Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Rational design of a nanometer-sized covalent octahedron

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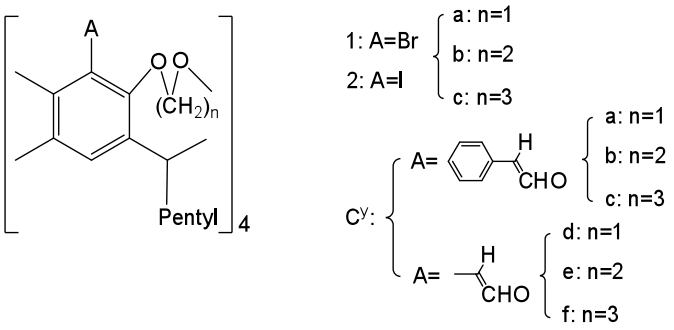
Table of Content

1. Experimental Procedures

1.1 General: Reagents and chromatography solvents were purchased from Aldrich and used without further purification except that chloroform was passed through K_2CO_3 prior to use. THF was dried over Na/benzophenone and distilled under argon. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced to residual $CHCl_3$ at δ_H = 7.26. ^{13}C NMR spectra recorded in $CDCl_3$ were referenced to $^{13}CDCl_3$ at δ_C = 77.5 ppm. Mass spectra were recorded on an Applied Biosystems Voyager DE-Pro mass spectrometer (MALDI-TOF). External standards were used for calibration and 2,4,6-trihydroxylacetophenone (THAP) as matrix. Gel permeation chromatography (GPC) was performed on a Thermo SpectraSYSTEM HPLC system equipped with dual wavelength UV/Vis detector (280 nm), Eppendorf CH-30 column heater and two Jordi GPC columns (cross linked DVB; 103 Å pore size; MW cutoff ~ 25,000; 7.8mm × 30cm) with CH_2Cl_2/1% NEt_3 as mobile phase at a flow of 1 mL/min. Approximate molecular weights of analytes were determined from a semilogarithmic calibration plot.

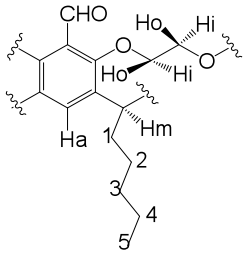


Components	C^a	C^b	C^c [1]
H_2N NH_2 **L^a**	**Complex Mixture**	**$C^b_2L^a_4$**	**Complex Mixture**
H_2N NH_2 **L^b**	**$C^a_4L^b_8$**	**$C^b_6L^b_{12}$**	**Complex Mixture**
H_2N NH_2 **L^c**	**$C^a_4L^c_8$**	**$C^b_6L^c_{12}$**	**Complex Mixture**
H_2N NH_2 **L^d**	**$C^a_4L^d_8$**	**$C^b_2L^c_4$**	**Complex Mixture**
NH_2 H_2N NH_2 **T**	**$C^a_6T_{12}$**	**$C^b_6T_{12}$**	**NA**

Table 1: TFA-catalyzed condensation products

1.2 Cavitand C[e]

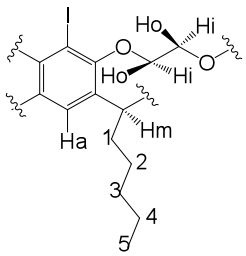
Tetrabromocavitand **1b**[2] (520 mg, 0.53 mmol) was dried under vacuum overnight at 100 ℃ and then dissolved in 20 mL THF under argon. THF (10 mL) was added to a second dried flask, which was charged with PrMgBr/THF solution (2.6 mL, 2 mol/L) and anhydrous LiCl (216 mg, 5.10 mmol). The suspension was stirred under argon untill all LiCl was dissolved. Then, the resulting solution was cannulated to the solution of **1c** at -78℃. After the Br/MgBr exchange, which was monitored by ^{1}H NMR spectroscopy, was complete, anhydrous DMF (0.43 mL, 6.33 mmol) was injected to the solution. After 1 hr, the reaction was quenched with aqueous HCl solution (10 mL, 1M). The product was extracted with ethyl acetate (3×30 mL). The combined organic solution was washed with sat. NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The product was further purified by silica gel column chromatography with THF/CH_2Cl_2=2/98 as the mobile phase. The white solid was obtained in 25% yield.



^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃): δ_H 10.35 (s, 4H, -C*H*O), 7.56 (s, 4H, H_a), 5.35 (t, *J*=8.1 Hz, 4H, Hm), 4.51 (m, 8H, Ho), 3.67 (m, 8H, Hi), 2.10 (m, 8H, H1), 1.42-1.18 (m, 24H, H2, H3 and H4), 0.88 (t, *J*=7.1Hz, 12H, H5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃): δ_C 190.24, 155.85, 137.37, 130.17, 125.13, 74.42, 34.50, 33.32, 32.28, 27.87, 23.07, 14.53. Ms (Maldi-tof) m/z: 1007.4911 (M+Na^+, 100%); Calcd for $C_{60}H_{72}O_{12}$ +Na^+: 1007.4916.

1.3 Cavitand 2b

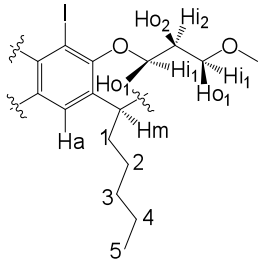
Tetrabromocavitand **1b** (530 mg, 0.54 mmol) was dried overnight under vacuum at 100 ℃ and then dissolved in 30 mL THF under argon. At -78℃, BuLi/Hexane (1.6 mL, 2.5M) was injected into the above solution. After 3 hours, I_2 (1.3 g, 5.12 mmol) was added to the solution. The reaction was quenched with water. The product was extracted with ethyl acetate (3×30 mL) and then the combined organic solution was washed with $Na_2S_2O_3$ solution (20 mL, 10%), water and sat. NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The product was further purified by silica gel column chromatography with CH_2Cl_2/Hexane=1/1 as mobile phase. The slightly yellow solid was obtained in 81% yield.



^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃): δ_H 7.29 (s, 4H, H_a), 5.27 (t, *J*=8.2 Hz, 4H, Hm), 4.46 (m, 8H, Ho), 3.76 (m, 8H, Hi), 2.04 (m, 8H, H1), 1.38-1.15 (m, 24H, H2, H3 and H4), 0.86 (t, *J*=7.2 Hz, 12H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 154.88, 136.98, 125.25, 90.36, 70.89, 36.05, 35.24, 32.31, 27.87, 23.05, 14.54. Ms (Maldi-tof) m/z: 1399.1543 ($M+Na^+$, 100%); Calcd for $C_{56}H_{68}O_8I_4+Na^+$: 1399.0984.

1.4 Cavitand 2c

Cavitand **1c**[2] (1.03 g, 0.99 mmol) was dried overnight under vacuum at 100 ℃ and then dissolved in 40 mL THF under argon. THF (10 mL) was added to a second dried flask, which was charged with PrMgBr/THF solution (5 mL, 2 mol/L) and anhydrous LiCl (420 mg, 9.91 mmol). The suspension was stirring under argon until all LiCl was dissolved. Then, the resulting solution was cannulated to the solution of **1c** at -78℃. After the Br/MgBr exchange, which was monitored by ^{1}H NMR spectroscopy, was complete, I_2 (2.52 g, 9.92 mmol) was added at the same temperature. The reaction was quenched with water. The product was extracted with ethyl acetate (3×50 mL). The combined organic solution was washed with $Na_2S_2O_3$ solution (50 mL, 10%), water and sat. NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The product was further purified by silica column with Hexane/EtOAc=1/4 as the mobile phase. The slightly yellow product was obtained in 70%.

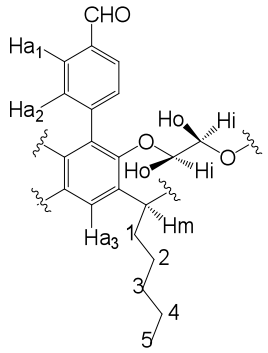


^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃): δ_H 7.04 (s, 4H, H_a), 4.91 (t, *J*=7.5 Hz, 4H, Hm), 4.67 (m, 8H, Ho_2), 3.94 (m, 8H, Hi_2), 2.32 (m, 4H, Ho_1), 2.08 (m, 4H, Hi_2), 1.93 (m, 8H, H1), 1.36-1.14 (m, 24H, H2, H3 and H4), 0.86 (t, J=6.9 Hz, 12H, H5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃): δ_C 157.18, 134.89, 125.78, 90.23, 70.29, 36.46, 36.22, 34.45, 29.85, 27.74, 23.03, 14.59. Ms (Maldi-tof) m/z: 1455.1230 ($M+Na^+$, 100%); Calcd for $C_{60}H_{76}O_8I_4$ $+Na^+$: 1455.1611.

1.5 Cavitand C[b]

A Schlenk flask was charged with cavitand **2b** (176.5 mg, 177.4 μmol), potassium (4-formylphenyl)trifluoroborate (225.6 mg, 1.06 mmol), $Pd(OAc)_2$ (17.3 mg, 71 μmol), PPh_3 (37.2 mg, 142 μmol), and K_2CO_3 (294 mg, 2.13 mmol) and was evacuated and refilled with argon 3 times. After adding THF (10 mL) and deionized water (1mL), the flask was sealed and kept stirring at 100 ℃ overnight. Then, the solution was acidified with aqueous HCl (3mL, 1M) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with sat. NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The pure product was obtained as a white solid in 65.4% yield

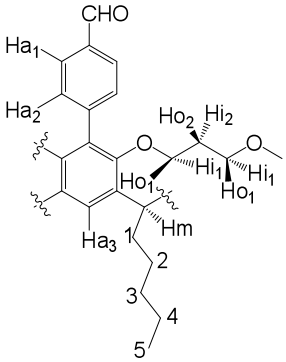
by using silica gel column with EtOAc/CH_2Cl_2=5/95 as the mobile phase.



^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 10.03 (s, 4H, -C*H*O), 7.89 (d, *J*=8.0, 8H, Ha_1), 7.63 (s, 4H, Ha_3), 7.34 (d, *J*=8.0 Hz, 8H, Ha_2), 5.26 (t, *J*=8.4, 4H, Hm), 3.84 (m, 8H, Ho), 3.41 (m, 8H, Hi), 2.23 (m, 8H, H1), 1.47-1.18 (m, 24H, H2, H3 and H4), 0.91 (t, J=6.8 Hz, 12H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 192.18, 151.88, 142.38, 136.83, 136.02, 131.04, 130.58, 129.76, 125.16, 72.76, 35.22, 34.41, 32.37, 28.09, 23.16, 14.60. Ms (Maldi-tof) m/z: 1311.6413 ($M+Na^+$, 100%); Calcd for $C_{84}H_{88}O_{12}+Na^+$: 1311.6167.

1.6 Cavitand C[c]

A Schlenk flask was charged with cavitand **2c** (103.15 mg, 72 μmol), potassium (4-formylphenyl)trifluoroborate (92 mg, 432.2 μmol), $Pd(OAc)_2$ (3.5 mg, 14.4 μmol), PPh_3 (7.5 mg, 28.8 μmol), and K_2CO_3 (119.3 mg, 864.4 μmol) and was evacuated and refilled with argon 3 times. After adding THF (10 mL) and deionized water (1mL), the flask was sealed and kept stirring at 100 ℃ overnight. Then, the solution was acidified with aqueous HCl (3 mL, 1M) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with sat. NaCl solution, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The pure product was then obtained as a white solid in 71% yield by using silica column with EtOAc/CH_2Cl_2=1/35 as the mobile phase.



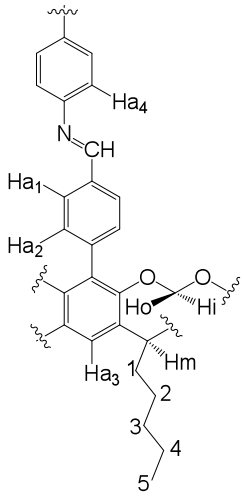
^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 10.04 (s, 4H, -C*H*O), 7.88 (d, *J*=8.0, 8H, Ha_1), 7.54 (d, *J*=8.0 Hz, 8H, Ha_2), 7.46 (s, 4H, Ha_3), 5.01 (t, *J*=8.0, 4H, Hm), 3.79 (m, 8H, Ho_2), 3.52 (m, 8H, Hi_2), 2.12 (m, 8H, H1), 1.87 (m, 4H, Ho_1), 1.54 (m, $H, Hi_1), 1.44-1.20 (m, 24H, H2, H3 and H4), 0.90 (t, J=6.8 Hz, 12H, H5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃): δ_C 192.54, 154.37, 143.57, 135.54, 134.38, 132.15, 129.50, 128.39, 125.72, 71.79, 36.53, 34.68, 32.49, 30.32, 27.99, 23.18, 14.62. Ms (Maldi-tof) m/z: 1367.6341 ($M+Na^+$, 100%); Calcd for $C_{88}H_{96}O_{12}+Na^+$: 1367.6799.

1.7 General procedure for synthesis of nanocapsules (Procedure A)

Stock solutions of the tetraformylcavitand (10 mg/mL), of the di- or triamine linker (10 mg/mL) and of TFA (1% v/v) in $CDCl_3$ were prepared. Then, the solutions of cavitand and linker were mixed in stoichiometric ratio followed by the addition of catalytic amount TFA solution. Several molecular sieves were added to above solution. After 1-2 hours, the solution was diluted to 0.5 ml with $CDCl_3$, if necessary, and transferred into a NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy. After completion, the solvent was removed.

