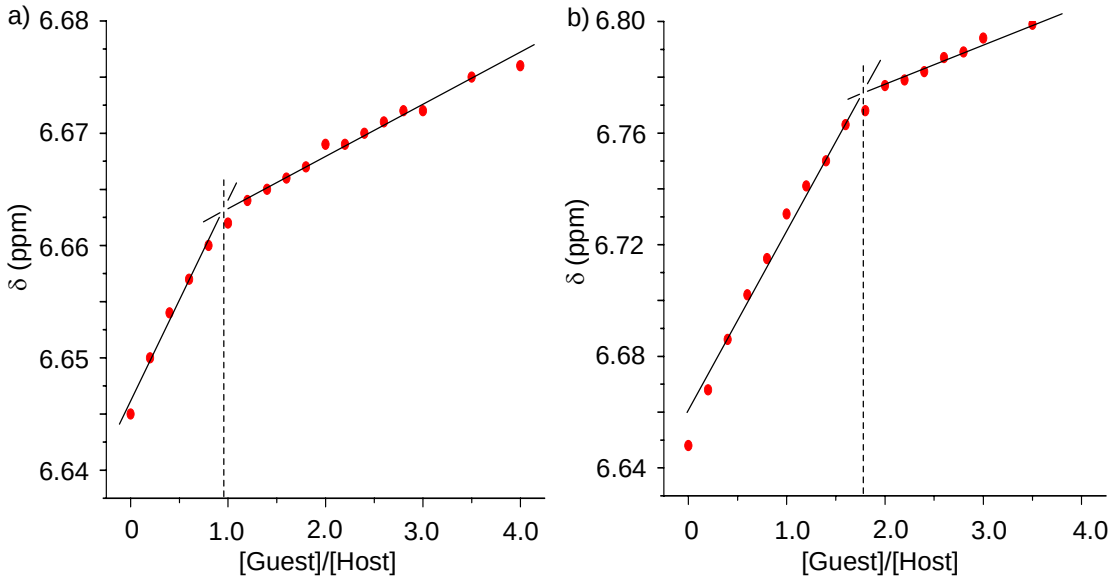

Figure S21. Molar ratio plot for the binding of OTA with (a) PA[9], (b) PA[10] in chloroform-*d* at 25 °C.

