Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Switchable silver-ion complexation by triazolated calix[4]semitubes

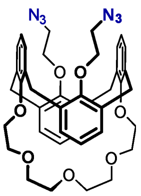
Maria Malakhova, Alexander Gorbunov, Ivan Lentin, Vladimir Kovalev and Ivan Vatsouro

Supplementary Information

Contents

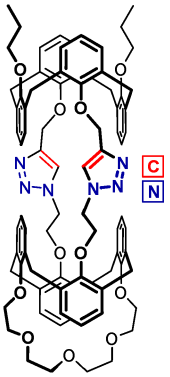
Synthesis and characterization of novel compounds

General experimental methods: NMR spectra were acquired on a Bruker Avance 400 instrument at 20 ºC if not stated otherwise, and chemical shifts are reported as ppm referenced to solvent signals. ESI mass spectra were obtained from Sciex TripleTOF 5600+ spectrometers. Chemicals received from commercial sources were used without further purification. Calixarenes **1**,[S1] **2**–**4**,[S2] **11**, **12**,[S1] **13**,[S3] **14**,[S1] **16**, **17**[S2] were prepared according to the published procedures.

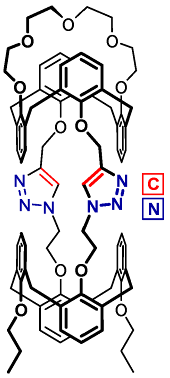


Calix[4]arene bis(azide) ***15***. A suspension of calixarene **14** (0.843 g, 1.50 mmol), anhydrous Cs_2CO_3 (1.462 g, 4.50 mmol) and tetraethylene glycol ditosylate (0.831 g, 1.65 mmol) in dry DMF (70 ml) was stirred at room temperature for 48 h. The solvent was evaporated, methylene chloride was added to the residue, and the mixture was washed with 2 M HCl. The organic layer was separated, washed with water, dried with and concentrated to dryness. The residue was purified by column chromatography (gradient from hexane to hexane/ethyl acetate (4:1)). The product was re-crystallized from methanol. Yield 0.382 g (35%), white solid. M.p. 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.07 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.91 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.90 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 3.90 (d, 4H, $^2J_{HH}$ = 16.5 Hz; $ArCH_2Ar$), 3.84 (d, 4H, $^2J_{HH}$ = 16.5 Hz; $ArCH_2Ar$), 3.59–3.50 (m, 8H; OCH_2CH_2O), 3.46–3.37 (m, 8H; OCH_2CH_2O), 3.13–3.07 (m, 4H; OCH_2), 2.75–2.69 (m, 4H; CH_2N_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.41, 155.59, 134.07, 133.79 (C_{Ar}), 129.33, 129.05, 123.11, 122.82 (CH_{Ar}), 72.67, 70.63, 69.74, 68.26, 67.37 (OCH_2), 49.71 (CH_2N_3), 37.92 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 759.2908 $[M+K]^+$ for $C_{40}H_{44}KN_6O_7$ (759.2903).

General procedure for the preparation of calix[4]semitubes. To a stirred mixture of calixarene (bis)alkyne and (bis)azide in THF, Cu(I)-catalyst was added ($CuSO_4{\cdot}5H_2O$/sodium ascorbate mixture dissolved in water). The mixture was stirred at 60 °C for 24 h, and then concentrated under reduced pressure. The residue was parted between dichloromethane and 2 M HCl at vigorous stirring for at least 2 h. The organic layer was separated, washed water and dried with $MgSO_4$. The solvent was removed and the residue was subjected to column chromatography. The two-step column separation was applied in several cases: from the first column, a polymeric material was first eluted followed by a semitube-containing fraction, which was then evaporated to dryness and subjected to the second column (with the same or different eluent) for the final purification.

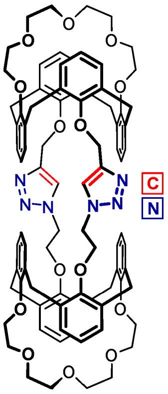


Bis(calix[4]arene) **5** was prepared according to *General procedure* from calixarene **15** (0.122 g, 0.17 mmol), calixarene **11** (0.100 g, 0.17 mmol), $CuSO_4 \cdot 5H_2O$ (0.042 g, 0.17 mmol) and sodium ascorbate (0.067 g, 0.34 mmol) in a mixture of THF (20 ml) and water (4 ml). The residue was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (40:1)). Yield 0.056 g (21%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.04 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.98 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.97 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.86 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.77 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.73 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.35 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.19 (s, 2H; ArH_{Trz}), 4.78 (s, 4H; OCH_2Trz), 4.30–4.23 (m, 4H; NCH_2), 4.07–4.01 (m, 4H; $NCH_2C\underline{H}_2$), 3.95 (d, 4H, $^2J_{HH}$ = 16.6 Hz; $ArCH_2Ar$), 3.87 (d, 4H, $^2J_{HH}$ = 16.6 Hz; $ArCH_2Ar$), 3.76 (d, 4H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.68–3.63 (m, 4H; OCH_2CH_2), 3.61–3.54 (m, 4H; OCH_2CH_2), 3.58 (d, 4H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.53–3.46 (m, 4H; OCH_2CH_2), 3.37–3.31 (m, 4H; $OC\underline{H}_2CH_2CH_3$), 3.12–3.05 (m, 4H; OCH_2CH_2), 1.39–1.29 (m, 4H; $CH_2C\underline{H}_2CH_3$), 0.69 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.95, 156.27, 155.60, 154.86 (C_{Ar}), 144.38 ($C_{Ar\ Trz}$), 134.38, 134.30, 134.03, 133.45 (C_{Ar}), 129.86, 129.65, 129.19, 128.39 (CH_{Ar}), 124.03 ($CH_{Ar\ Trz}$), 123.66, 123.00, 121.16 (CH_{Ar}), 73.09, 71.84, 70.83, 69.40, 68.52, 67.49, 63.53 (OCH_2), 48.63 (NCH_2), 38.20, 37.98 ($ArCH_2Ar$), 22.94 ($\underline{C}H_2CH_3$), 10.08 (CH_3) ppm. ESI-MS *m/z*: 1322.6532 $[M+NH_4]^+$ for $C_{80}H_{88}N_7O_{11}$ (1322.6536).

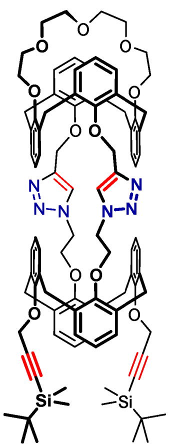


Bis(calix[4]arene) **6** was prepared according to *General procedure* from calixarene **13** (0.112 g, 0.17 mmol), calixarene **12** (0.200 g, 0.17 mmol), $CuSO_4 \cdot 5H_2O$ (0.042 g, 0.17 mmol) and sodium ascorbate (0.067 g, 0.34 mmol) in a mixture of THF (20 ml) and water (4 ml). The residue was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (40:1)). Yield 0.055 g (25%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.07 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.95 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.92 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.88 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.83 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.65 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.42 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.09 (s, 2H; ArH_{Trz}), 4.77 (s, 4H; OCH_2Trz), 4.43–4.36 (m, 4H; NCH_2), 4.07–3.99 (m, 4H; $NCH_2C\underline{H}_2$), 3.89 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.82 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.81 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.63 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.57–3.52 (m, 8H; OCH_2CH_2), 3.41–3.35 (m, 4H; $OC\underline{H}_2CH_2CH_3$), 3.34–3.30 (m, 4H; OCH_2CH_2), 3.27–3.20 (m, 4H; OCH_2CH_2), 1.20–1.08 (m, 4H; $CH_2C\underline{H}_2CH_3$), 0.69 (t, 6H, $^3J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.08, 156.17, 155.66, 154.95

(C_{Ar}), 144.12 ($C_{Ar\ Trz}$), 134.48, 134.35, 134.24, 133.36 (C_{Ar}), 130.01, 129.65, 128.97, 128.41 (CH_{Ar}), 124.12 ($CH_{Ar\ Trz}$), 123.47, 123.19, 122.48, 121.95 (CH_{Ar}), 72.35, 71.44, 70.34, 70.08, 68.83, 68.75, 63.37 (OCH_2), 48.86 (NCH_2), 38.35, 38.06 ($ArCH_2Ar$), 22.12 ($\underline{C}H_2CH_3$), 9.85 (CH_3) ppm. ESI-MS *m*/*z*: 1322.6538 $[M+NH_4]^+$ for $C_{80}H_{88}N_7O_{11}$ (1322.6536).

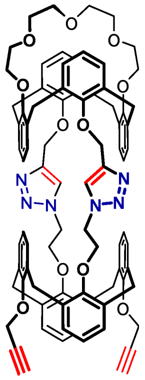


Bis(calix[4]arene) ***7*** was prepared according to *General procedure* from calixarene **15** (0.065 g, 0.09 mmol), calixarene **13** (0.059 g, 0.09 mmol), $CuSO_4\cdot5H_2O$ (0.022 g, 0.09 mmol) and sodium ascorbate (0.036 g, 0.18 mmol) in a mixture of THF (10 ml) and water (2 ml). The residue was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (40:1)). Yield 0.051 g (41%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 7.12 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.97 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.95 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.93 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.80 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.69 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.40 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.06 (s, 2H; ArH_{Trz}), 4.76 (s, 4H; OCH_2Trz), 4.39–4.34 (m, 4H; NCH_2), 4.04–3.99 (m, 4H; $NCH_2C\underline{H}_2$), 3.92 (d, 4H, ${}^2J_{HH}$ = 16.6 Hz; $ArCH_2Ar$), 3.85 (d, 4H, ${}^2J_{HH}$ = 16.6 Hz; $ArCH_2Ar$), 3.81 (d, 4H, ${}^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.68–3.64 (m, 4H; OCH_2), 3.62 (d, 4H, ${}^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.60–3.57 (m, 4H; OCH_2), 3.56–3.52 (m, 8H; OCH_2), 3.51–3.47 (m, 4H; OCH_2), 3.37–3.33 (m, 4H; OCH_2), 3.26–3.22 (m, 4H; OCH_2), 3.12–3.07 (m, 4H; OCH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.19, 156.14, 155.65, 154.91 (C_{Ar}), 144.13 ($C_{Ar\ Trz}$), 134.48, 134.30, 134.23, 133.43 (C_{Ar}), 129.76, 129.66, 128.92, 128.35 (CH_{Ar}), 124.02 ($CH_{Ar\ Trz}$), 123.67, 123.50, 123.08, 121.97 (CH_{Ar}), 73.18, 72.36, 70.86, 70.35, 70.07, 69.35, 68.96, 68.73, 67.37, 63.38 (OCH_2), 48.80 (NCH_2), 38.24, 38.06 ($ArCH_2Ar$). ESI-MS *m*/*z*: 1396.6535 $[M+NH_4]^+$ for $C_{82}H_{90}N_7O_{14}$ (1396.6540).