1.7.1 Tetracavitand capsule $C^a{}_4L^b{}_8$

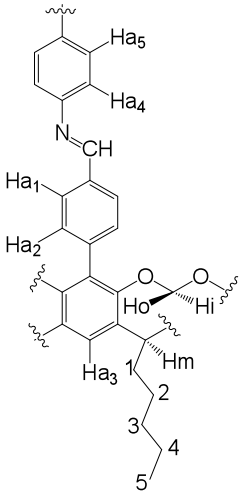
From **C**$^{a[1]}$ (3.58 mg, 2.91 μmol), 1,4-phenylenediamine (0.63 mg, 5.81 μmol) and TFA (4 μL, 1%v/v in $CDCl_3$) according to **procedure A.** Based on GPC, the purity is 90% and the rest are hexacavitand-aggregates.



^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^b{}_8$: δ_H 8.53 (s, 8H, -C*H*N-), 8.51 (s, 8H, -C*H*N-), 7.94 (d, *J*=7.5 Hz, 16H, Ha_1), 7.83 (d, *J*=7.5 Hz, 16H, Ha_1), 7.38 (s, 8H, Ha_3), 7.35 (s, 8H, Ha_3), 7.29 (s, 16H, Ha_4), 7.27 (d, *J*=8.6 Hz, 16H, Ha_2), 7.24 (s, 16H, Ha_4), 7.08 (d, *J*=8.6 Hz, 16H, Ha_2), 5.48-5.30 (m, 12H, Ho), 4.97-4.78 (m, 16H, Hm), 4.64 (m, 4H, Hi), 4.51-4.30 (m, 12H, Hi), 3.56 (m, 4H, Ho), 2.47-2.2 (m, 32H, H1), 1.57-1.34 (m, 96H, H2, H3 and H4), 1.04-0.86 (m, 48H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^b{}_8$: δ_C 159.92, 159.08, 153.33, 153.08, 152.86, 152.77, 150.68, 149.78, 139.06, 138.99, 138.92, 138.77, 137.74, 137.69, 135.78, 135.70, 131.03, 130.76, 129.64, 129.17, 128.81, 122.57, 122.33, 122.26, 120.81, 120.67, 101.57, 101.41, 99.43, 37.70, 37.61, 32.59, 32.58, 32.55, 31.09, 30.89, 30.43, 28.23, 28.20, 28.16, 23.24, 23.21, 23.18, 14.64, 14.63. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^b{}_8$: D=2.50*10^{-10} m^2/s. Ms (Maldi-tof) of $C^a{}_4L^b{}_8$ m/z: 5511.6259 (M+H$^+$, 100%); Calcd for $C_{368}H_{352}O_{32}N_{16}$ +H$^+$: 5511.6503.

1.7.2 Tetra-cavitand capsule $C^a{}_4L^c{}_8$

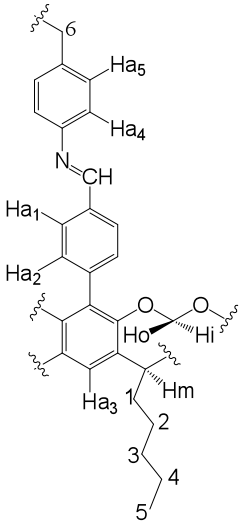
From **C**$^{a[1]}$ (2.33 mg, 1.88 μmol), benzidine (0.69 mg, 3.77 μmol) and TFA (2 μL, 1%v/v in $CDCl_3$) according to **procedure A.** Based on GPC, the purity is 80% and the rest are hexacavitand-aggregates.



^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^c{}_8$: δ_H 8.48 (s, 8H, -C*H*N-), 8.45 (s, 8H, -C*H*N-), 7.88 (d, *J*=8.6 Hz, 16H, Ha_1), 7.79 (d, *J*=8.6 Hz, 16H, Ha_1), 7.60 (d, *J*=8.6 Hz, 16H, Ha_5), 7.54 (d, *J*=8.6 Hz, 16H, Ha_5), 7.32 (s, 8H, Ha_3), 7.30 (s, 8H, Ha_3), 7.25 (d, *J*=8.4 Hz, 16H, Ha_4), 7.20 (d, *J*=8.4 Hz, 16H, Ha_4), 7.14 (d, *J*=7.8 Hz, 16H, Ha_2), 7.04 (d, *J*=7.8 Hz, 16H, Ha_2), 5.35-5.28 (m, 12H, Ho), 4.85-4.79 (m, 16H, Hm), 4.70 (m, 4H, Hi), 4.37-4.29 (m, 12H, Hi), 3.65 (m, 4H, Ho), 2.37-2.24 (m, 32H, H1), 1.49-1.32 (m, 96H, H2, H3 and H4), 0.96-0.86 (m, 48H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^c{}_8$: δ_C 160.39, 160.27, 159.56, 153.30, 153.07, 152.95, 152.82, 151.82, 151.70, 151.01, 139.02, 138.95, 138.80, 137.86, 137.79, 137.63, 135.75, 135.70, 135.62, 131.00, 130.77, 129.65, 129.23, 129.14, 128.87, 128.16, 128.09, 127.77, 122.04, 121.92, 121.89, 120.82, 120.71, 115.91, 101.44, 101.16, 99.77, 37.69, 37.64, 32.59, 31.06, 30.98, 30.53, 28.19, 23.22, 14.65. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^c{}_8$: D=2.14*10^{-10} m^2/s. Ms (Maldi-tof) of $C^a{}_4L^c{}_8$ m/z: 6119.9712 ($M+H^+$, 100%); Calcd for $C_{416}H_{384}O_{32}N_{16}$ +H^+: 6119.9100.

1.7.3 Tetra-cavitand capsule $C^a{}_4L^d{}_8$

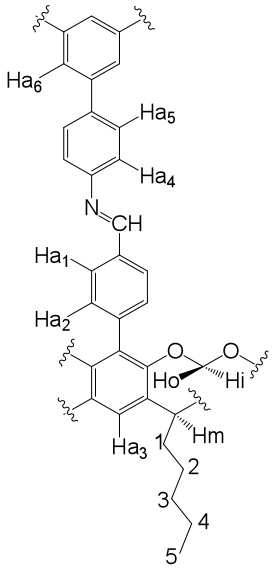
From **C^a**[1] (2.35 mg, 1.90 μmol), 1,4-ethylenedianiline (0.81 mg, 3.81 μmol) and TFA (2 μL, 1%v/v in $CDCl_3$) according to **procedure A.** Based on GPC, the purity is 80% and the rest are di- and hexacavitand-aggregates.



^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^d{}_8$: δ_H 8.50 (s, 8H, -C*H*N-), 8.47 (s, 8H, -C*H*N-), 7.92 (d, *J*=7.7 Hz, 16H, Ha_1), 7.85 (d, *J*=7.7 Hz, 16H, Ha_1), 7.37 (s, 8H, Ha_3), 7.36 (s, 8H, Ha_3), 7.34 (d, *J*=8.2 Hz, 16H, Ha_5), 7.29 (d, *J*=8.2 Hz, 16H, Ha_5), 7.24-7.16 (m, 48H, Ha_4 and Ha_2), 7.12 (d, *J*=7.6 Hz, 16H, Ha_2), 5.41-5.27 (m, 12H, Ho), 4.95-4.86 (m, 16H, Hm and Hi), 4.42-4.29 (m, 12H, Hi), 3.88 (m, 4H, Ho), 2.94 (s, 16H, H6), 2.91 (s, 16, H6), 2.46-2.27 (m, 32H, H1), 1.61-1.36 (m, 96H, H2, H3 and H4), 1.03-0.92 (m, 48H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^d{}_8$: δ_C 159.88, 159.52, 153.22, 153.06, 152.98, 152.87, 150.57, 150.24, 140.70, 140.52, 139.04, 139.00, 138.97, 138.81, 137.74, 137.67, 135.76, 135.73, 130.91, 130.71, 129.98, 129.72, 129.64, 129.45, 129.40, 129.30, 128.77, 121.59, 121.52, 120.77, 120.66, 115.70, 101.37, 100.16, 38.46, 38.43, 37.67, 37.62, 32.59, 31.01, 30.60, 28.19, 23.24, 23.21, 14.64. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^a{}_4L^d{}_8$: D=2.06*10^{-10} m^2/s. Ms (Maldi-tof) of $C^a{}_4L^d{}_8$ m/z: 6345.1584 (M+H$^+$, 100%); Calcd for $C_{432}H_{416}O_{32}N_{16}$ +H$^+$: 6345.1495.

1.7.4 Hexa-cavitand capsule $C^a{}_6T_{12}$

From **C^a**[1] (2.41 mg, 1.90 µmol), 1,3,5-tris(4-aminophenyl)benzene (0.91 mg, 2.61 µmol) and TFA (2 µL, 1%v/v in $CDCl_3$) according to **procedure A.** Based on GPC, the purity is >95%.

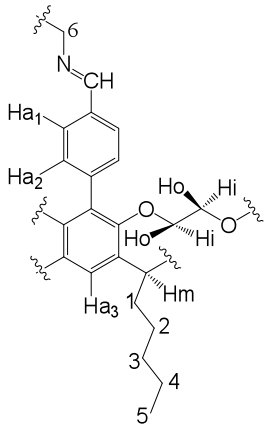


^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 8.53 (s, 24H, -C*H*N-), 7.92 (d, *J*=8.3 Hz, 48H, Ha_1), 7.82 (s, 24H, Ha_3), 7.76 (d, *J*=8.3 Hz, 48H, Ha_5), 7.39 (s, 24H, Ha_6), 7.32 (d, *J*=8.3 Hz, 48H, Ha_4), 7.19 (d, *J*=8.3 Hz, 48H, Ha_2), 5.24 (m, 24H, Ho), 4.89 (t, *J*=7.8 Hz , 24H, Hm), 4.25 (m, 24H, Hi), 2.39 (m, 48H, H1), 1.58-1.35 (m, 144H, H2, H3 and H4), 0.98 (t, *J*=6.7 Hz, 72H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 160.48, 153.03, 152.10, 142.30, 139.21, 138.94, 138.14, 135.58, 130.68, 129.53, 128.90, 124.54, 125.02, 121.85, 120.72, 101.05, 37.59, 32.59, 30.84, 28.20, 23.21. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃): D=1.85*10^{-10} m^2/s. Ms (Maldi-tof) m/z: 9779.8018 (M+H$^+$, 100%); Calcd for $C_{672}H_{600}O_{48}N_{24}$ +H$^+$: 9780.5500

1.7.5 Hemicarcerand $C^b{}_2L^a{}_4$

From **C^b** (2.08 mg, 1.61 µmol), 1,2-ethylenediamine (0.19 mg, 3.23 µmol) and TFA (2 µL,

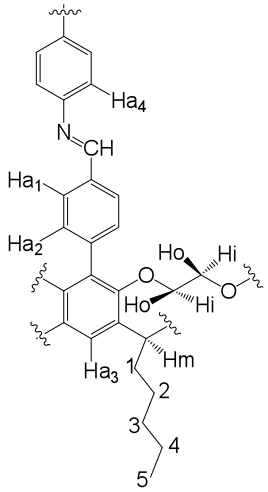
1%v/v in $CDCl_3$) according to **procedure A.** NMR shows that the purity is >95%.



^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃): δ_H 8.46 (s, 8H, -C*H*N-), 7.83 (d, *J*=8.6 Hz, 16H, Ha_1), 7.65 (s, 8H, Ha_3), 7.23 (d, *J*=8.6 Hz, 48H, Ha_1), 5.28 (t, *J*=7.8 Hz, 8H, Hm), 3.97-3.72 (m, 32H, Ho and H6), 3.39 (m, 16H, Hi), 2.24 (m, 16H, H1), 1.50-1.18 (m, 48H, H2, H3 and H4), 0.90 (t, *J*=7.1 Hz, 24H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 161.86, 151.89, 137.93, 136.31, 135.75, 130.63, 130.08, 128.23, 124.37, 72.53, 62.95, 34.95, 34.14, 32.19, 27.94, 22.92. Ms (Maldi-tof) m/z: 2676.5396 ($M+H^+$, 100%); Calcd for $C_{176}H_{192}O_{16}N_8$ $+H^+$: 2676.4652

1.7.6 Hexa-cavitand capsule $C^b_6L^b_{12}$

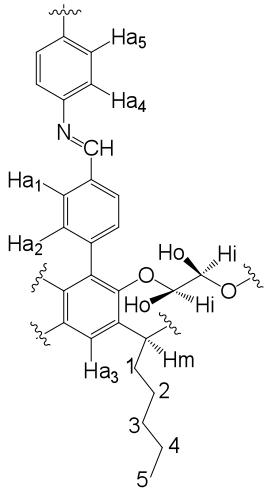
From $\mathbf{C^b}$ (2.32 mg, 1.80 μmol), 1,4-phenylenediamine (0.40 mg, 3.6 μmol) and TFA (2.5 μL, 1%v/v in $CDCl_3$) according to **procedure A.** NMR shows that the purity is >95%.