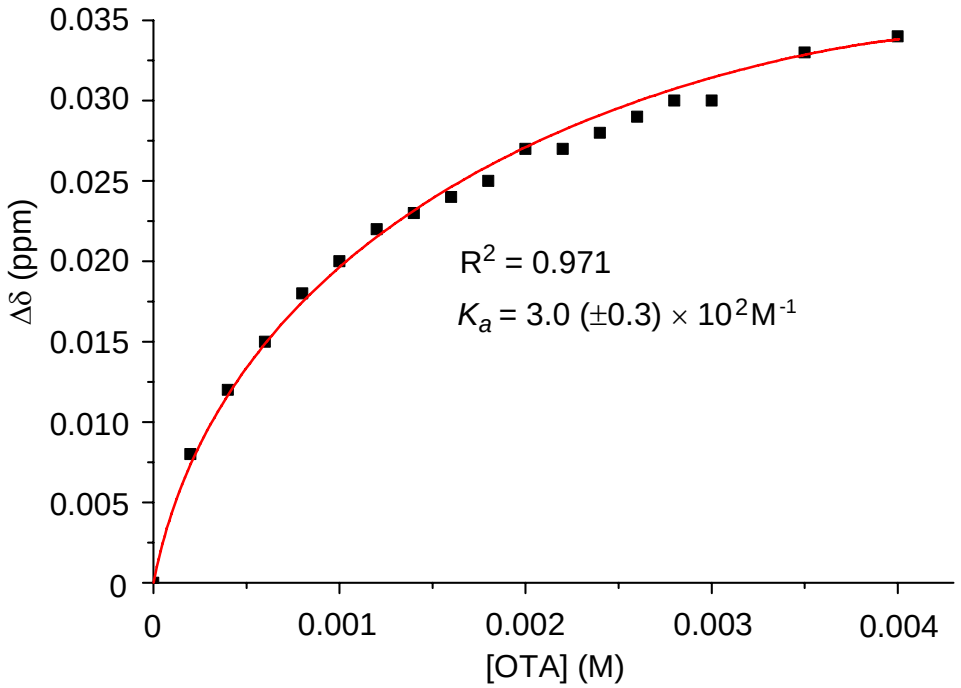

Figure S22. Changes of the chemical shift changes of Ar*H* on PA[9] with addition of OTA. The red solid line was obtained from the non-linear curve-fitting using Eq. 1.

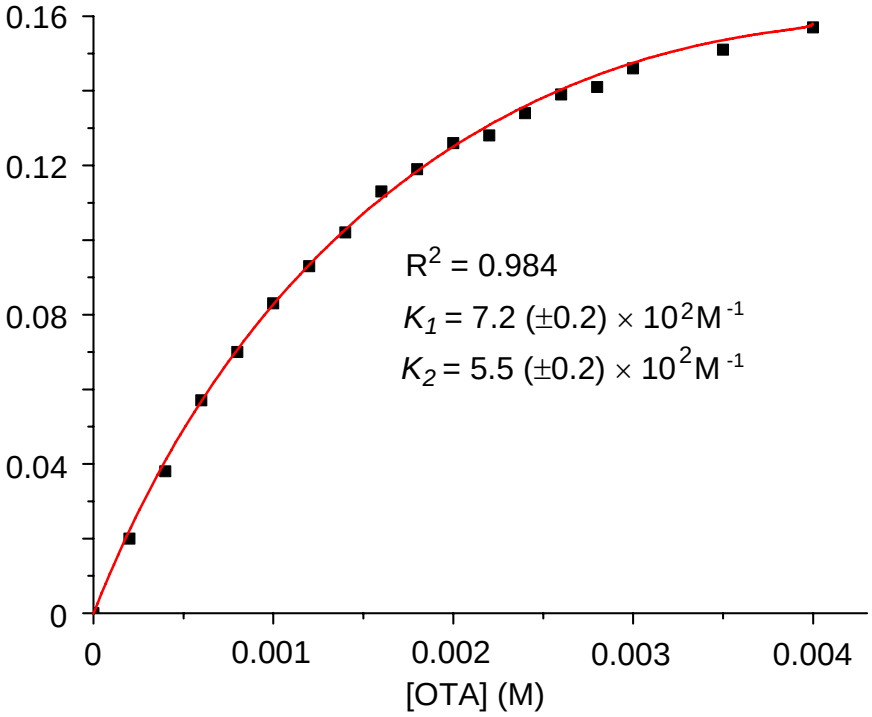

Figure S23. Changes of the chemical shift changes of Ar*H* on PA[10] with addition of OTA. The red solid line was obtained from the non-linear curve-fitting using Eq. 2.