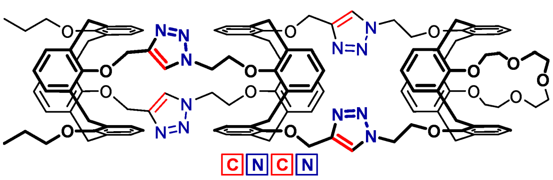


Bis(calix[4]arene) ***18*** was prepared according to *General procedure* from calixarene **13** (0.350 g, 0.53 mmol), calixarene **17** (0.461 g, 0.53 mmol), $CuSO_4\cdot5H_2O$ (0.132 g, 0.53 mmol) and sodium ascorbate (0.210 g, 1.06 mmol) in a mixture of THF (75 ml) and water (15 ml). The residue was purified by column chromatography. Column 1: gradient from dichloromethane to dichloromethane/ethanol (20:1). Column 2: gradient from hexane to hexane/ethyl acetate (1:1). Yield 0.346 g (43%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 7.12 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.96 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.90 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.88 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.85 (d, 4H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.64 (t, 2H, ${}^3J_{HH}$ = 7.5 Hz; ArH), 6.44 (t, 2H,

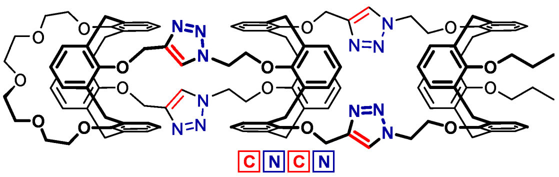
$^3J_{HH}$ = 7.5 Hz; ArH), 6.08 (s, 2H; ArH_{Trz}), 4.78 (s, 4H; OCH_2Trz), 4.49–4.43 (m, 4H; NCH_2), 4.10–4.06 (m, 4H; $NCH_2C\underline{H_2}$), 4.03 (s, 4H; OCH_2CC), 4.02 (d, 4H, $^2J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.84 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.73 (d, 4H, $^2J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.66 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.57–3.52 (m, 8H; OCH_2CH_2O), 3.35–3.29 (m, 4H; OCH_2CH_2O), 3.25–3.19 (m, 4H; OCH_2CH_2O), 0.86 (s, 18H; $C(CH_3)_3$), 0.07 (s, 12H; $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.20, 155.60, 155.59, 154.84 (C_{Ar}), 144.08 ($C_{Ar\,Trz}$), 135.25, 134.51, 134.26, 133.51 (C_{Ar}), 130.33, 129.60, 128.90, 128.42 (CH_{Ar}), 124.35 ($CH_{Ar\,Trz}$), 123.67, 123.49, 123.10, 122.03 (CH_{Ar}), 102.55 ($OCH_2\underline{C}$), 90.09 ($OCH_2C\underline{C}$), 72.41, 70.34, 70.07, 68.91, 68.71, 63.16 (OCH_2), 58.33 ($O\underline{C}H_2CC$), 49.17 (NCH_2), 38.25, 38.14 ($ArCH_2Ar$), 25.95 ($C(\underline{C}H_3)_3$), 16.38 ($\underline{C}(CH_3)_3$), –4.84 ($SiCH_3$) ppm. ESI-MS *m*/*z*: 1564.6962 $[M+K]^+$ for $C_{92}H_{104}KN_6O_{11}Si_2$ (1564.6972).



Bis(calix[4]arene) ***19***. To a suspension of bis(calix[4]arene) **18** (0.346 g, 0.23 mmol) in THF (5 ml) a solution of $nBu_4NF\cdot3H_2O$ (0.058 g, 0.18 mmol) in THF (5 ml) and water (0.10 ml) was added. The mixture was stirred at 50 °C for 12 h and cooled to room temperature. The solvent was removed and the residue was dissolved in dichloromethane. Hexane was added, and the solid formed was collected and dried. Yield 0.241 g (81%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.13 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.96 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.94 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.93 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.85 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.68 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.43 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.09 (s, 2H; ArH_{Trz}), 4.79 (s, 4H; OCH_2Trz), 4.48–4.42 (m, 4H; NCH_2), 4.11–4.06 (m, 4H; $NCH_2C\underline{H_2}$), 4.03 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.87 (d, 4H, $^4J_{HH}$ = 2.4 Hz; $OC\underline{H_2}CCH$), 3.84 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.77 (d, 4H, $^2J_{HH}$ = 16.1 Hz; $ArCH_2Ar$), 3.66 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.57–3.52 (m, 8H; OCH_2CH_2O), 3.35–3.29 (m, 4H; OCH_2CH_2O), 3.25–3.19 (m, 4H; OCH_2CH_2O), 2.34 (t, 2H, $^4J_{HH}$ = 2.4 Hz; CCH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.17, 155.60, 155.42, 154.79 (C_{Ar}), 144.08 ($C_{Ar\,Trz}$), 135.18, 134.49, 134.22, 133.50 (C_{Ar}), 130.51, 129.59, 128.88, 128.64 (CH_{Ar}), 124.26 ($CH_{Ar\,Trz}$), 123.96, 123.48, 123.31, 121.96 (CH_{Ar}), 80.07 ($\underline{C}CH$), 74.80 ($C\underline{C}H$), 72.36, 70.31, 70.03, 68.98, 68.68, 63.11 (OCH_2), 57.80 ($O\underline{C}H_2CCH$), 49.06 (NCH_2), 38.23, 38.10 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1335.5200 $[M+K]^+$ for $C_{80}H_{76}KN_6O_{11}$ (1335.5209).

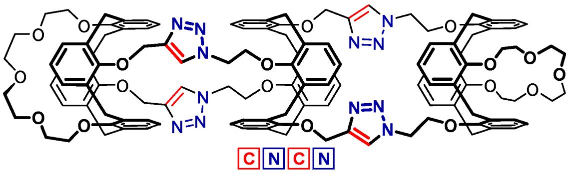


Tris(calix[4]arene) ***8*** was prepared according to *General procedure* from calixarene **16** (0.095 g, 0.08 mmol), calixarene **15** (0.056 g, 0.08 mmol), $CuSO_4\cdot5H_2O$ (0.019 g, 0.08 mmol) and sodium ascorbate (0.031 g, 0.16 mmol) in a mixture of THF (10 ml) and water (2 ml). Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). The residue was dissolved in dichloromethane, methanol was added, and the solid formed was collected and dried. Yield 0.050 g (33%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 7.05 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 7.01–6.96 (m, 6H; ArH), 6.94 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.90–6.84 (m, 6H; ArH), 6.81 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.76 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.68 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.48 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.36 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.13 (s, 2H; ArH_{Trz}), 6.05 (s, 2H; ArH_{Trz}), 4.79 (s, 4H; OCH_2Trz), 4.76 (s, 4H; OCH_2Trz), 4.48–4.40 (m, 8H; NCH_2), 4.13–4.06 (m, 4H; $NCH_2C\underline{H_2}$), 4.06–4.00 (m, 4H; $NCH_2C\underline{H_2}$), 3.94 (d, 4H, $^{2}J_{HH}$ = 16.7 Hz; $ArCH_2Ar$), 3.85 (d, 4H, $^{2}J_{HH}$ = 16.7 Hz; $ArCH_2Ar$), 3.80 (d, 4H, $^{2}J_{HH}$ = 16.3 Hz; $ArCH_2Ar$), 3.79 (d, 4H, $^{2}J_{HH}$ = 15.4 Hz; $ArCH_2Ar$), 3.70–3.67 (m, 4H; OCH_2), 3.66 (d, 4H, $^{2}J_{HH}$ = 16.3 Hz; $ArCH_2Ar$), 3.61–3.56 (m, 4H; OCH_2), 3.60 (d, 4H, $^{2}J_{HH}$ = 15.4 Hz; $ArCH_2Ar$), 3.53–3.47 (m, 4H; OCH_2), 3.35–3.28 (m, 4H; OCH_2), 3.12–3.06 (m, 4H; OCH_2), 1.33–1.25 (m, 4H; $C\underline{H_2}CH_3$), 0.67 (t, 6H, $^{3}J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.99, 156.16, 155.84, 155.61, 154.95, 154.67 (C_{Ar}), 144.36, 143.80 ($C_{Ar\,Trz}$), 134.46, 134.37, 134.31, 134.02, 133.85, 133.39 (C_{Ar}), 129.82, 129.75, 129.45, 128.94, 128.75, 128.32 (CH_{Ar}), 124.25, 124.07 ($CH_{Ar\,Trz}$), 123.74, 123.68, 123.11, 123.08, 122.96, 121.37 (CH_{Ar}), 73.21, 71.66, 70.88, 69.32, 69.03, 68.68, 67.33, 63.23, 63.09 (OCH_2), 48.90, 48.85 (NCH_2), 38.31, 38.28, 38.16 ($ArCH_2Ar$), 22.87 ($\underline{C}H_2CH_3$), 10.08 (CH_3) ppm. ESI-MS *m*/*z*: 991.9295 $[M+H+K]^{2+}$ for $C_{118}H_{119}KN_{12}O_{15}$ (991.9288).



Tris(calix[4]arene) **9** was prepared according to *General procedure* from calixarene **19** (0.115 g, 0.09 mmol), calixarene **12** (0.057 g, 0.09 mmol), $CuSO_4\cdot5H_2O$ (0.022 g, 0.09 mmol) and sodium ascorbate (0.036 g, 0.18 mmol) in a mixture of THF (10 ml) and water (2 ml). Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). The residue was dissolved in dichloromethane, methanol was added, and the solid formed was collected and dried. Yield 0.024 g (14%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 7.09 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.99–6.91 (m, 10H; ArH), 6.90–6.86 (m, 6H; ArH), 6.84 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.74 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.64 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.48 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.41 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.10 (s, 2H; ArH_{Trz}), 6.05 (s, 2H; ArH_{Trz}), 4.78 (s, 4H; OCH_2Trz), 4.77 (s, 4H; OCH_2Trz), 4.52–4.47 (m, 4H; NCH_2), 4.47–4.42 (m, 4H; NCH_2), 4.11–4.01 (m, 8H; $NCH_2C\underline{H_2}$), 3.91 (d, 4H, $^{2}J_{HH}$ = 16.3 Hz; $ArCH_2Ar$), 3.84 (d, 4H, $^{2}J_{HH}$ = 16.8 Hz; $ArCH_2Ar$), 3.81 (d, 4H, $^{2}J_{HH}$ = 16.3 Hz; $ArCH_2Ar$), 3.79 (d, 4H, $^{2}J_{HH}$ = 16.8 Hz;

ArCH$_2$Ar), 3.68 (d, 4H, $^2J_{HH}$ = 16.8 Hz; ArCH$_2$Ar), 3.64 (d, 4H, $^2J_{HH}$ = 16.8 Hz; ArCH$_2$Ar), 3.57–3.53 (m, 8H; OCH$_2$), 3.42–3.36 (m, 4H; OCH$_2$), 3.36–3.31 (m, 4H; OCH$_2$), 3.25–3.19 (m, 4H; OCH$_2$), 1.21–1.10 (m, 4H; C$\underline{H}_2$CH$_3$), 0.70 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.13, 156.21, 155.88, 155.64, 154.96, 154.75 (C$_{Ar}$), 144.14, 143.77 (C$_{Ar\ Trz}$), 134.52, 134.43, 134.34, 134.21, 133.84, 133.33 (C$_{Ar}$), 130.08, 129.61, 129.56, 128.83, 128.72, 128.39 (CH$_{Ar}$), 124.22, 124.19 (CH$_{Ar\ Trz}$), 123.68, 123.53, 123.28, 122.96, 122.48, 122.02 (CH$_{Ar}$), 72.43, 71.44, 70.37, 70.04, 68.96, 68.93, 68.64, 63.16, 63.11 (OCH$_2$), 49.00, 48.98 (NCH$_2$), 38.39, 38.30, 38.14 (ArCH$_2$Ar), 22.11 ($\underline{C}$H$_2$CH$_3$), 9.85 (CH$_3$) ppm. ESI-MS *m*/*z*: 991.9290 [M+H+K]$^{2+}$ for C$_{118}$H$_{119}$KN$_{12}$O$_{15}$ (991.9288).