^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 8.53 (s, 24H, -C*H*N-), 7.93 (d, *J*=8.3 Hz, 48H, Ha_1), 7.67 (s, 24H, Ha_3), 7.31 (d, *J*=8.3 Hz, 48H, Ha_1), 7.26 (s, 48H, Ha_4), 5.30 (t, *J*=7.2 Hz, 24H, Hm), 3.89 (m, 48H, Ho), 3.46 (m, 48H, Hi), 2.26 (m, 48H, H1), 1.52-1.22 (m, 144H, H2, H3 and H4), 0.92 (t, *J*=6.4 Hz, 72H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 159.81, 152.10, 150.45, 139.22, 136.68, 135.88, 130.82, 130.74, 128.88, 124.81, 122.32, 72.78, 35.20, 34.50, 32.47, 28.22, 23.19, 14.63. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃): D=2.11*10^{-10} m^2/s. Ms (Maldi-tof) m/z: 8603.1035 ($M+H^+$, 100%); Calcd for $C_{576}H_{576}O_{48}N_{24}$ $+H^+$: 8603.3647

1.7.7 Hexa-cavitand capsule $C^b_6L^c_{12}$

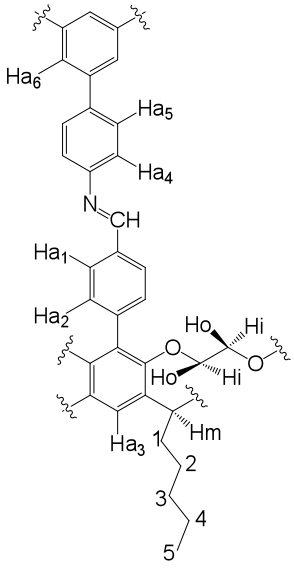
From **C^b** (2.07 mg, 1.61 μmol), benzidine (0.59 mg, 3.22 μmol) and TFA (2 μL, 1%v/v in $CDCl_3$) according to **procedure A.** NMR shows that the purity is >95%.



^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 8.55 (s, 24H, -C*H*N-), 7.94 (d, *J*=7.8 Hz, 48H, Ha_1), 7.75-7.60 (m, 72H, Ha_3 and Ha_2), 7.41-7.25 (m, 96H, Ha_4 and Ha_5), 5.31 (t, *J*=8.1 Hz, 24H, Hm), 3.91 (m, 48H, Ho), 3.48 (m, 48H, Hi), 2.26 (m, 48H, H1), 1.49-1.28 (m, 144H, H2, H3 and H4), 0.92 (t, *J*=6.8 Hz, 72H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 160.09, 152.10, 151.51, 139.22, 138.86, 136.69, 135.87, 130.82, 128.88, 128.11, 124.82, 121.89, 72.82, 35.24, 34.45, 32.48, 28.22, 23.20, 14.64. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃): D=1.73*10^{-10} m^2/s. Ms (Maldi-tof) m/z: 9516.8574 (M+H$^+$, 100%); Calcd for $C_{648}H_{624}O_{48}N_{24}$ +H$^+$: 9516.7676

1.7.8 Hexa-cavitand capsule $C^b_6T_{12}$

From **C^b** (1.88 mg, 1.46 μmol), 1,3,5-tris(4-aminophenyl)benzene (0.85 mg, 2.43 μmol) and TFA (2 μL, 1%v/v in $CDCl_3$) according to **procedure A.** NMR shows that the purity is >95%.

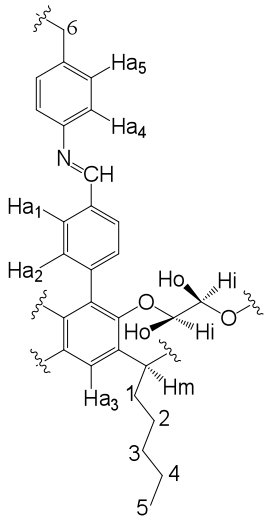


^{1}H NMR (300 MHz, $CDCl_3$, 25 ℃): δ_H 8.52 (s, 24H, -C*H*N-), 7.95 (d, *J*=8.2 Hz, 48H, Ha_1),

7.79 (s, 24H, Ha_3), 7.74 (d, J=8.2 Hz, Ha_2), 7.67 (s, 24H, Ha_6), 7.38-7.27 (m, 96H, Ha_4 and Ha_5), 5.32 (t, *J*=7.5 Hz, 24H, Hm), 3.87 (m, 48H, Ho), 3.68 (m, 48H, Hi), 2.28 (m, 48H, H1), 1.54-1.31 (m, 144H, H2, H3 and H4), 0.94 (t, *J*=6.8 Hz, 72H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃): δ_C 160.37, 152.11, 151.98, 142.50, 139.45, 139.29, 136.72, 135.82, 131.03, 130.85, 128.90, 128.65, 125.23, 124.76, 121.87, 72.65, 35.12, 34.56, 32.51, 28.26, 23.20, 14.84. Dosy NMR (500 MHz, $CDCl_3$, 25 ℃): D=1.80*10^{-10} m^2/s. Ms (Maldi-tof) m/z: 10117.4707 (M+H$^+$, 100%); Calcd for $C_{696}H_{648}O_{48}N_{24}$ +H$^+$: 10117.4104

1.7.9 Hemicarcerand capsule $C^b_2L^d_4$

From **C^b** (2.12 mg, 1.65 μmol), 1,2-ethylenedianiline (0.70 mg, 3.30 μmol) and TFA (2 μL, 1%v/v in $CDCl_3$) according to **procedure A.** NMR shows that the purity is 95% and the rest are larger aggregates.



^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃) of $C^b_2L^d_4$: δ_H 8.44 (s, 8H, -C*H*N-), 7.89 (d, *J*=7.7 Hz, 16H, Ha_2), 7.69 (s, 8H, Ha_3), 7.29 (d, *J*=7.7 Hz, 48H, Ha_2), 7.04 (d, *J*=8.3 Hz, 16H, Ha_4), 6.96 (d, *J*=8.3 Hz, 16H, Ha_5), 5.31 (t, *J*=8.3 Hz, 8H, Hm), 3.90 (m, 16H, Ho), 3.45 (m, 16H, Hi), 2.98 (s, 16H, H6), 2.25 (m, 16H, H1), 1.46-0.90 (t, *J*=7.1 Hz, 24H, H5). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃) of $C^b_2L^d_4$: δ_C 161.86, 151.89, 137.93, 136.31, 135.75, 130.63, 130.08, 128.23, 124.37, 72.53, 62.95, 34.95, 34.14, 32.19, 27.94, 22.92. Ms (Maldi-tof) of $C^b_2L^d_4$ m/z: 3284.6484 (M+H$^+$, 100%); Calcd for $C_{224}H_{224}O_{16}N_8$ +H$^+$: 3284.7094

Reference:

[1] C. B. Aakeroy, P. D. Chopade, *Org. Lett.* **2010**, *13*, 1-3.

[2] R. C. Helgeson, K. Paek, C. B. Knobler, E. F. Maverick, D. J. Cram, *J. Am. Chem. Soc.* **1996**, *118*, 5590-5604.

2. NMR Spectra, Maldi-TOF Mass Spectra and GPC Chromatograms

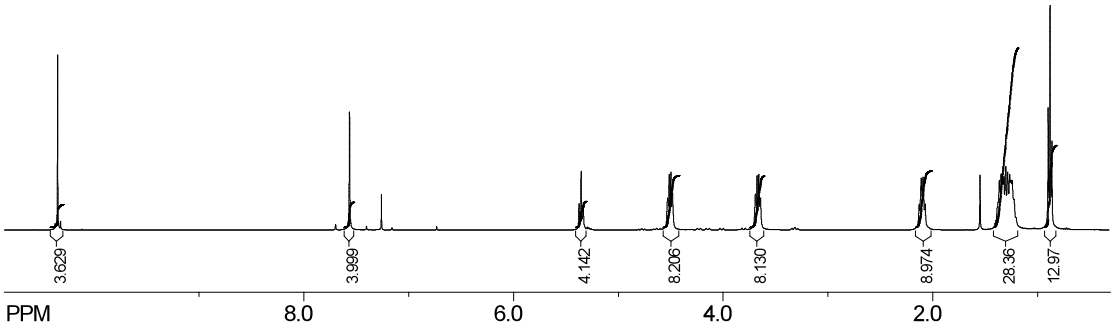


Figure S-1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ℃) of **C**^{e}

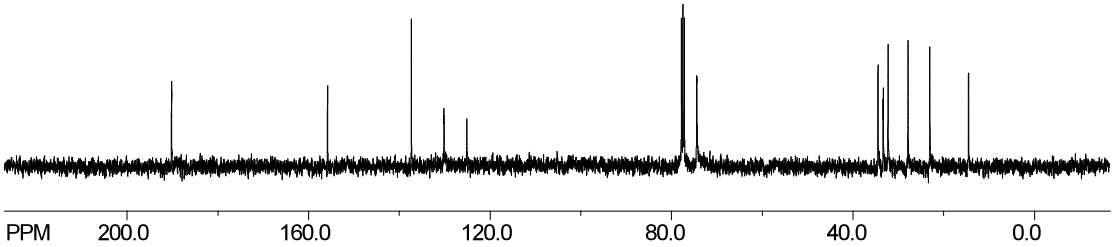


Figure S-2: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 ℃) of **C**^{e}

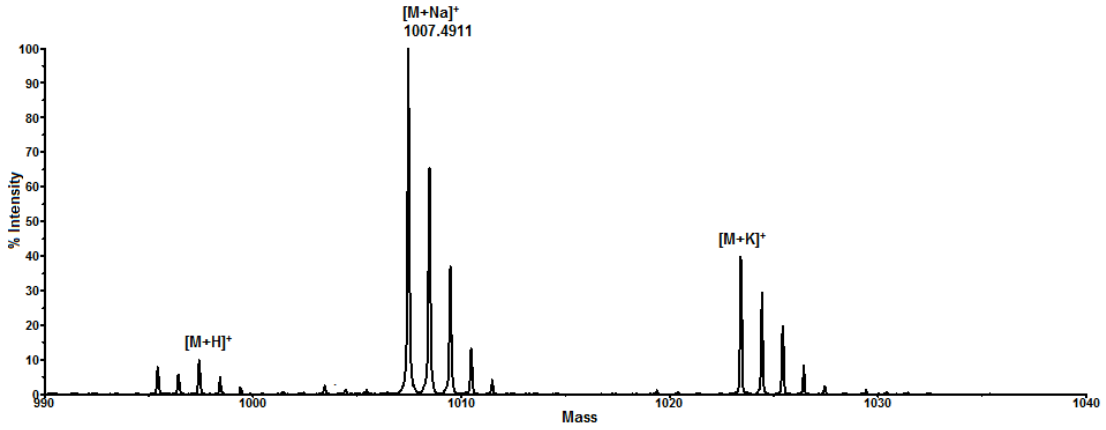


Figure s-3: Maldi-tof Mass Spectrum of **C**^{e}.

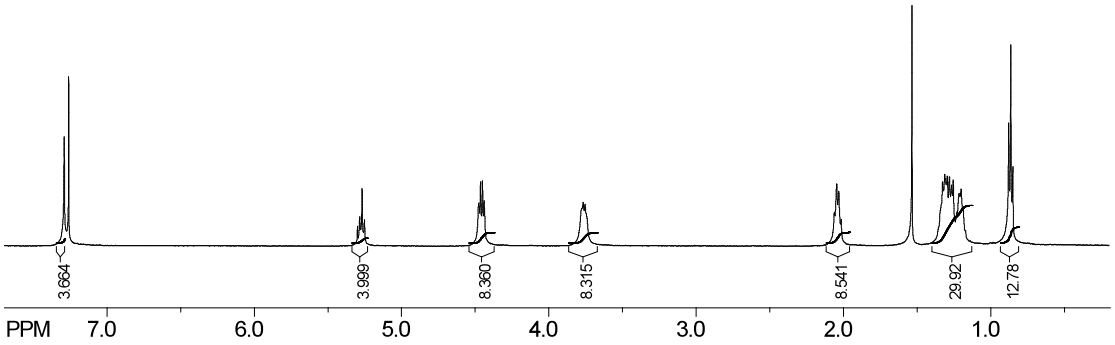


Figure S-4: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of **2b**.