7. HR ESI-MS experiments:

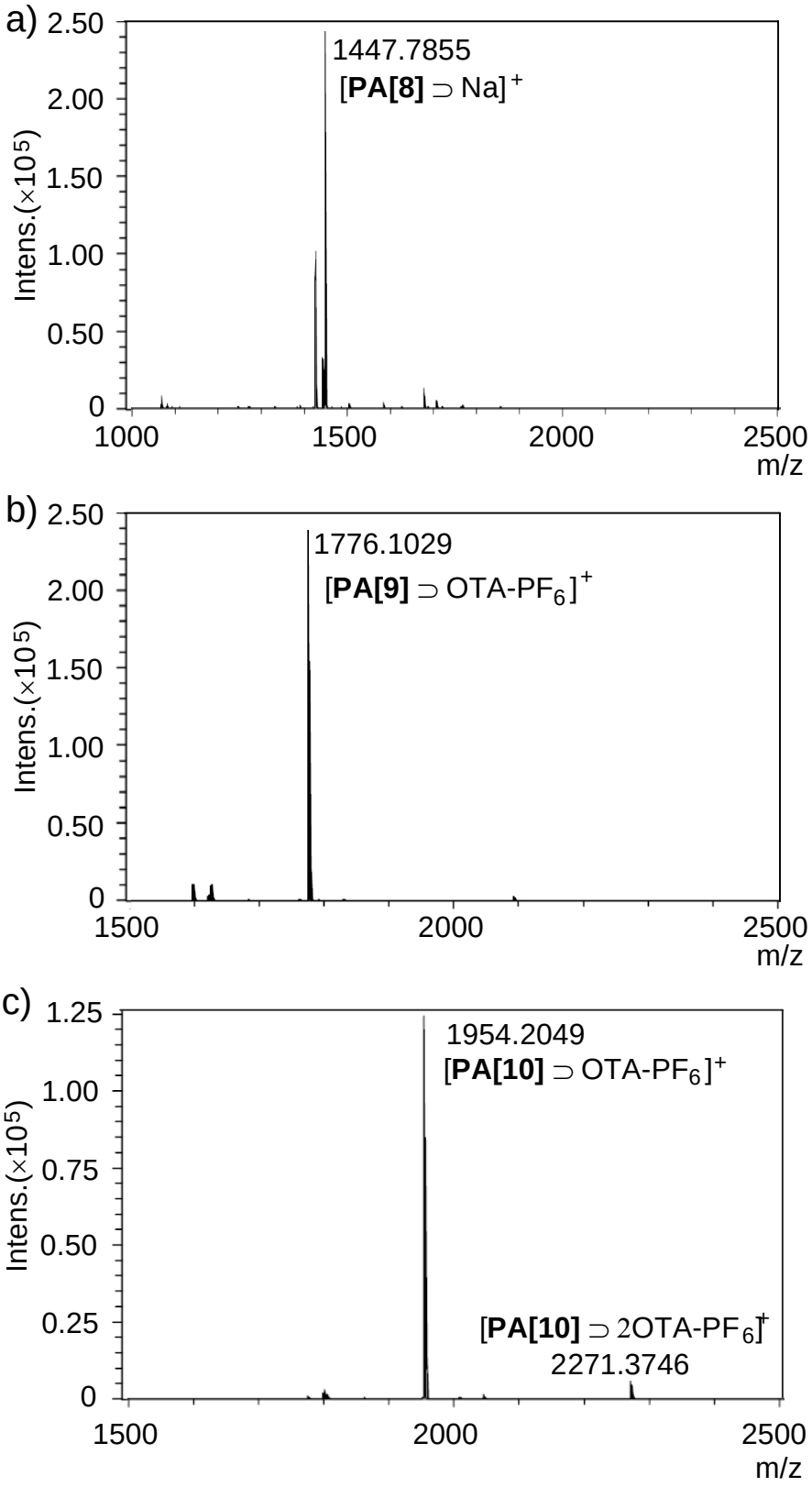

Figure S24. ESI-MS of the mixture of OTA (3.0 mM) with (a) PA[8] (0.5 mM), (b) PA[9] (0.5 mM) and (c) PA[10] (0.5 mM) in chloroform.