Tris(calix[4]arene) ***10*** was prepared according to *General procedure* from calixarene **19** (0.115 g, 0.09 mmol), calixarene **15** (0.064 g, 0.09 mmol), CuSO$_4$·5H$_2$O (0.022 g, 0.09 mmol) and sodium ascorbate (0.036 g, 0.18 mmol) in a mixture of THF (10 ml) and water (2 ml). Column 1: gradient from dichloromethane to dichloromethane/ethanol (20:1). Column 2: gradient from dichloromethane to dichloromethane/ethanol (50:1). The residue was dissolved in dichloromethane, methanol was added, and the solid formed was collected and dried. Yield 0.042 g (23%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.19 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.13 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.02–6.91 (m, 12H; ArH), 6.86 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.83 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.74 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.68 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.47 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.41 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.05 (s, 2H; ArH$_{Trz}$), 6.04 (s, 2H; ArH$_{Trz}$), 4.77 (s, 4H; OCH$_2$Trz), 4.75 (s, 4H; OCH$_2$Trz), 4.52–4.47 (m, 4H; NCH$_2$), 4.47–4.42 (m, 4H; NCH$_2$), 4.10–4.05 (m, 4H; NCH$_2$C$\underline{H}_2$), 4.05–4.00 (m, 4H; NCH$_2$C$\underline{H}_2$), 3.94 (d, 4H, $^2J_{HH}$ = 16.7 Hz; ArCH$_2$Ar), 3.85 (d, 4H, $^2J_{HH}$ = 16.7 Hz; ArCH$_2$Ar), 3.83 (d, 4H, $^2J_{HH}$ = 16.1 Hz; ArCH$_2$Ar), 3.78 (d, 4H, $^2J_{HH}$ = 16.9 Hz; ArCH$_2$Ar), 3.70–3.57 (m, 16H; ArCH$_2$Ar + OCH$_2$), 3.56–3.53 (m, 8H; OCH$_2$), 3.52–3.47 (m, 4H; OCH$_2$), 3.36–3.31 (m, 4H; OCH$_2$), 3.24–3.19 (m, 4H; OCH$_2$), 3.12–3.06 (m, 4H; OCH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 156.20, 156.16, 155.87, 155.59, 154.90, 154.73 (C$_{Ar}$), 144.13, 143.76 (C$_{Ar\ Trz}$), 134.51, 134.36, 134.31, 134.19, 133.83, 133.38 (C$_{Ar}$), 129.81, 129.60, 129.50, 128.81, 128.72, 128.31 (CH$_{Ar}$), 124.16, 124.09 (CH$_{Ar\ Trz}$), 123.74, 123.69, 123.52, 123.06, 122.96, 122.00 (CH$_{Ar}$), 73.20, 72.42, 70.87, 70.36, 70.02, 69.31, 69.00, 68.95, 68.63, 67.32, 63.15, 63.09 (OCH$_2$), 48.94, 48.89 (NCH$_2$), 38.27, 38.26, 38.12 (ArCH$_2$Ar) ppm. ESI-MS *m*/*z*: 1047.9067 [M+2K]$^{2+}$ for C$_{120}$H$_{120}$K$_2$N$_{12}$O$_{18}$ (1047.9069).

NMR spectra of novel compounds

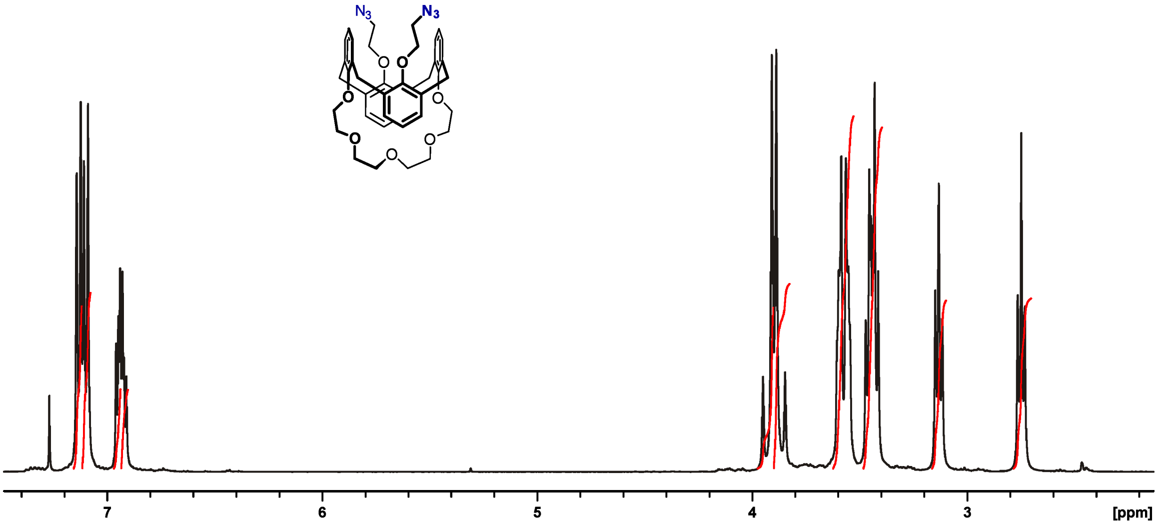


Figure S1. ^{1}H NMR spectrum of calix[4]arene **15** (400 MHz, $CDCl_3$).

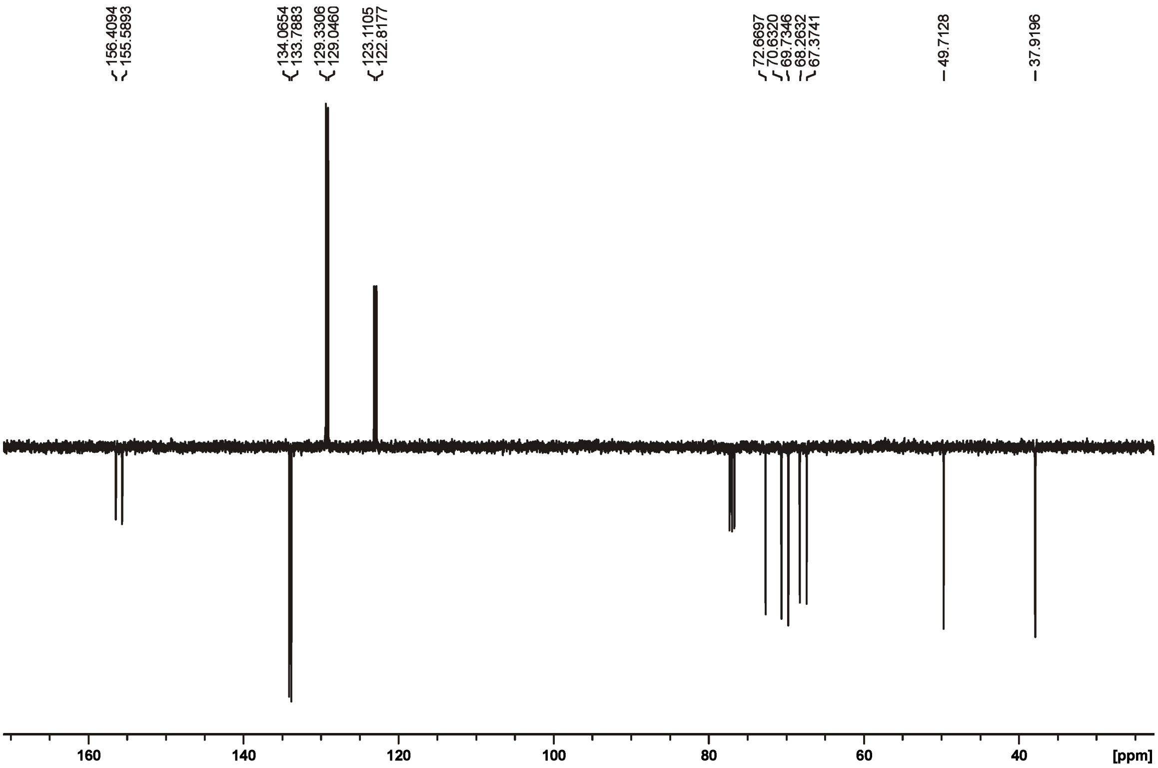


Figure S2. ^{13}C NMR spectrum (APT) of calix[4]arene **15** (100 MHz, $CDCl_3$).

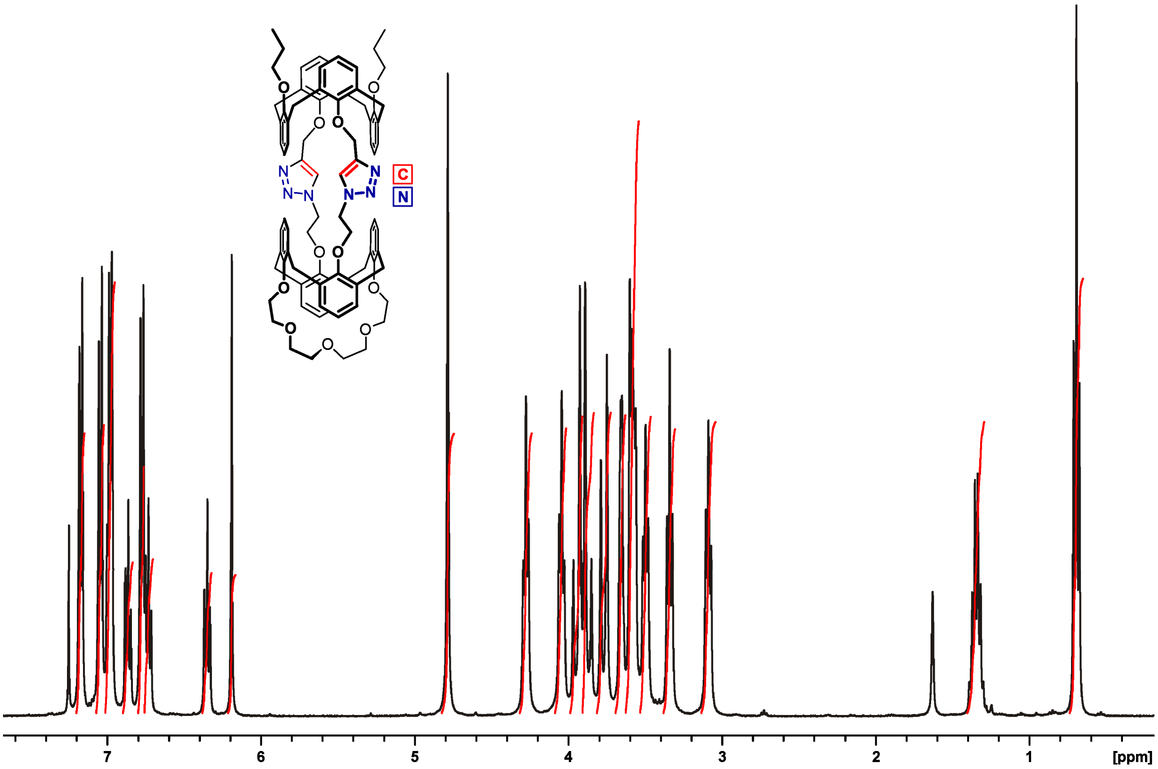


Figure S3. ^{1}H NMR spectrum of bis(calix[4]arene) **5** (400 MHz, $CDCl_3$).