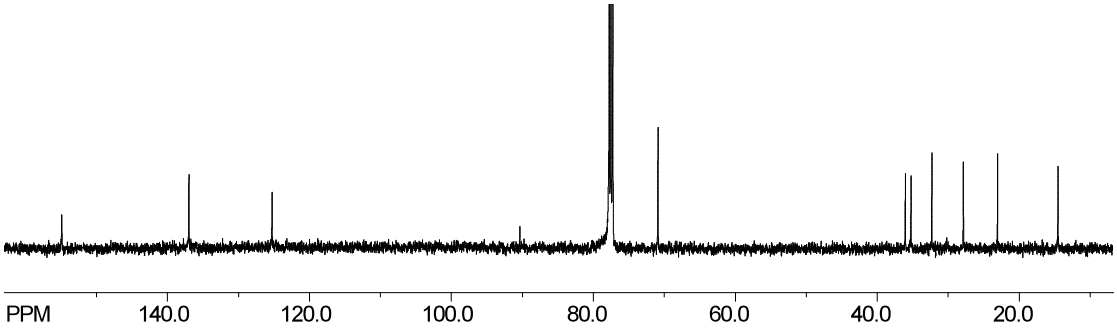


Figure S-5: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of **2b**

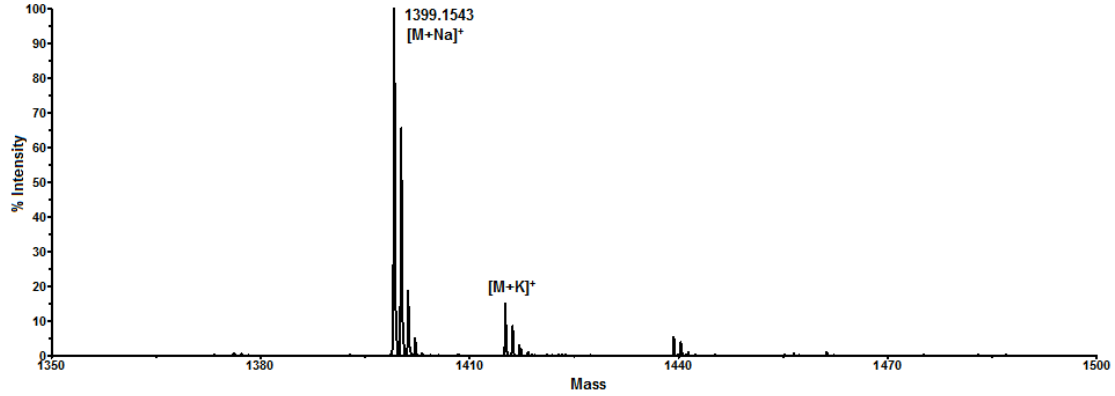


Figure S-6: Maldi-tof Mass Spectrum of **2b**.

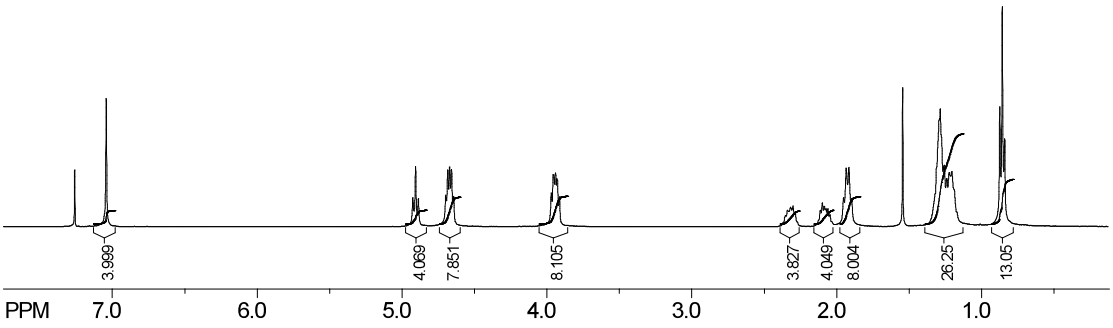


Figure S-7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ℃) of **2c**.

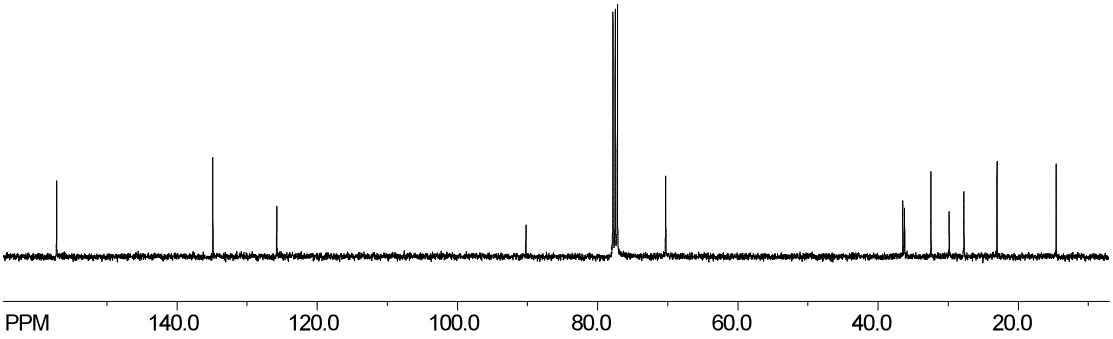


Figure S-8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 ℃) of **2c.**

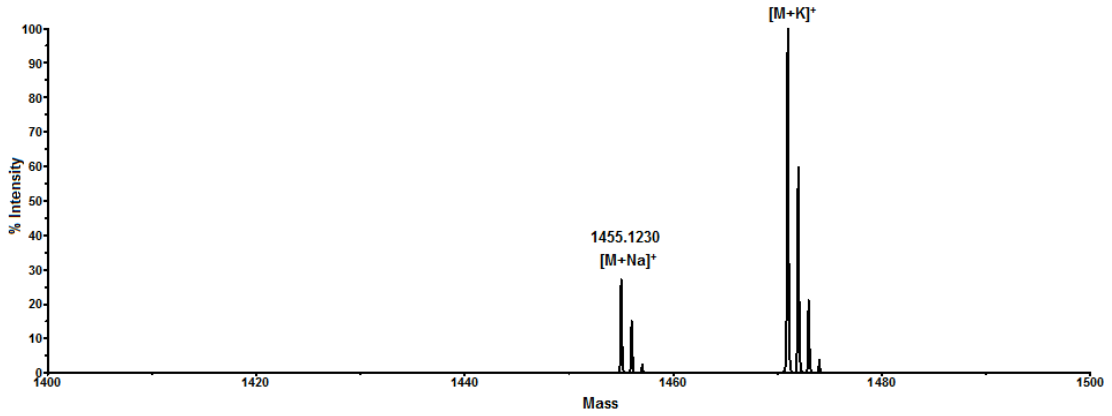


Figure S-9: Maldi-tof Mass Spectrum of **2c**.

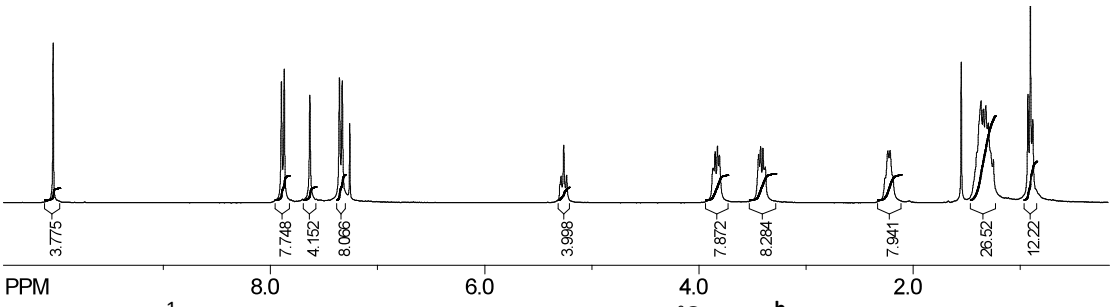


Figure S-10: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of **C^{b}**.

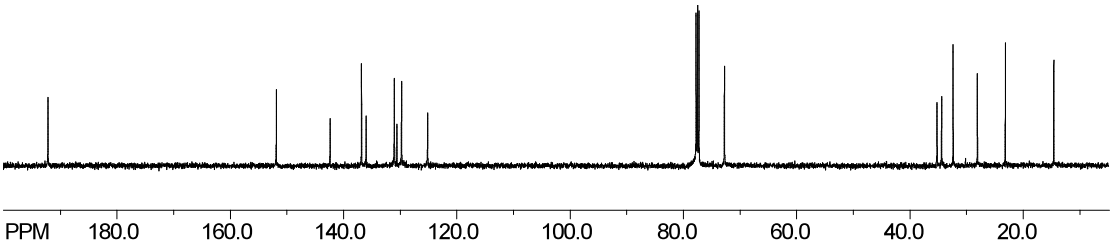


Figure S-11: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of **C^{b}.**

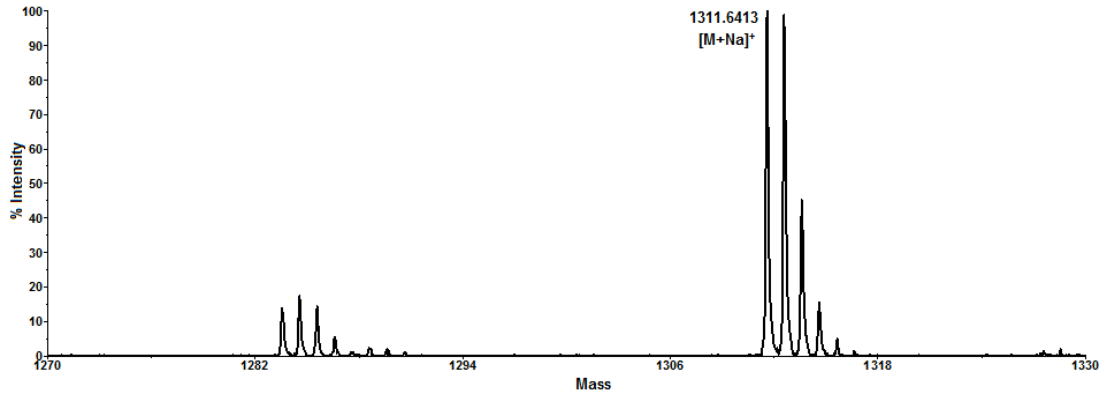


Figure S-12: Maldi-tof Mass Spectrum of **C^{b}.**

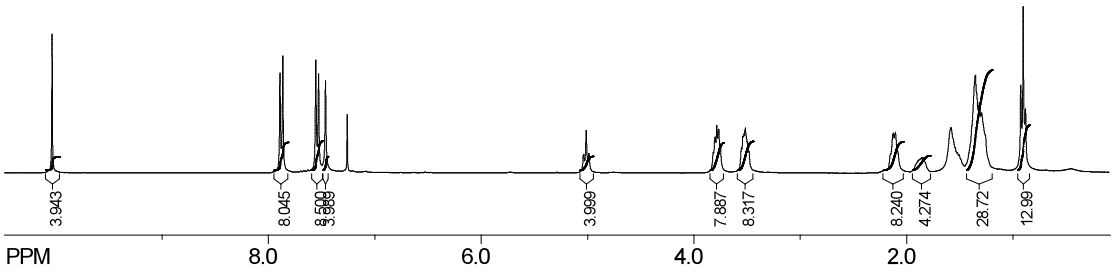


Figure S-13: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of **C**^{c}.

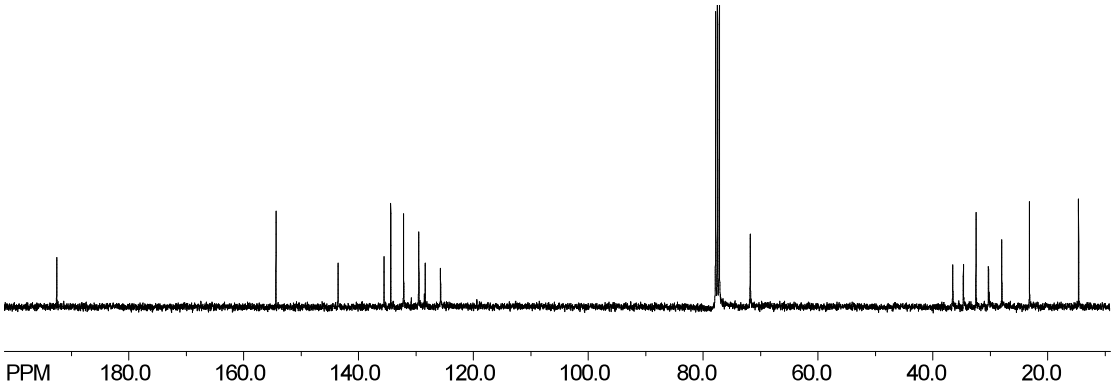


Figure S-14: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 ℃) of **C**$^{c.}$