8. 2D ^{1}H NMR NOESY experiment:

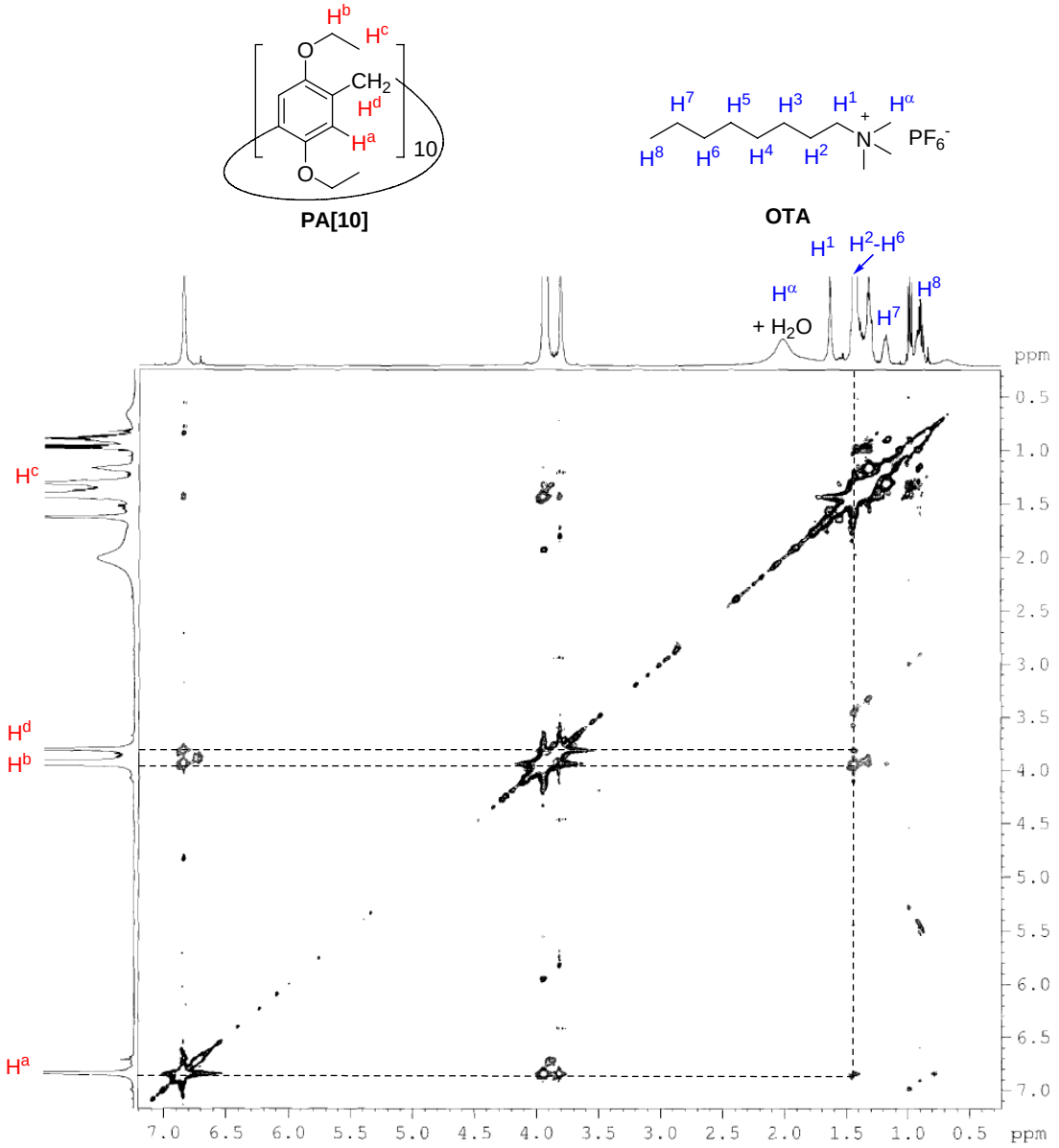

Figure S25. 2D ^{1}H NMR NOESY spectrum (mixing time = 500 ms) of PA[10] (6.0 mM) and OTA (48 mM) in $CDCl_3$ at 298 K.

9. References:

(1) Tao, H. Q.; Cao, D. R.; Liu, L. Z.; Kou, Y. H.; Wang, L. Y.; Meier, H. *Sci. China: Chem.* **2012**, *55*, 223-228.

(2) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305-1323.