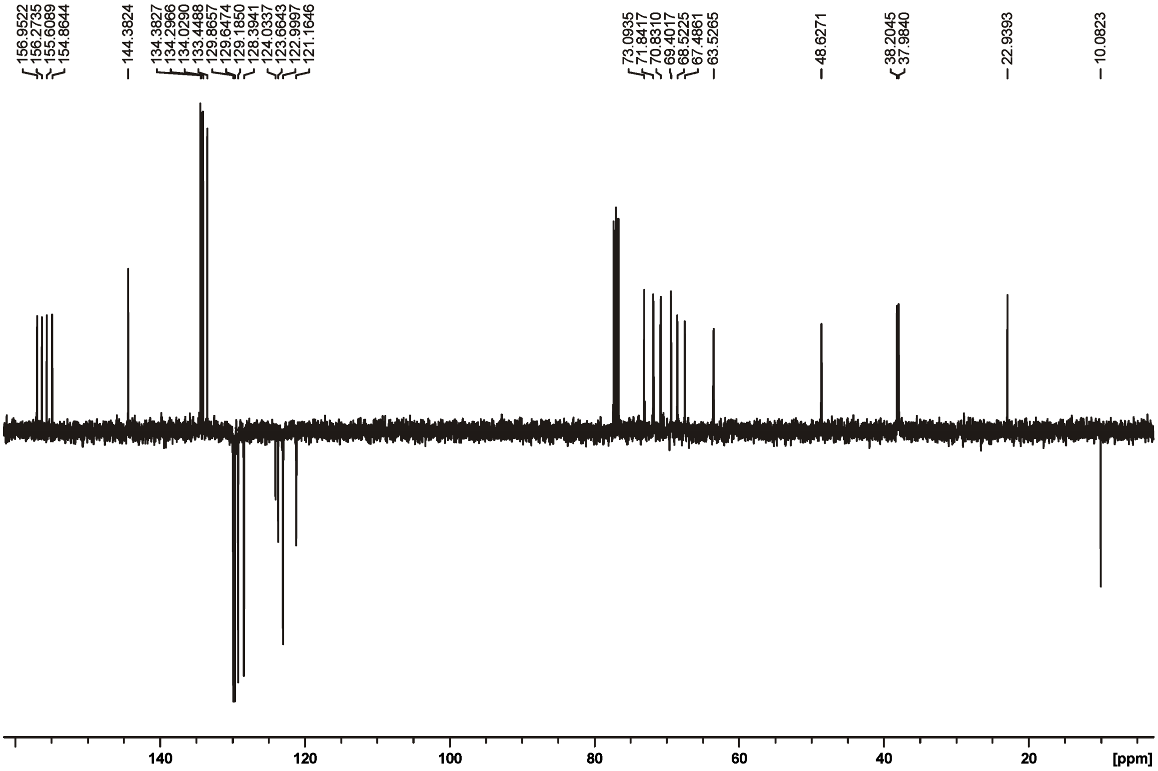


Figure S4. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **5** (100 MHz, $CDCl_3$).

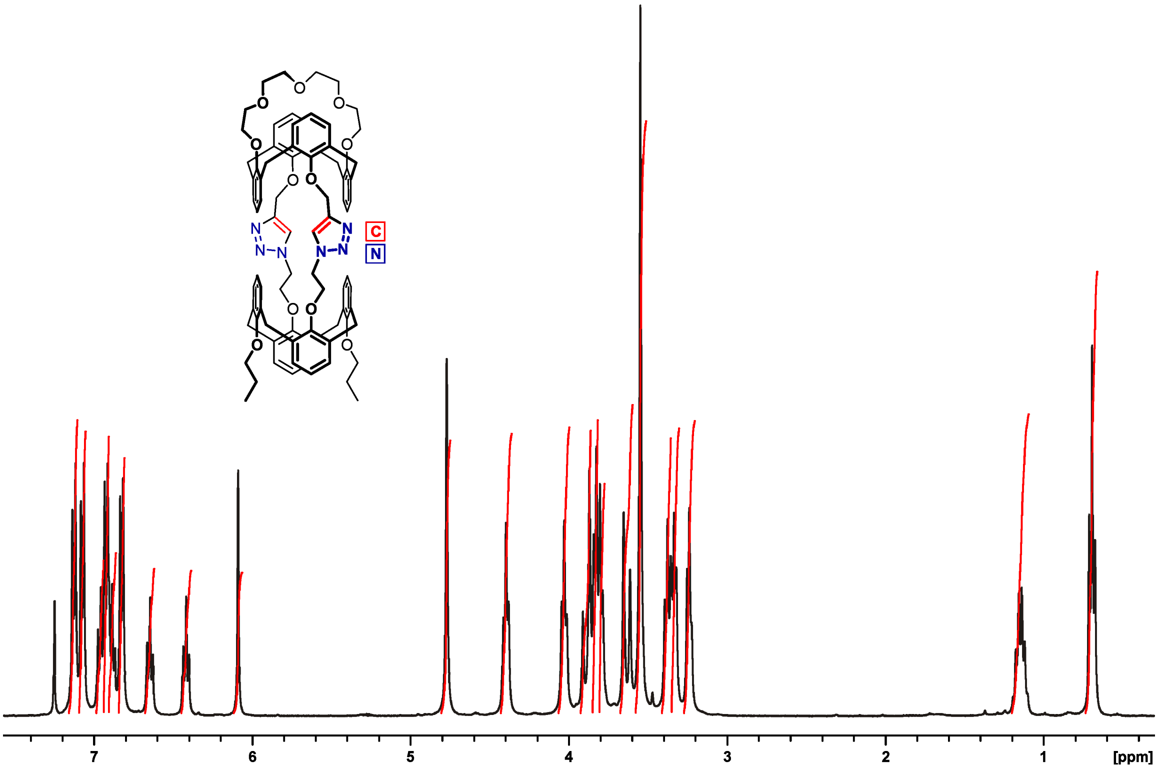


Figure S5. ^{1}H NMR spectrum of bis(calix[4]arene) **6** (400 MHz, $CDCl_3$).

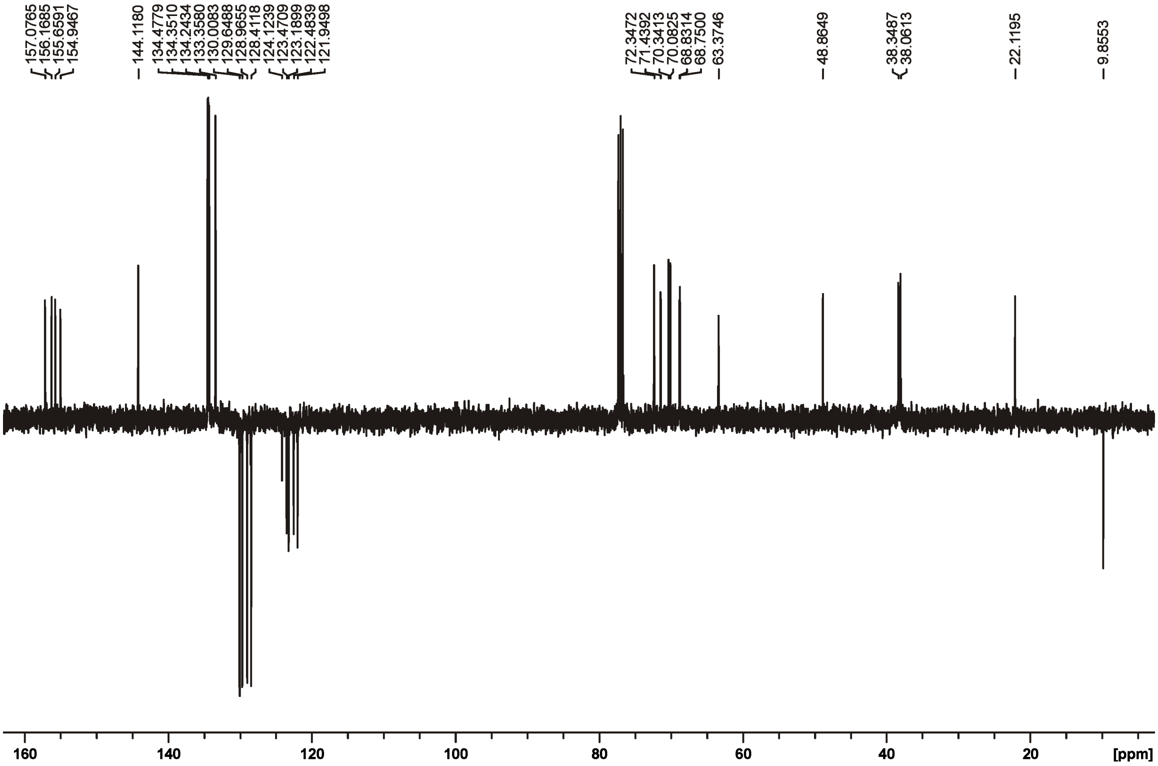


Figure S6. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **6** (100 MHz, $CDCl_3$).

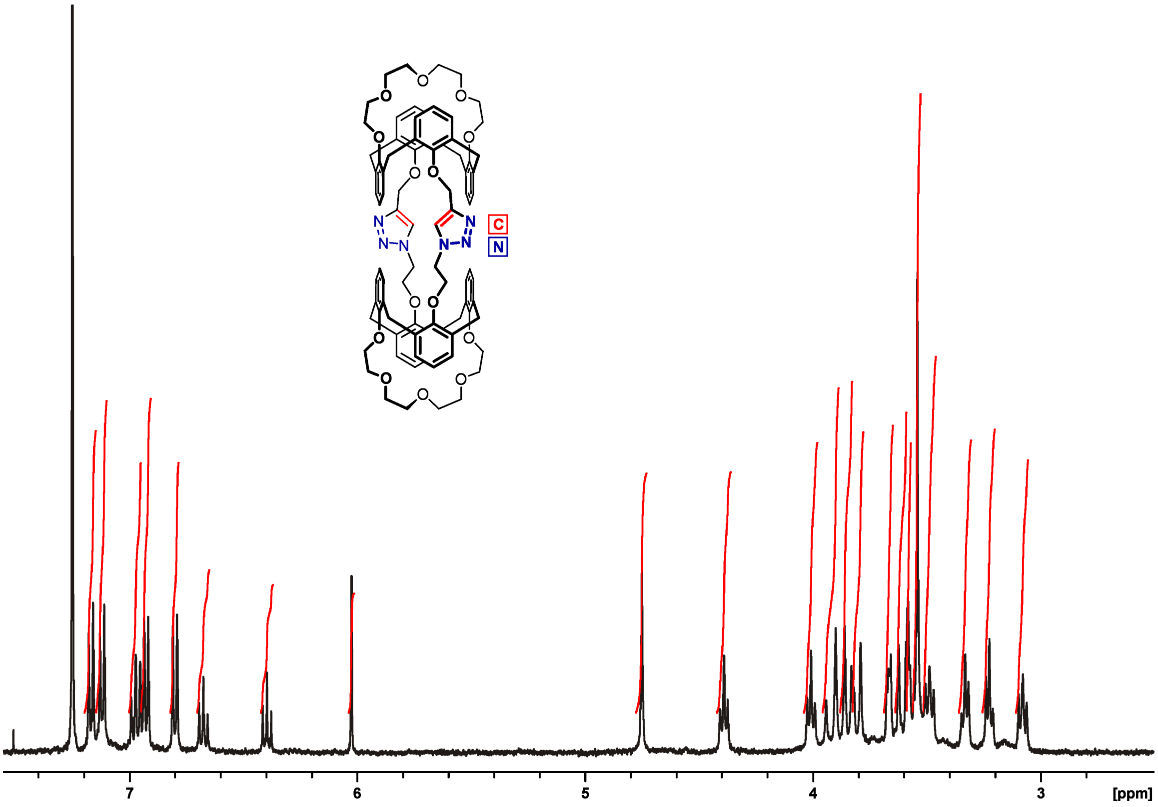


Figure S7. ^{1}H NMR spectrum of bis(calix[4]arene) **7** (400 MHz, $CDCl_3$).