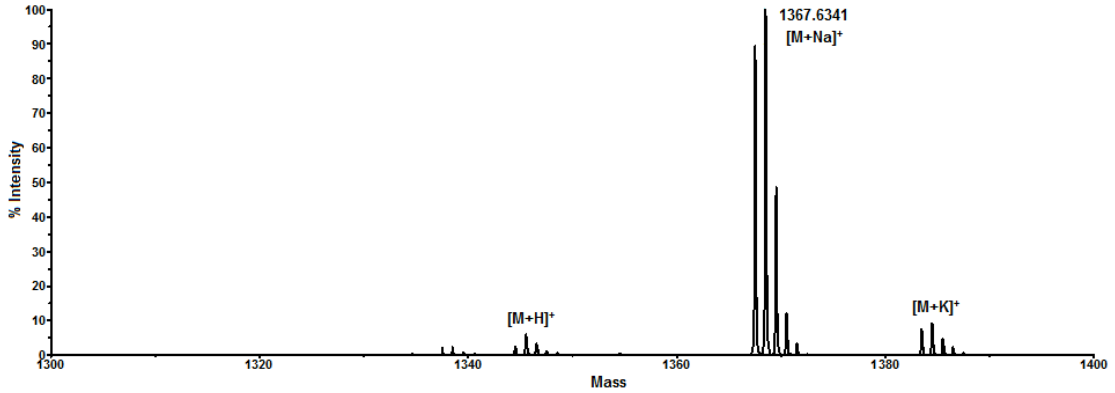


Figure S-15: Maldi-tof Mass Spectrum of **C**^{c}**.**

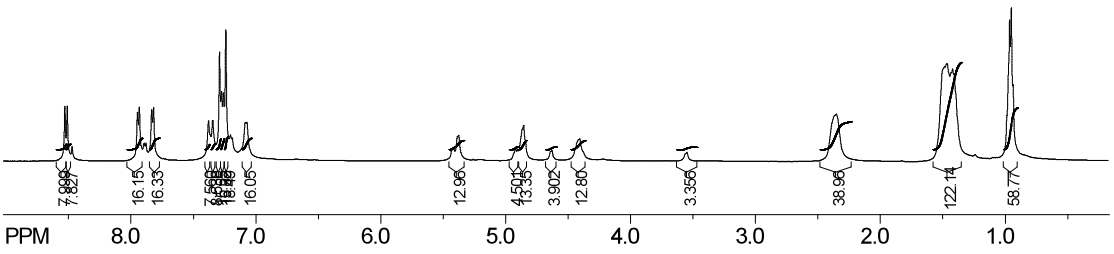


Figure S-16: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^b_8}$

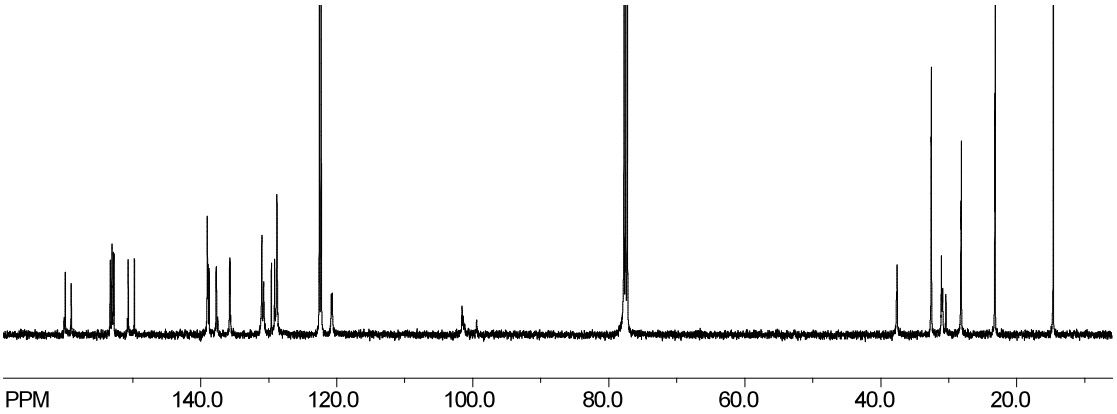


Figure S-17: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^b_8}$

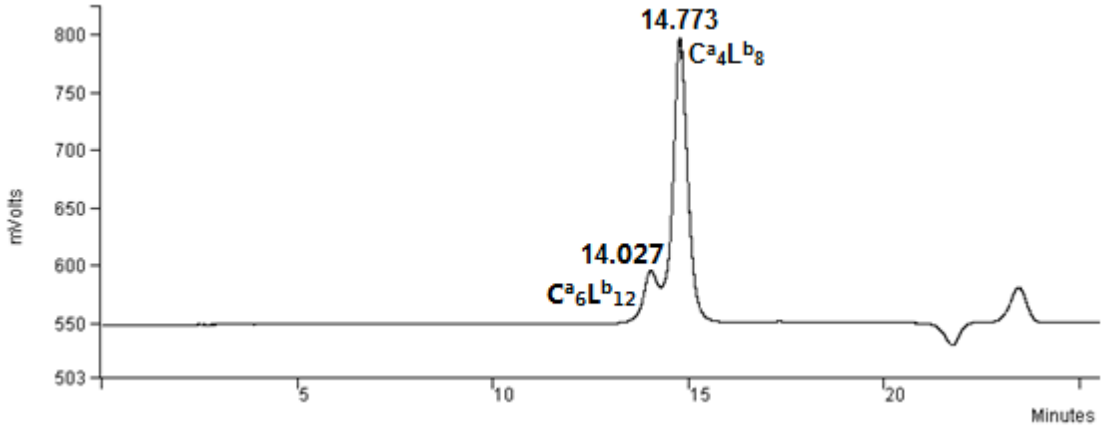


Figure S-18: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^a_4L^b_8}$

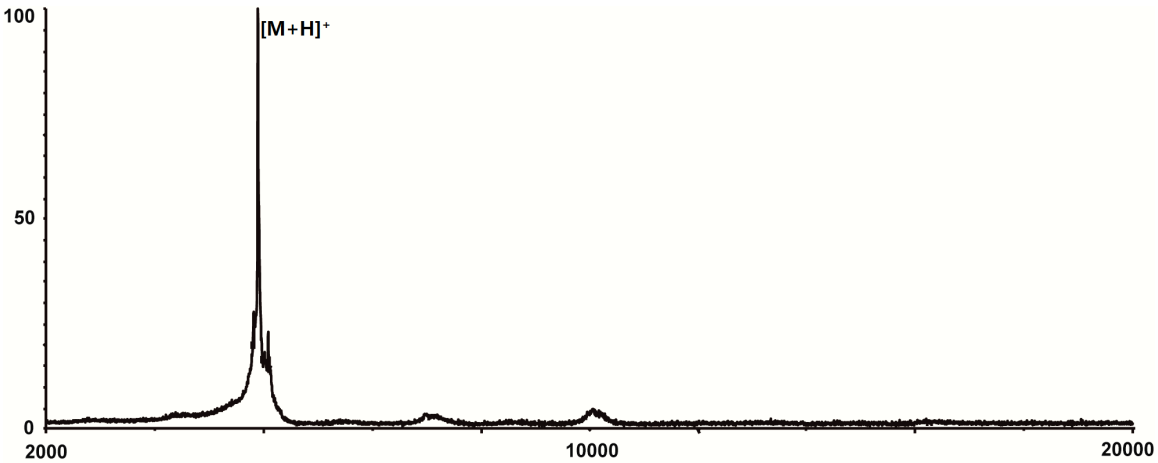


Figure S-19: Maldi-tof Mass Spectrum of $\mathbf{C^a_4L^b_8}$

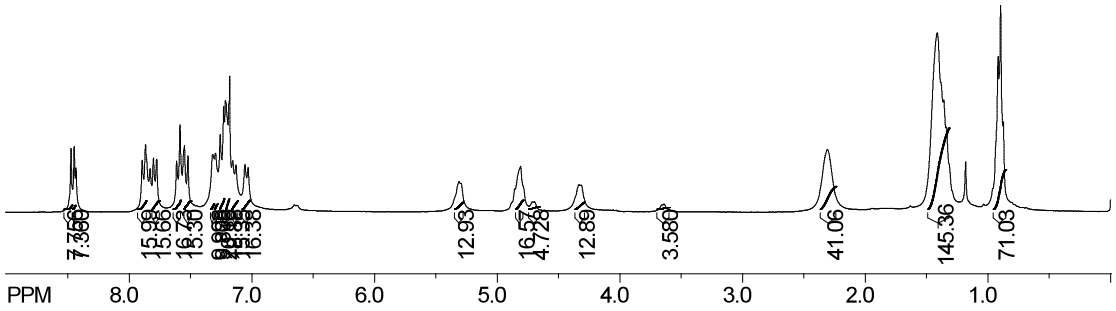


Figure S-20: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^c_8}$

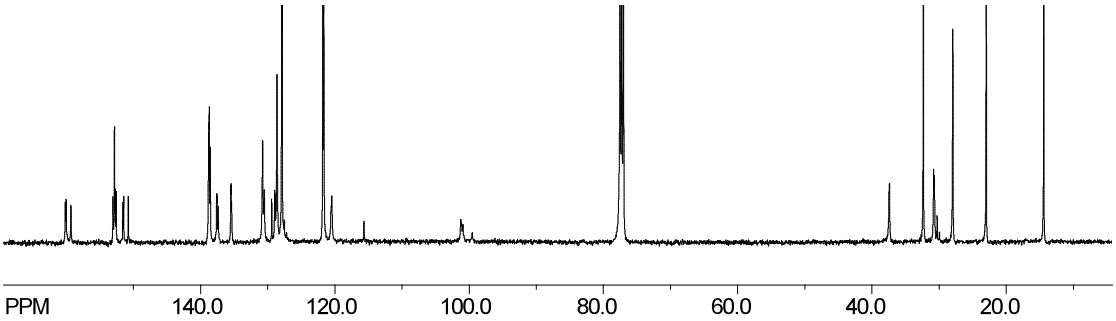


Figure S-21: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^c_8}$

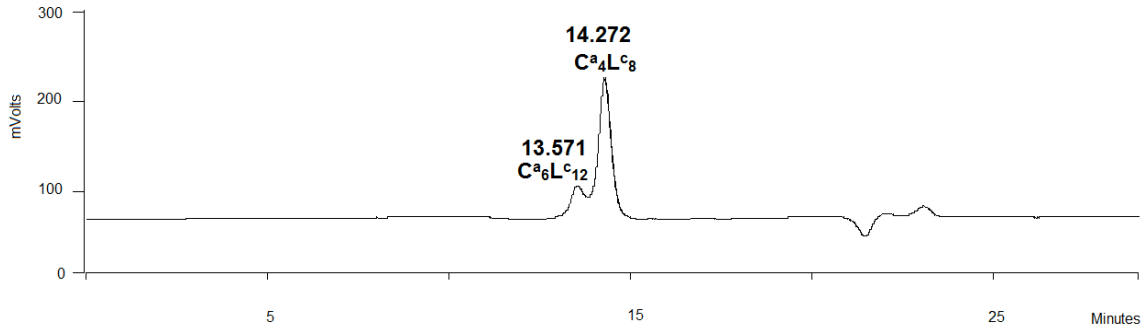


Figure S-22: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^a_4L^c_8}$