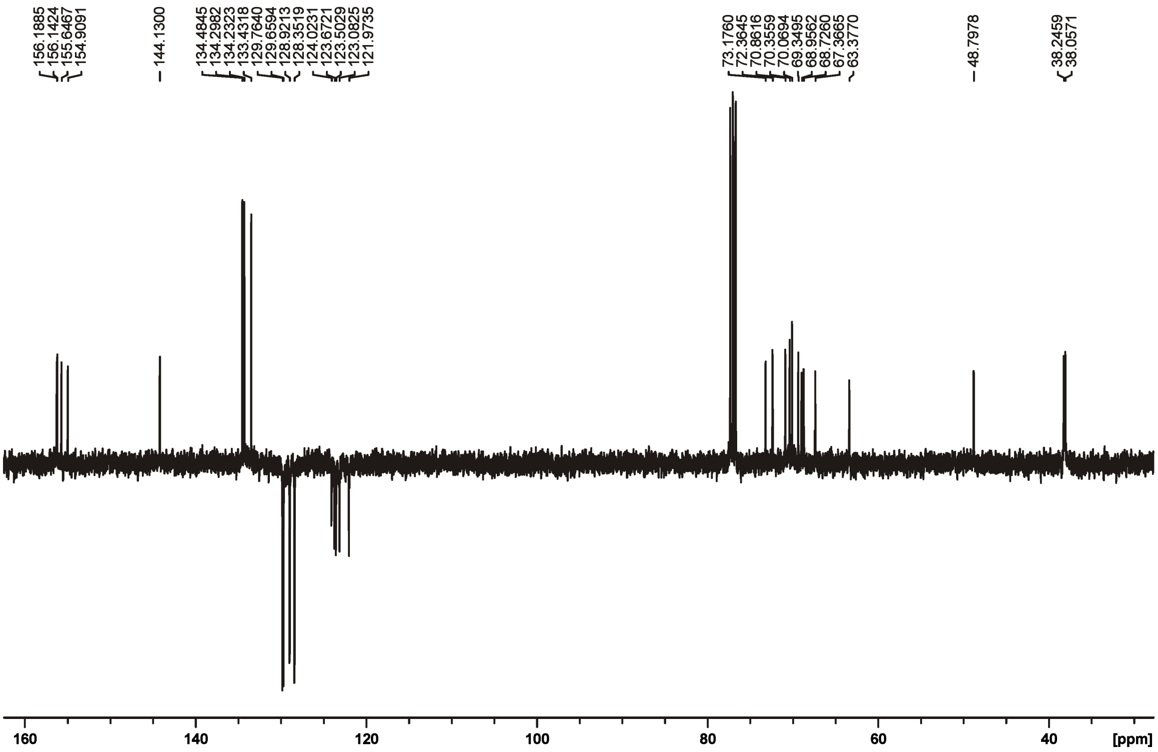


Figure S8. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **7** (100 MHz, $CDCl_3$).

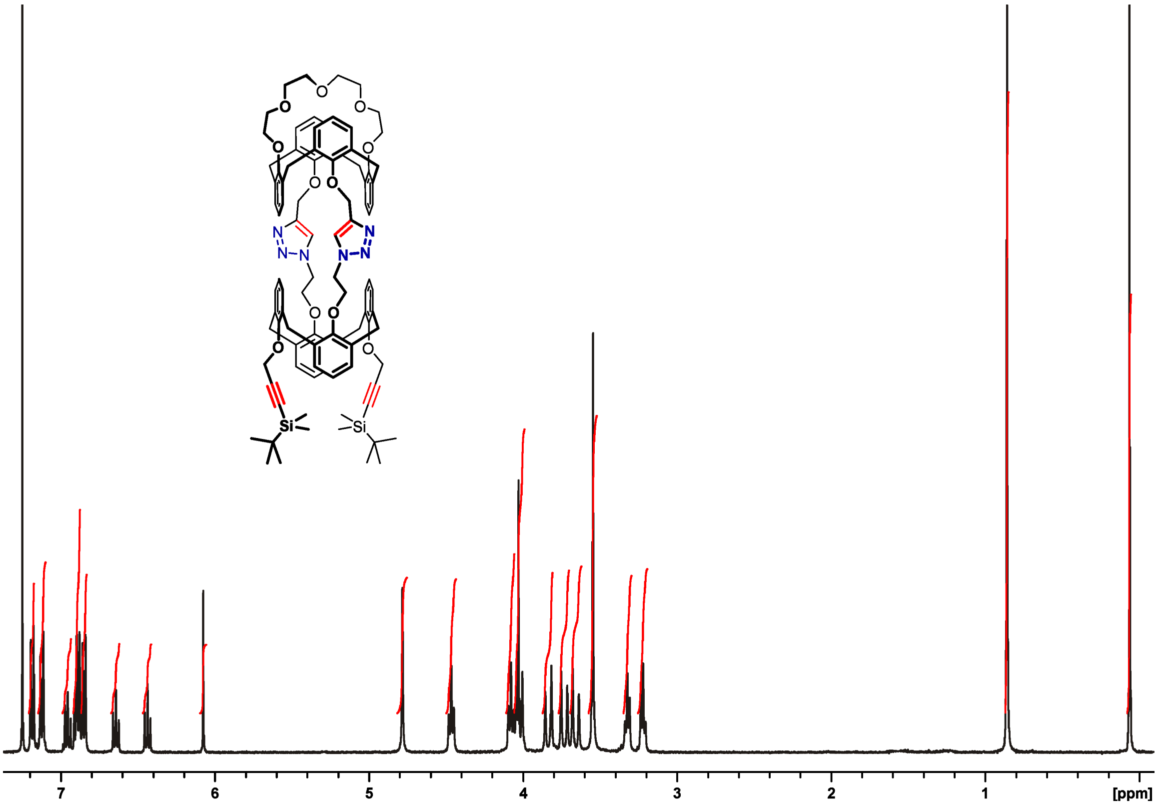


Figure S9. ^{1}H NMR spectrum of bis(calix[4]arene) **18** (400 MHz, CDCl$_3$).

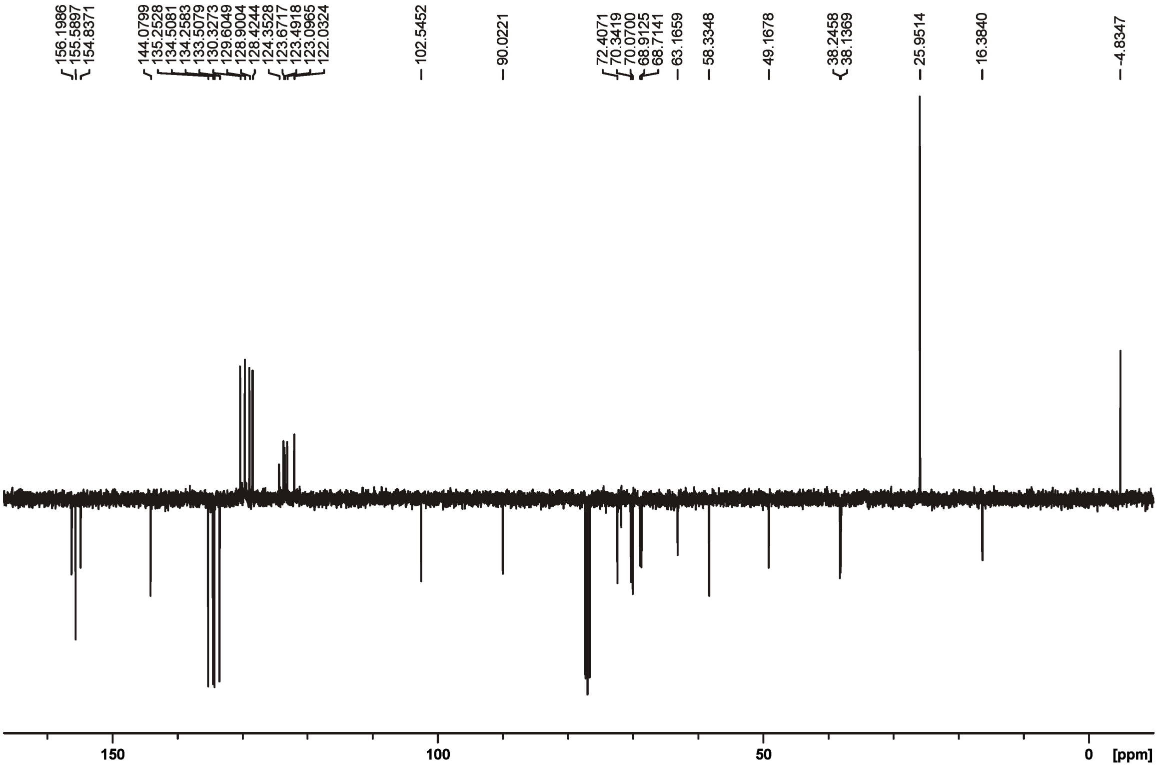


Figure S10. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **18** (100 MHz, CDCl$_3$).

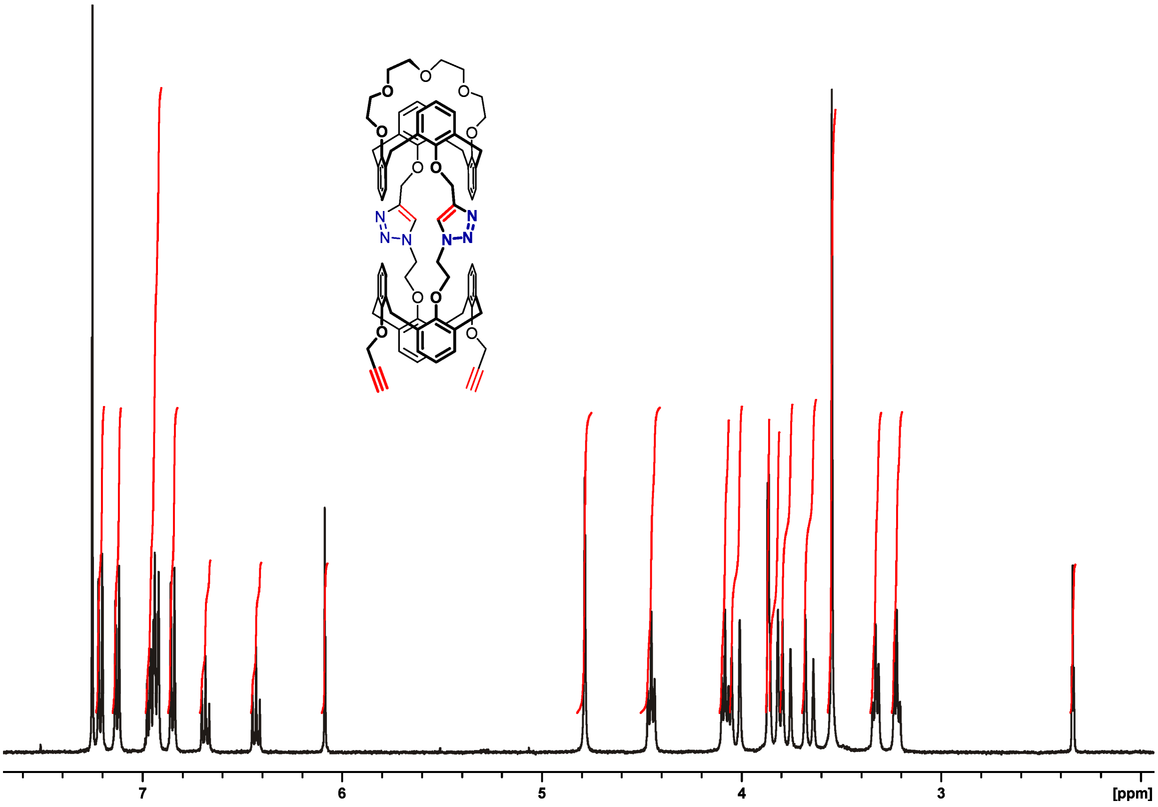


Figure S11. ^{1}H NMR spectrum of bis(calix[4]arene) **19** (400 MHz, $CDCl_3$).

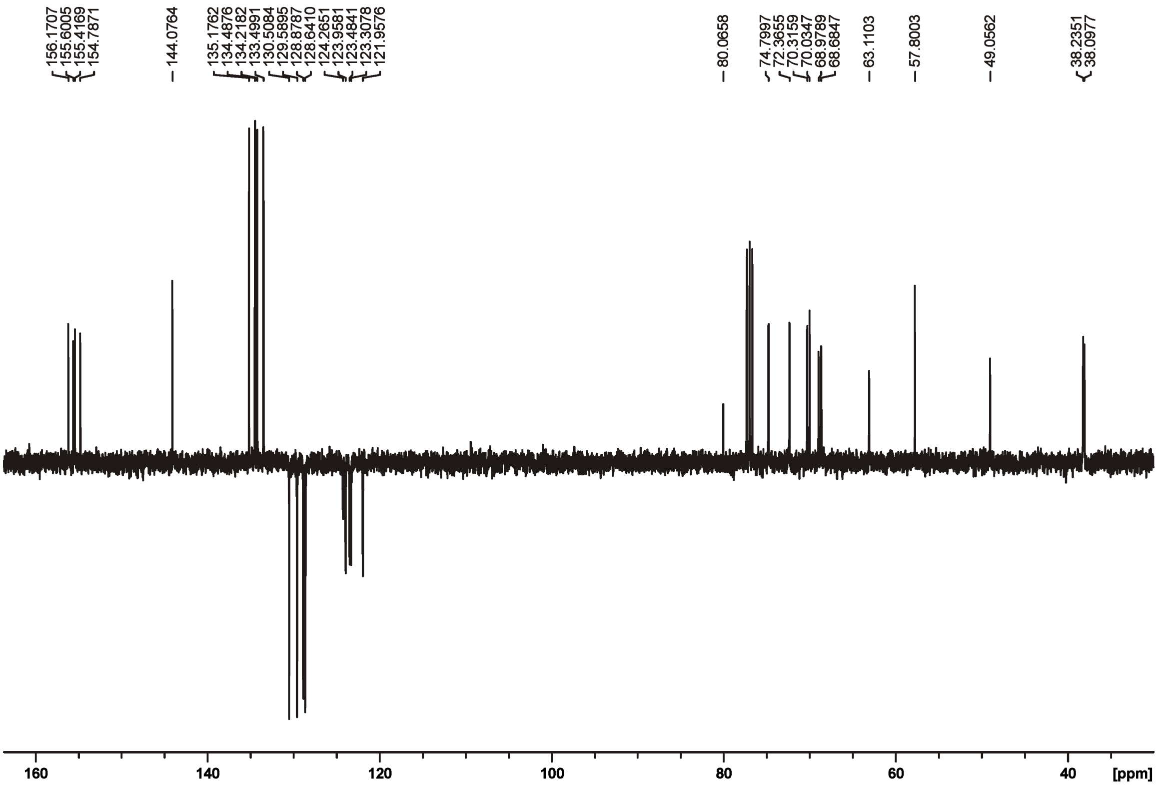


Figure S12. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **19** (100 MHz, $CDCl_3$).

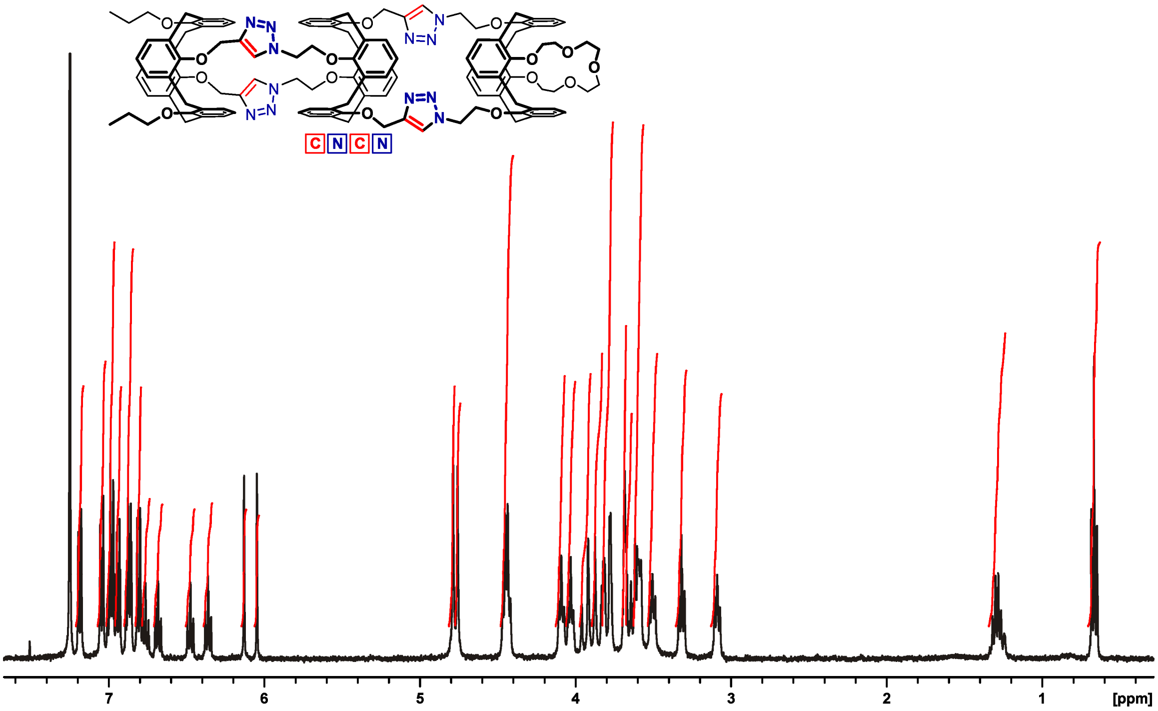


Figure S13. ^{1}H NMR spectrum of tris(calix[4]arene) **8** (400 MHz, $CDCl_3$).

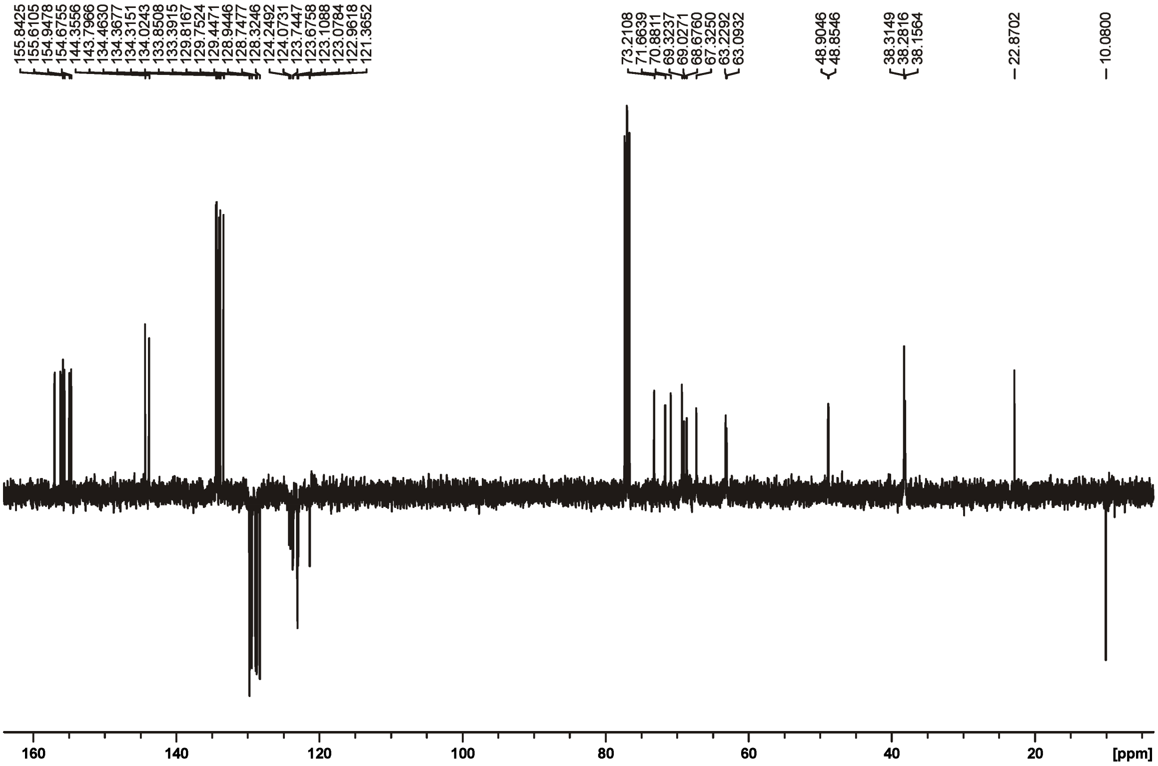


Figure S14. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **8** (100 MHz, $CDCl_3$).

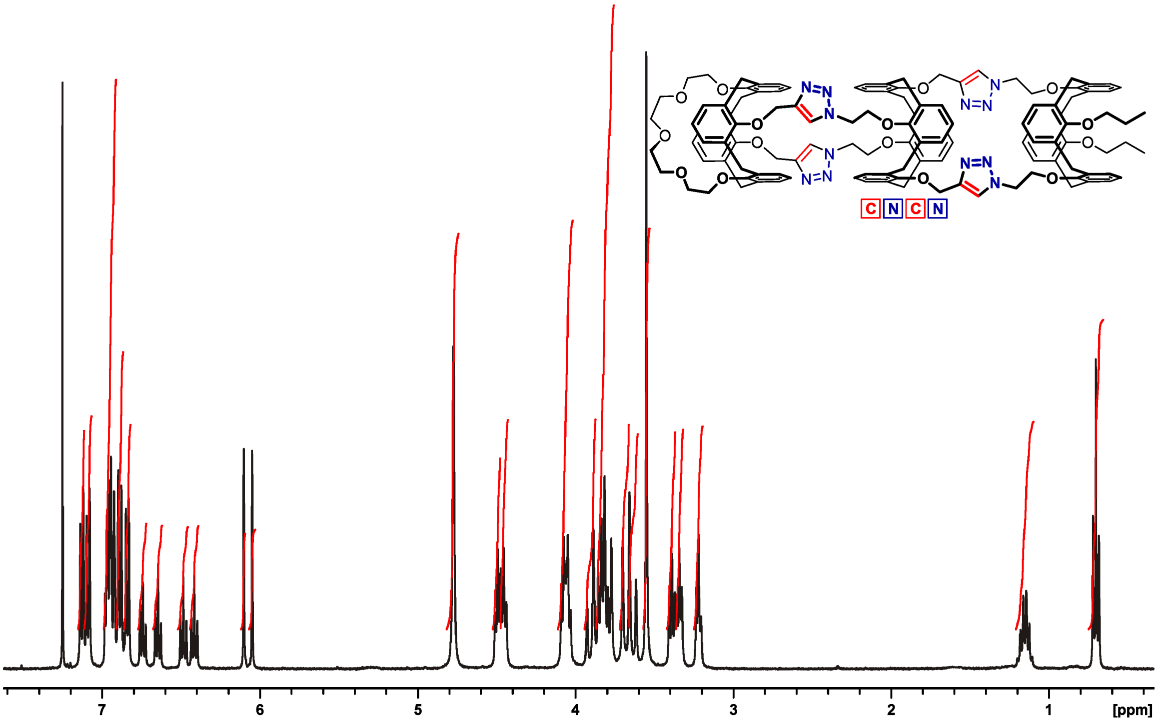


Figure S15. ^{1}H NMR spectrum of tris(calix[4]arene) **9** (400 MHz, CDCl$_3$).