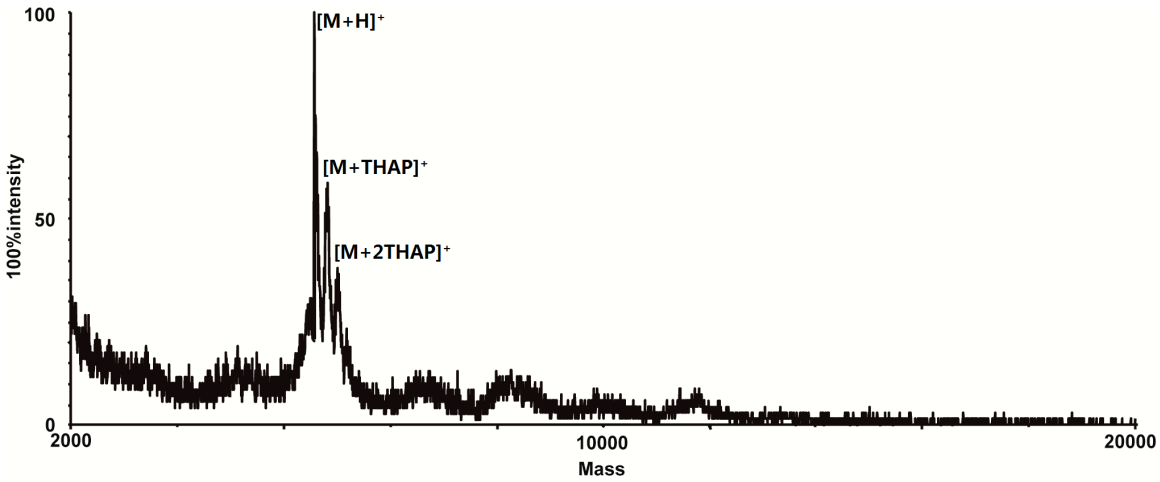


Figure S-23: Maldi-tof Mass spectrum of $\mathbf{C^a_4L^c_8}$

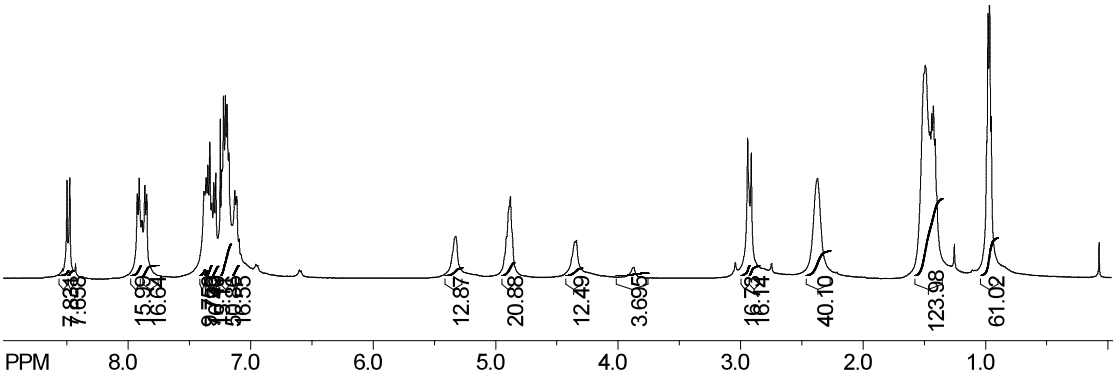


Figure S-24: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^d_8}$

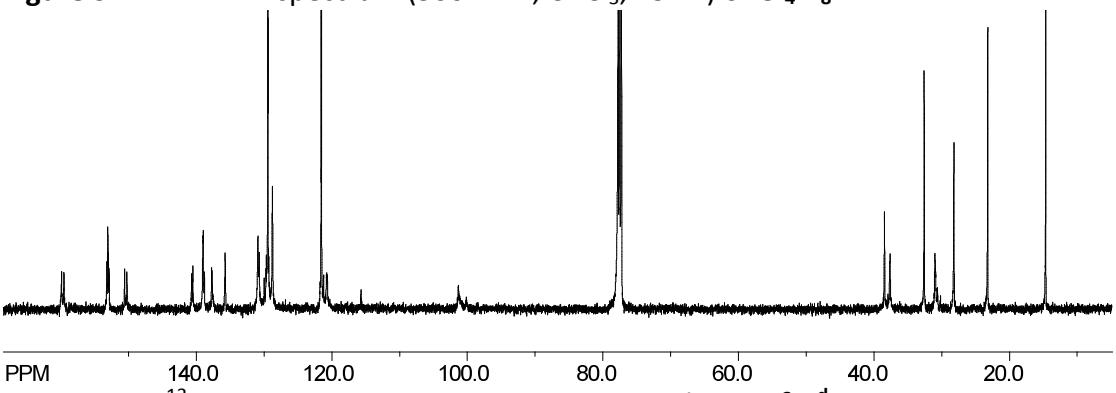


Figure S-25: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_4L^d_8}$

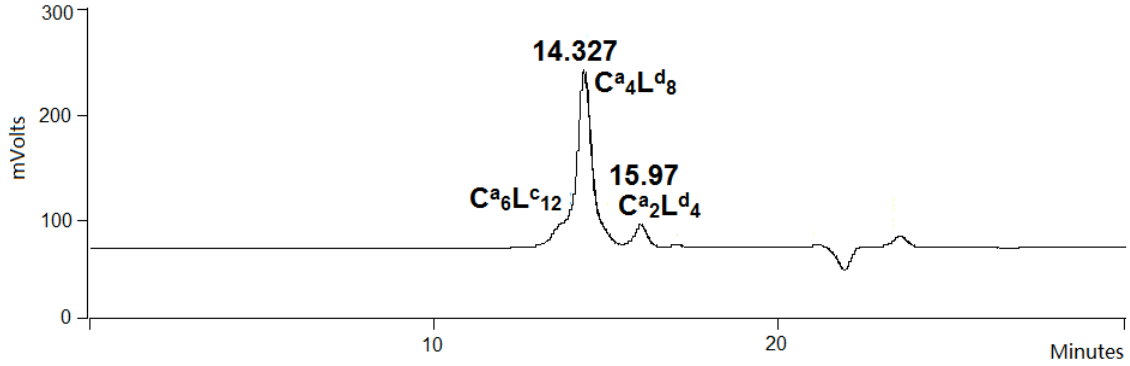


Figure S-26: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^a_4L^d_8}$

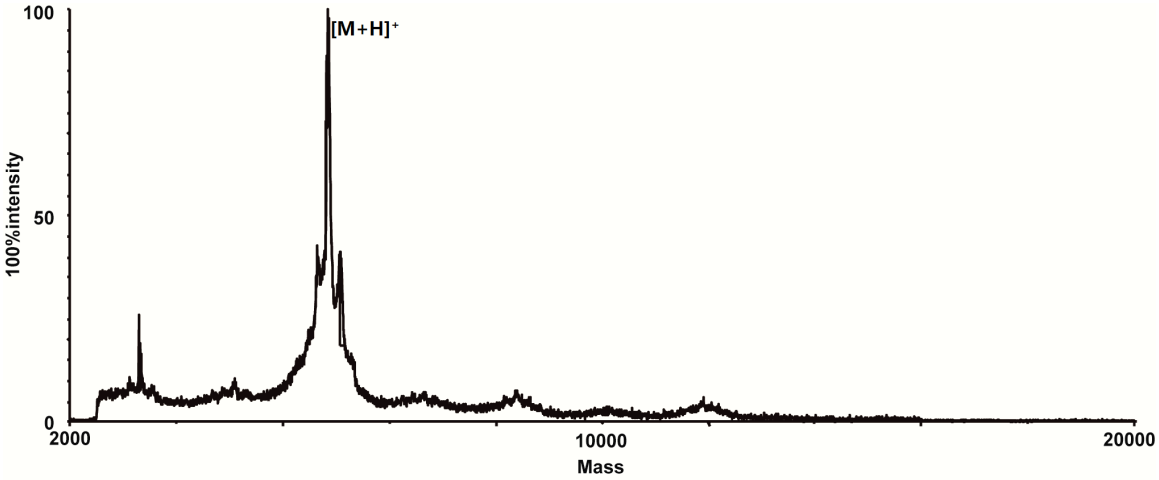


Figure S-27: Maldi-tof Mass spectrum of $\mathbf{C^a_4L^d_8}$

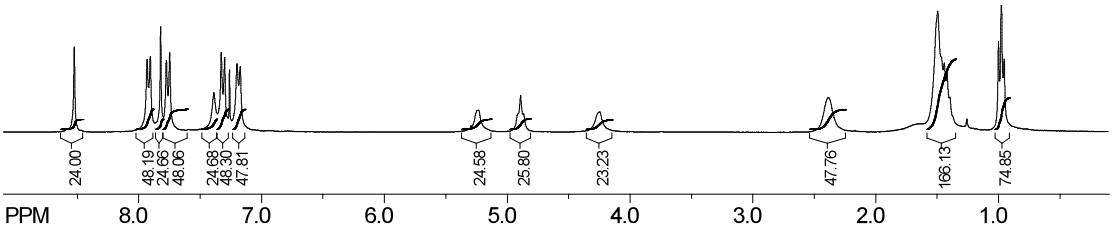


Figure S-28: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_6T_8}$

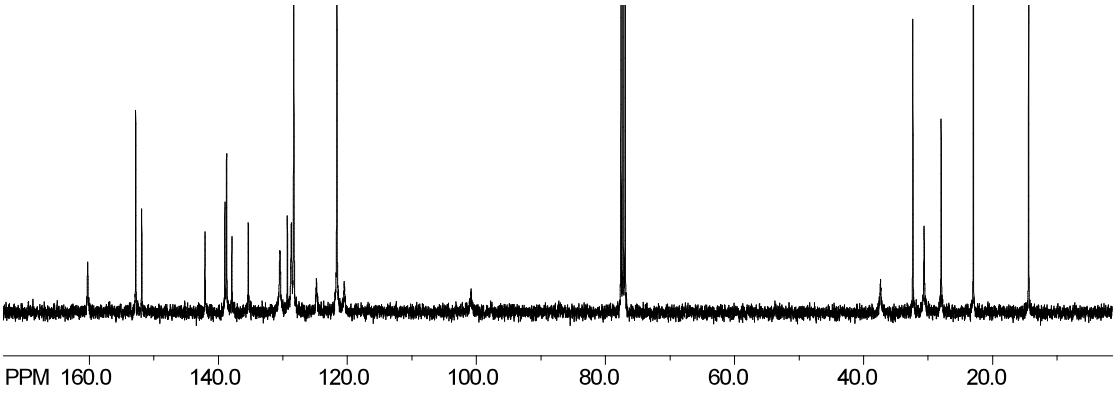


Figure S-29: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^a_6T_8}$

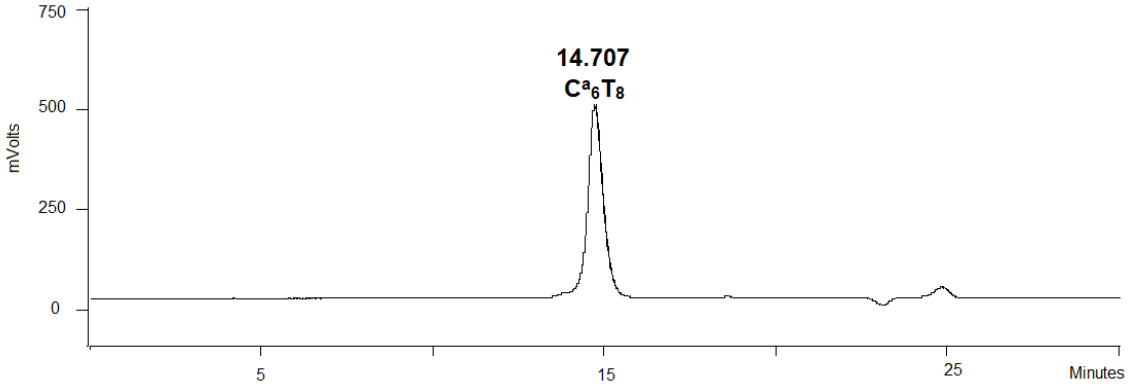


Figure S-30: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 0.9 ml/min) of $\mathbf{C^a_6T_8}$