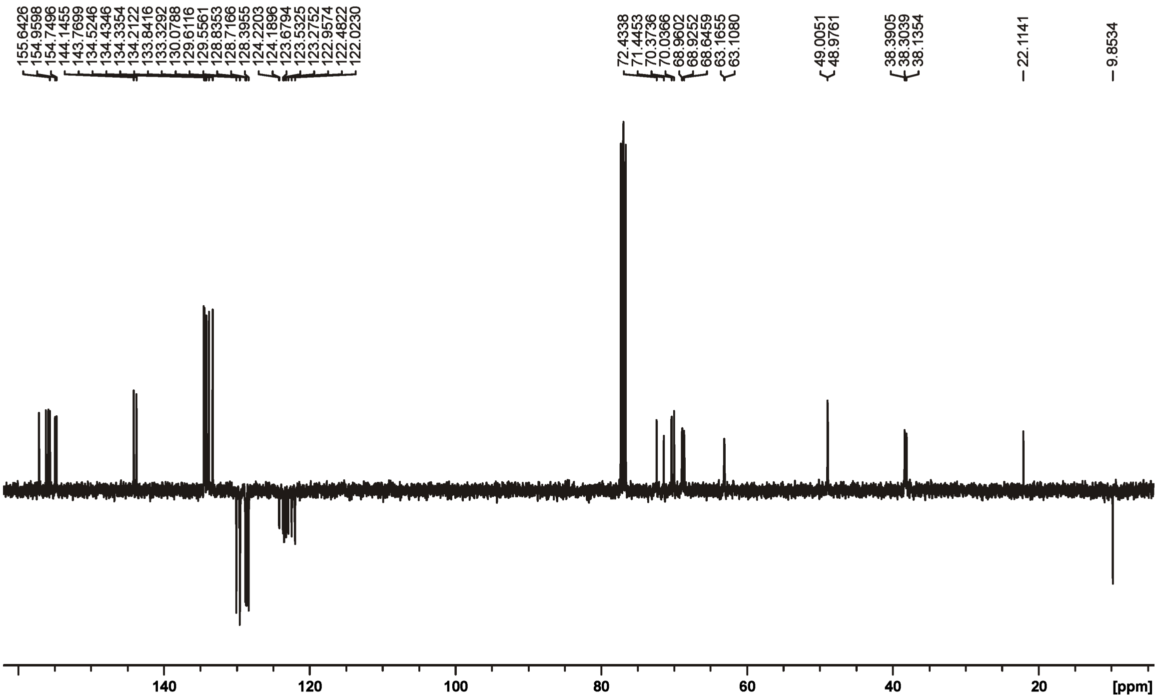


Figure S16. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **9** (100 MHz, CDCl$_3$).

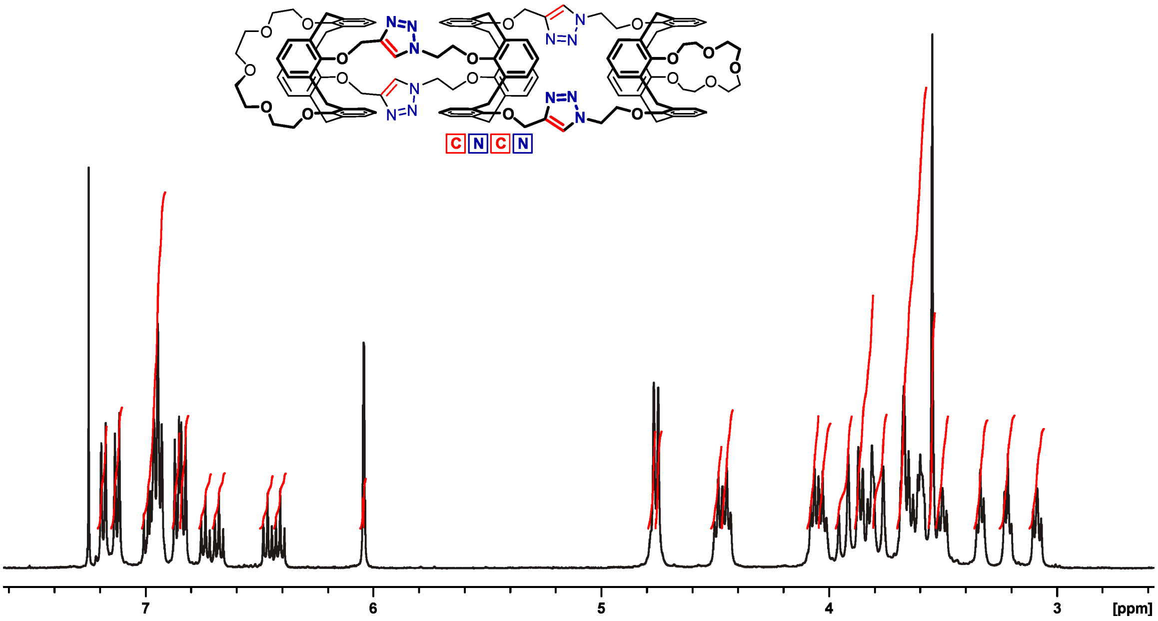


Figure S17. ^{1}H NMR spectrum of tris(calix[4]arene) **10** (400 MHz, CDCl$_3$).

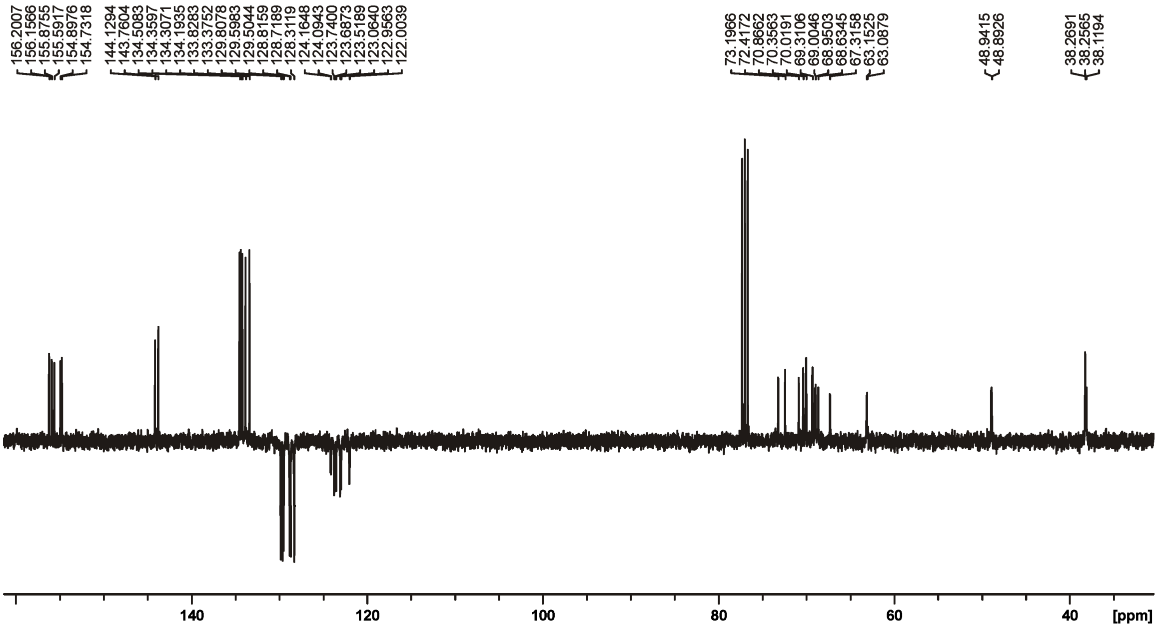
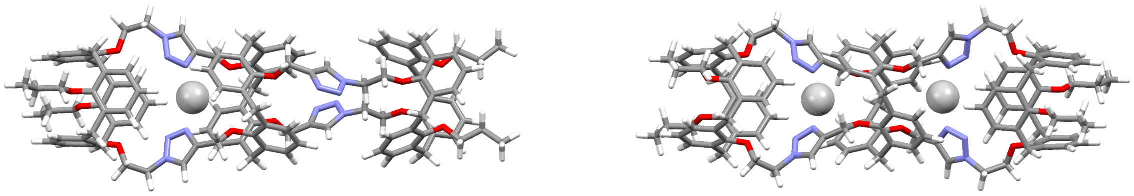


Figure S18. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **10** (100 MHz, CDCl$_3$).

Energy-minimized structures of Ag$^+$ and K$^+$ complexes

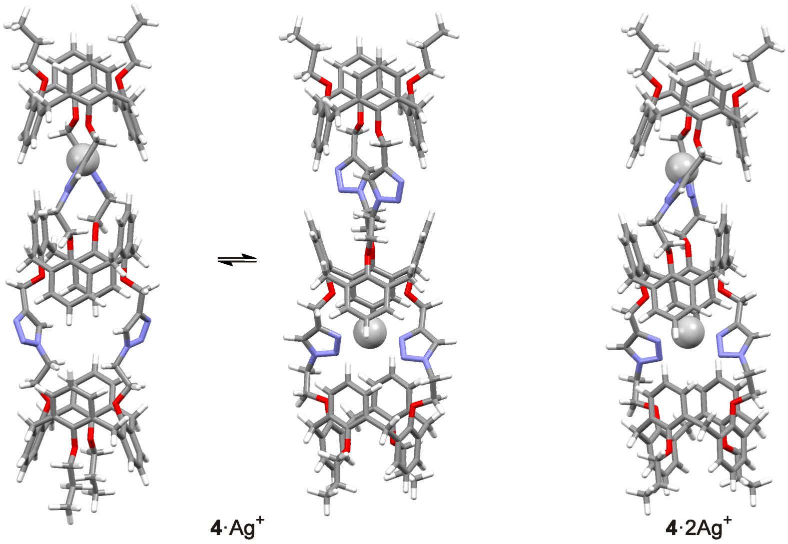
2$\cdot$Ag$^+$ **2**$\cdot$2Ag$^+$

Figure S19. Energy-minimized structures of the cationic parts of complexes **2**$\cdot$Ag$^+$ and **2**$\cdot$2Ag$^+$.[S4]



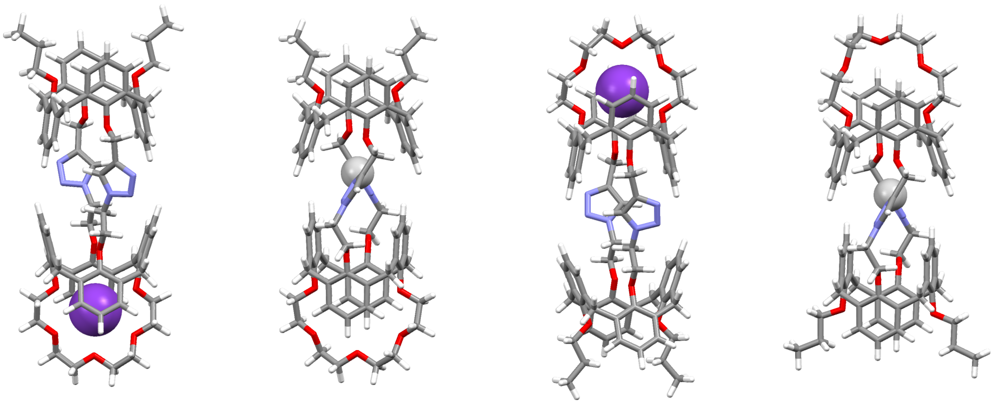
3$\cdot$Ag$^+$ **3**$\cdot$2Ag$^+$

Figure S20. Energy-minimized structures of the cationic parts of complexes **3**$\cdot$Ag$^+$ and **3**$\cdot$2Ag$^+$.