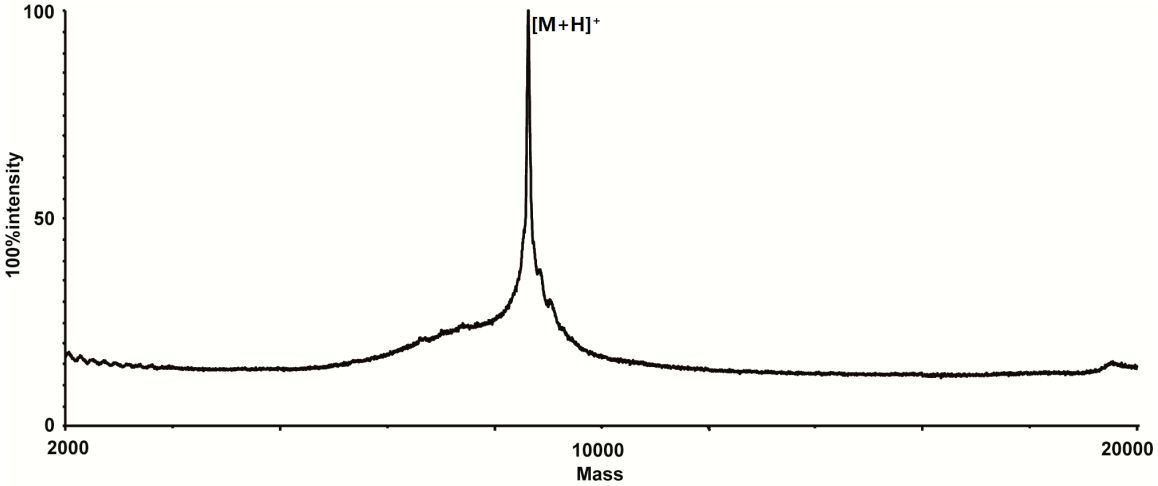


Figure S-31: Maldi-tof Mass spectrum of $\mathbf{C^a_6T_8}$

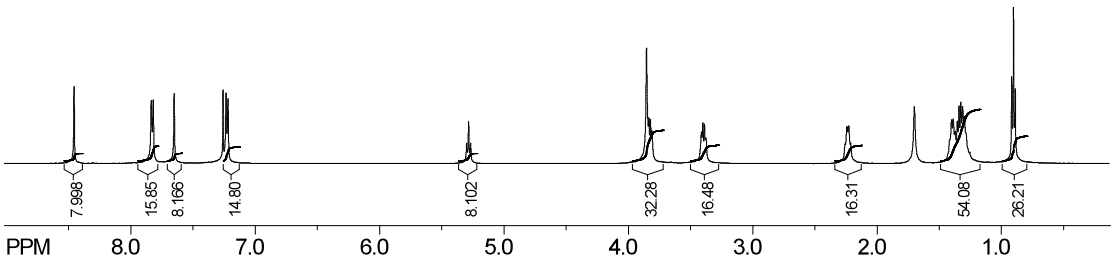


Figure S-32: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_2L^a_4}$

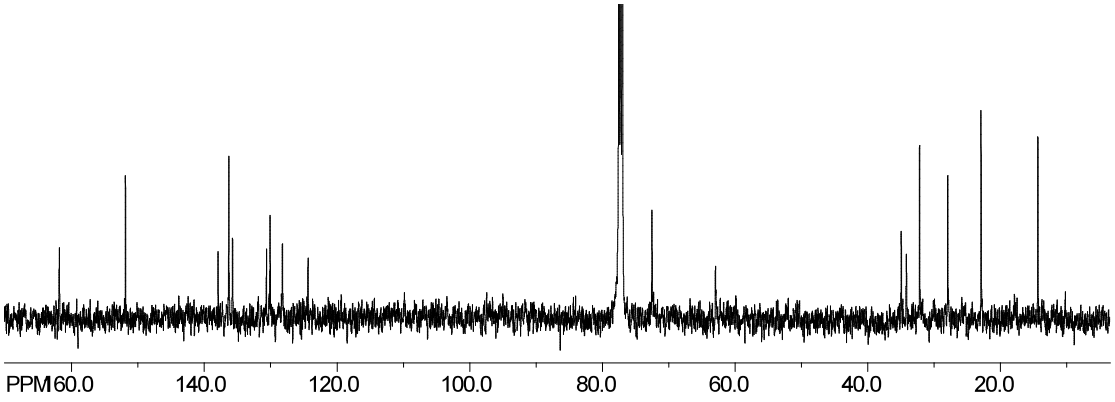


Figure S-33: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_2L^a_4}$

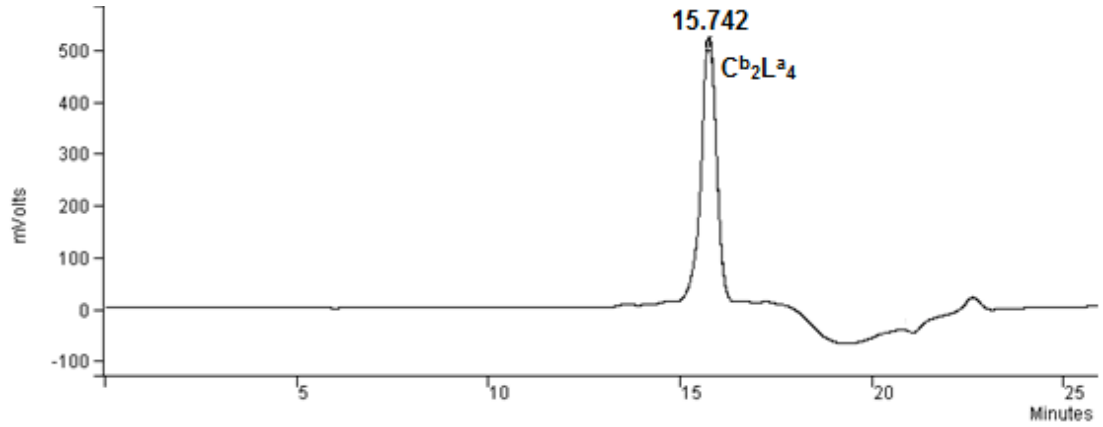


Figure S-34: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^b_2L^a_4}$

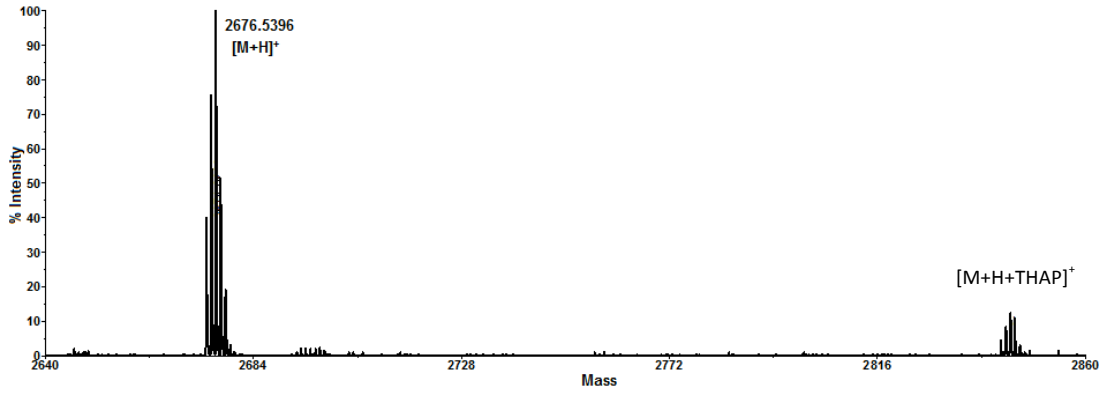


Figure S-35: Maldi-tof Mass spectrum of $\mathbf{C^b_2L^a_4}$

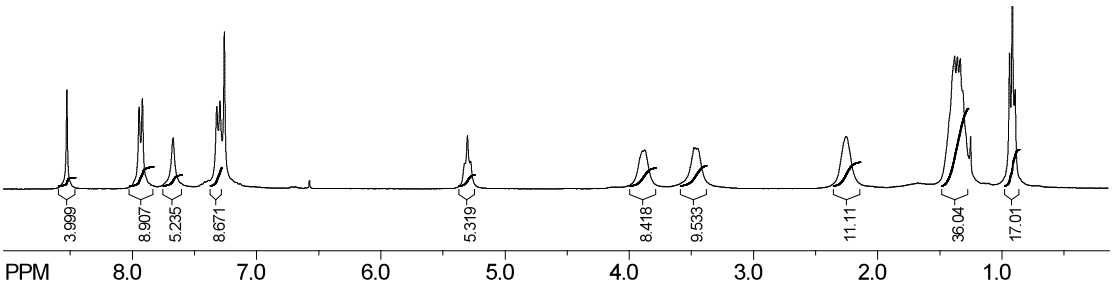


Figure S-36: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_6L^b_{12}}$

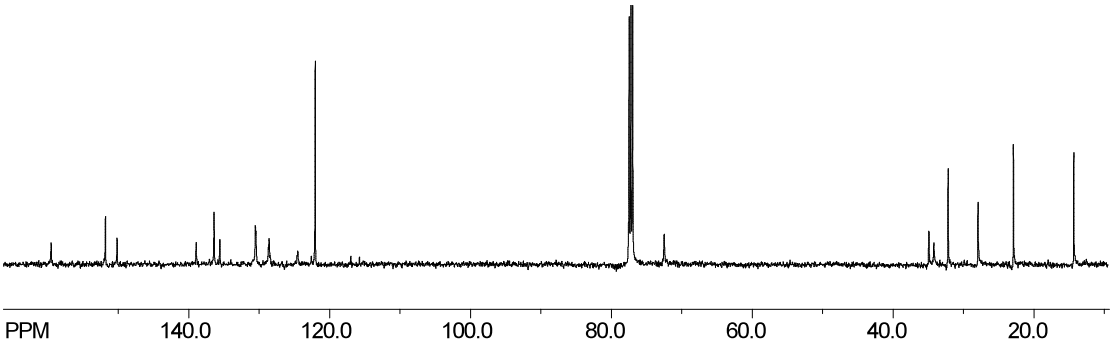


Figure S-37: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_6L^b_{12}}$

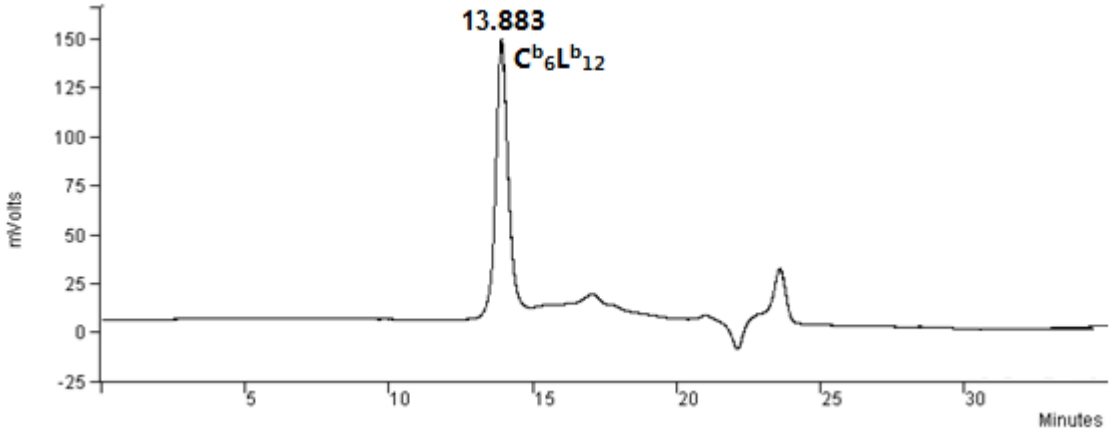


Figure S-38: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^b_6L^b_{12}}$

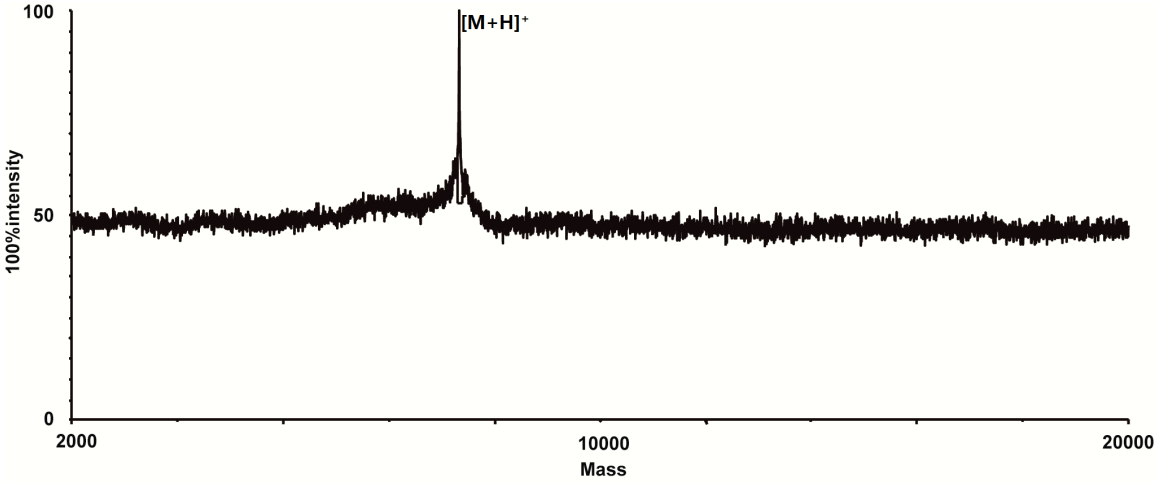


Figure S-39: Maldi-tof Mass spectrum of $\mathbf{C^b_6L^b_{12}}$

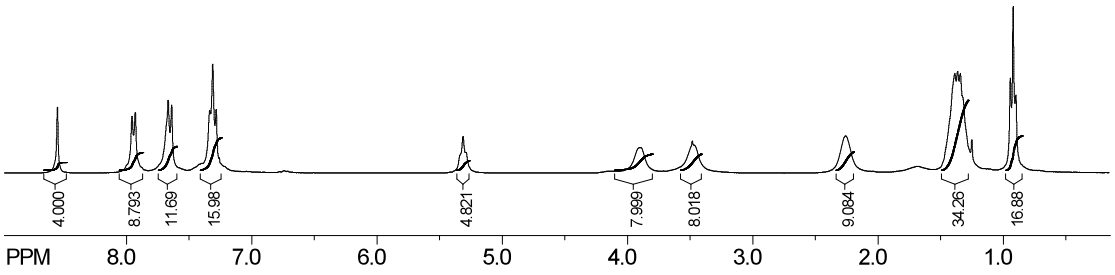


Figure S-40: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^{b}_{6}L^{c}_{12}}$

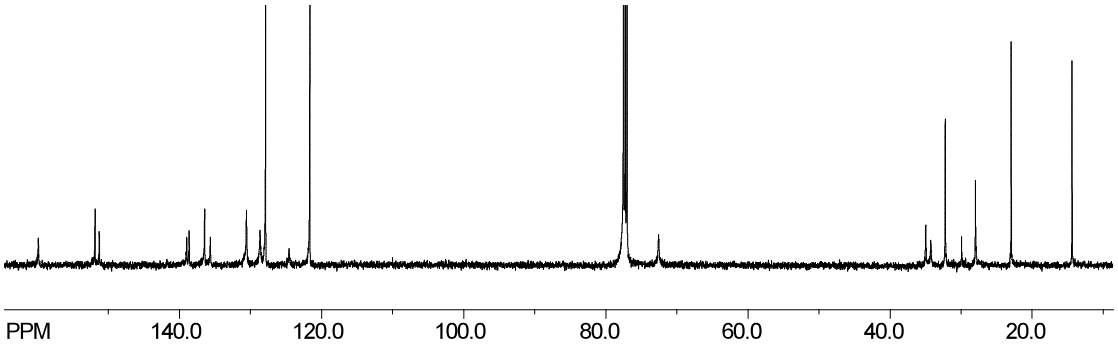


Figure S-41: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^{b}_{6}L^{c}_{12}}$

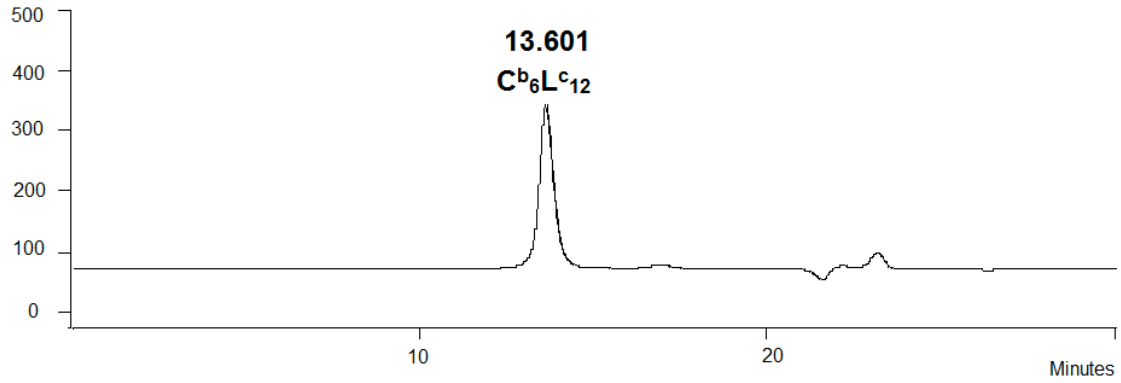


Figure S-42: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^{b}_{6}L^{c}_{12}}$

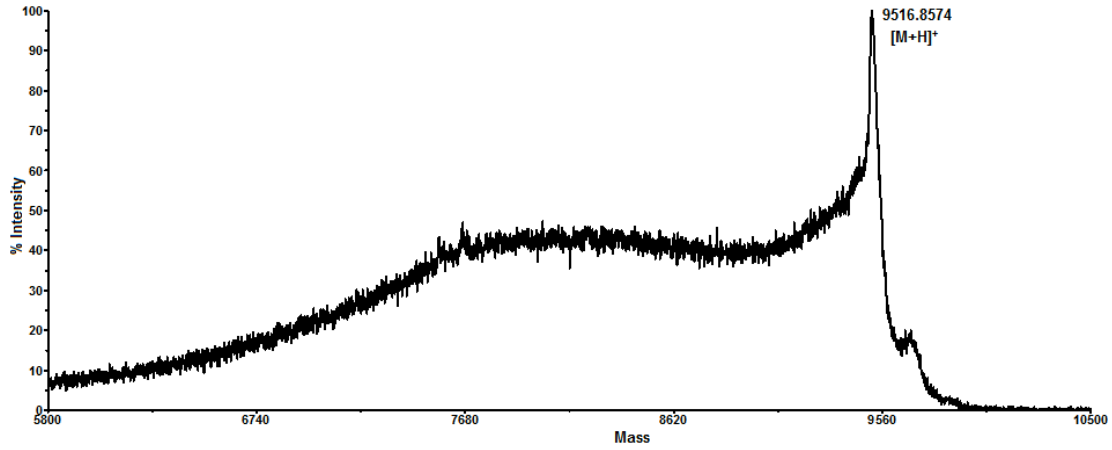


Figure S-43: Maldi-tof Mass spectrum of $\mathbf{C^{b}_{6}L^{c}_{12}}$

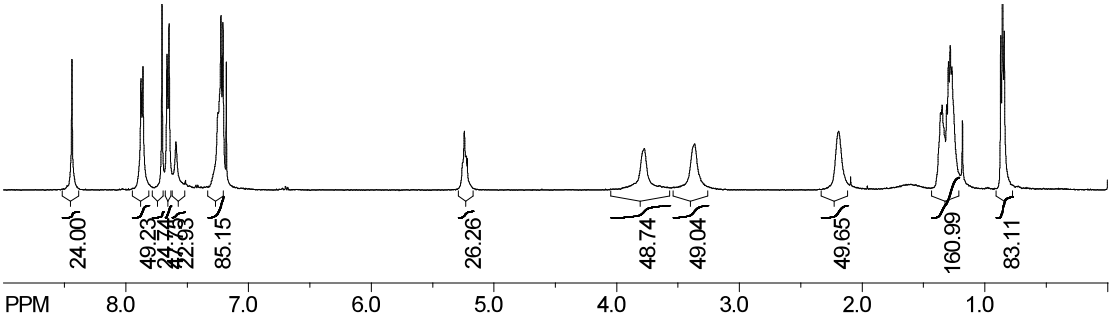


Figure S-44: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_6T_{12}}$

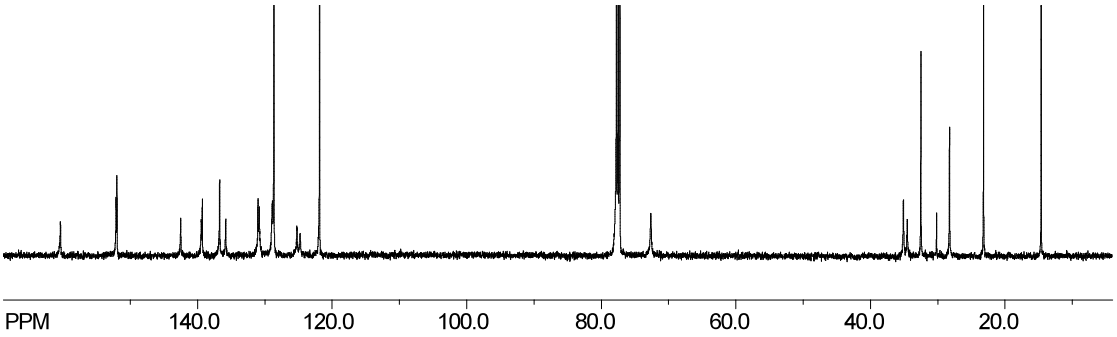


Figure S-45: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_6T_{12}}$

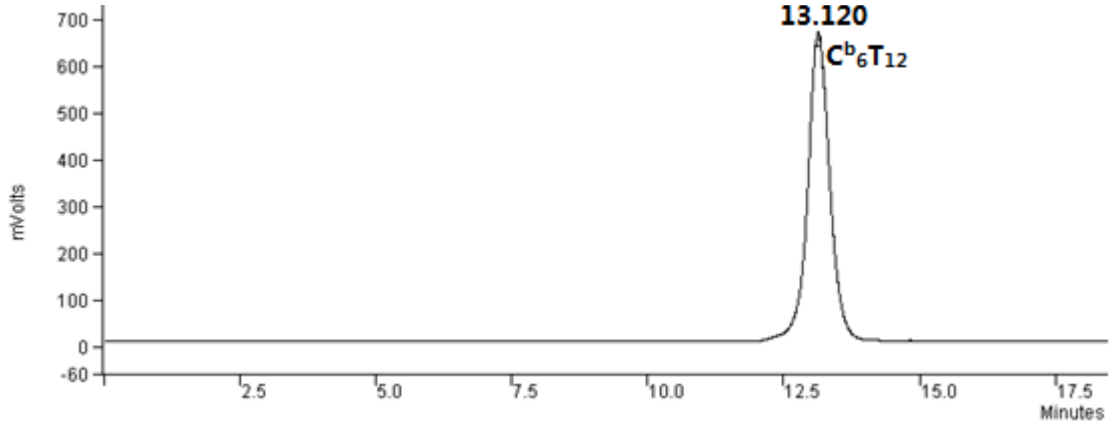


Figure S-46: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^b_6T_{12}}$

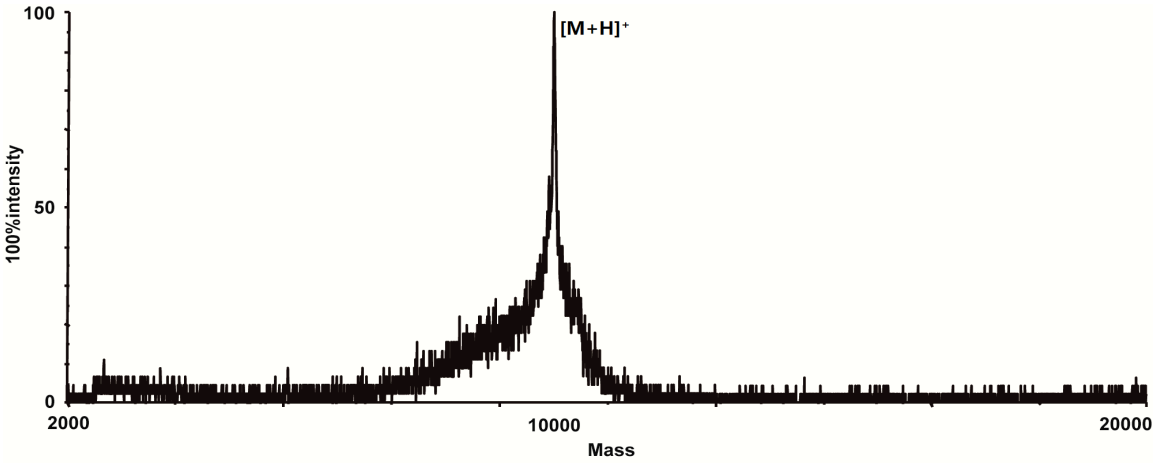


Figure S-47: Maldi-tof Mass spectrum of $\mathbf{C^b_6T_{12}}$

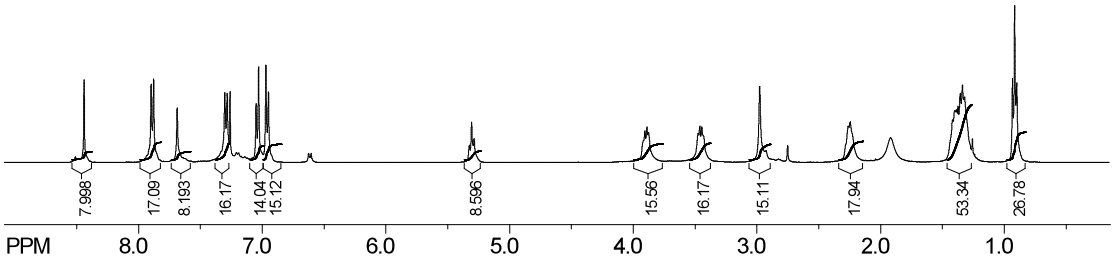


Figure S-48: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_2L^d_4}$

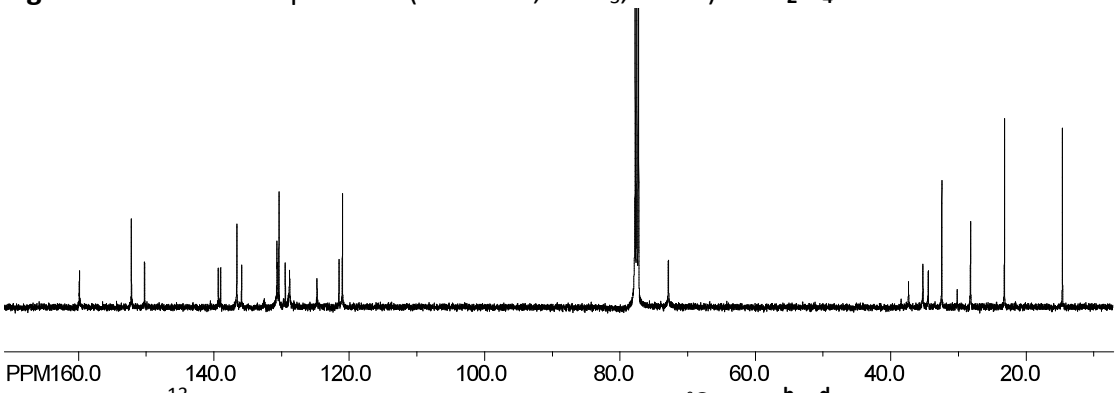


Figure S-49: ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of $\mathbf{C^b_2L^d_4}$

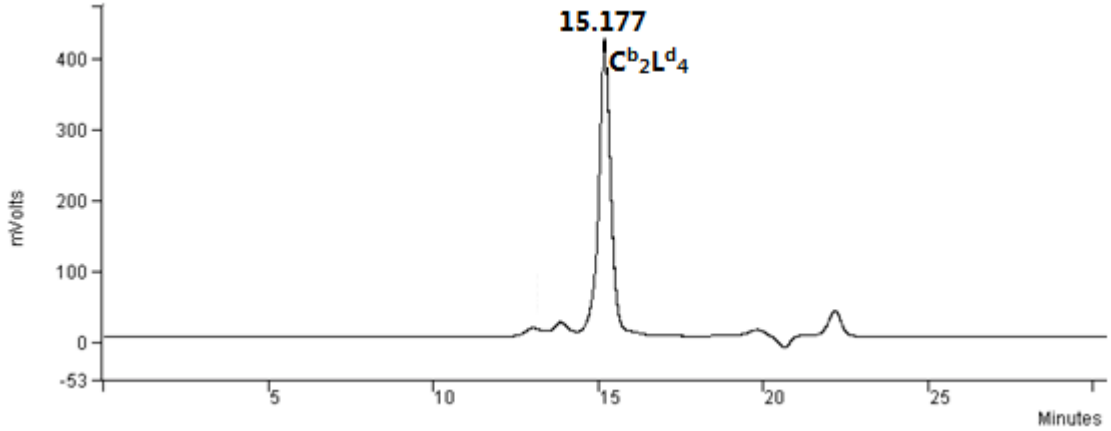


Figure S-50: GPC chromatogram (CH_2Cl_2+1% TEA, 60 ℃, 280 nm, 1 ml/min) of $\mathbf{C^b_2L^d_4}$

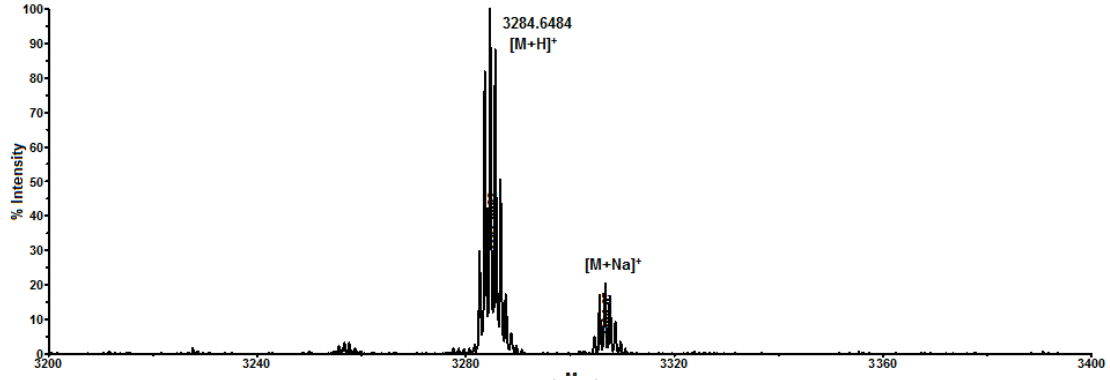


Figure S-51: Maldi-tof Mass spectrum of $\mathbf{C^b_2L^d_4}$