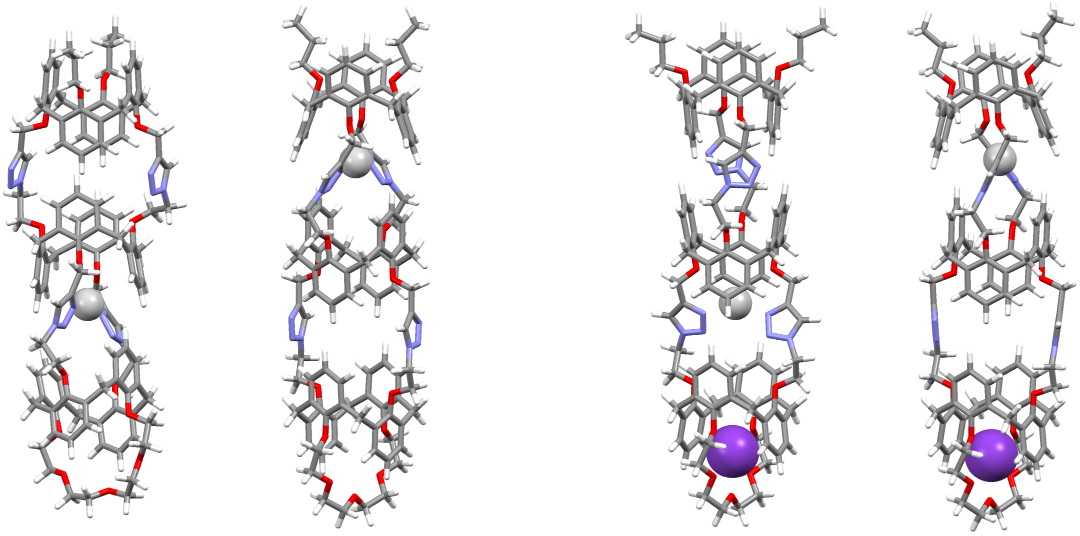
4$\cdot$Ag$^+$ **4**$\cdot$2Ag$^+$

Figure S21. Energy-minimized structures of the cationic parts of complexes **4**$\cdot$Ag$^+$ (two exchanging structures) and **4**$\cdot$2Ag$^+$.



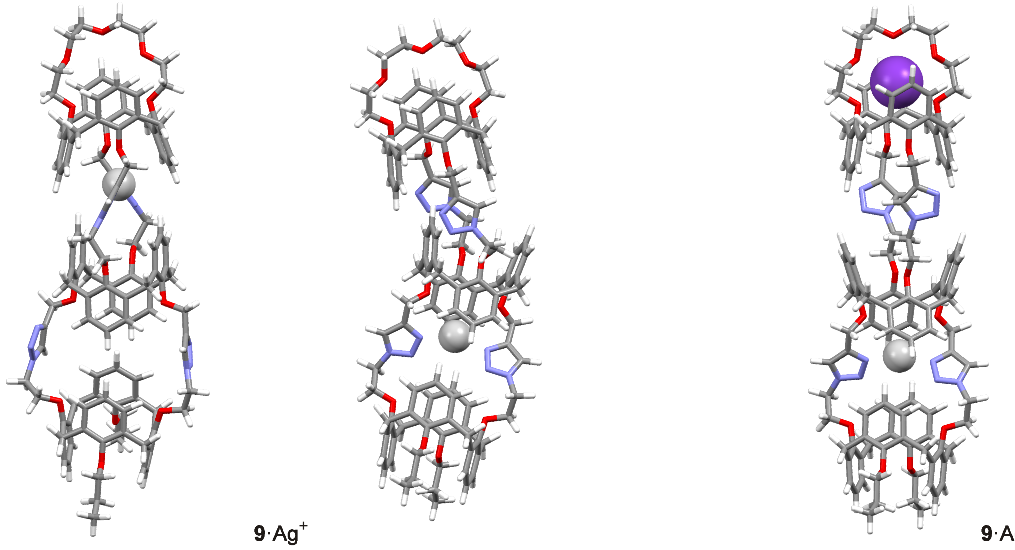
5·K^{+} **5**·Ag^{+} **6**·K^{+} **6**·Ag^{+}

Figure S22. Energy-minimized structures of the potassium and silver complexes of the crownated biscalixarene semitubes **5** and **6**.



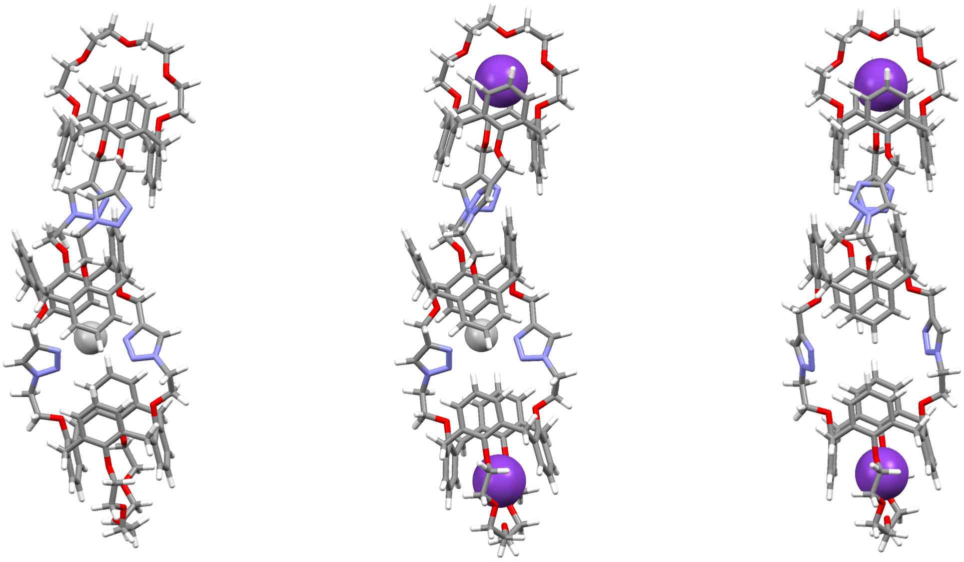
8·Ag^{+} **8**·Ag^{+}·K^{+}

Figure S23. Energy-minimized structures of complexes **8**·Ag^{+} (two exchanging structures) and **8**·Ag^{+}·K^{+} (two exchanging structures).



9·Ag^{+} **9**·Ag^{+}·K^{+}

Figure S24. Energy-minimized structures of complexes **9**·Ag^{+} (two exchanging structures) and **9**·Ag^{+}·K^{+}.



10·Ag$^+$ **10**·Ag$^+$·2K$^+$ **10**·2K$^+$

Figure S25. Energy-minimized structures of complexes **10**·Ag$^+$ (one of two possible structures), **10**·Ag$^+$·2K$^+$ and **10**·2K$^+$.

NMR-titration of tris(calixarene) 4 with $AgClO_4 \cdot H_2O$

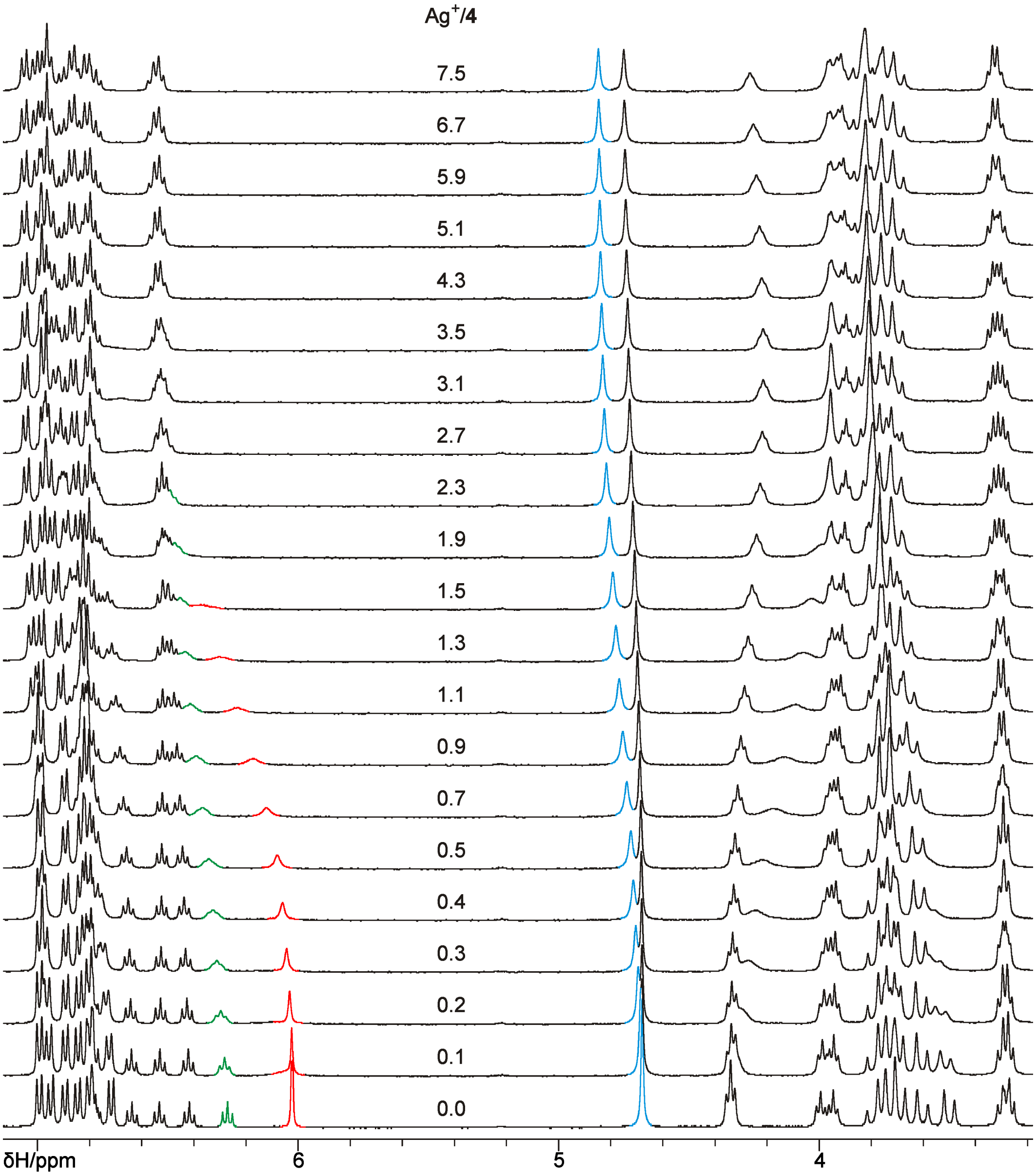


Figure S26. Parts of ^{1}H NMR spectra of tris(calixarene) **4** and its mixtures with increasing amount of $AgClO_4 \cdot H_2O$; 400 MHz, $CDCl_3/CD_3CN$ (4:1), *c*(**4**) $2.0 \cdot 10^{-3}$ M, 20 °C; the signals from the triazole protons of the semitube are colored red, the most affected signal from the calixarene aromatics is colored green, the signal tried for calculation of the complexation constant is colored light blue.

References

S1. A. Gorbunov, N. Ozerov, M. Malakhova, A. Eshtukov, D. Cheshkov, S. Bezzubov, V. Kovalev and I. Vatsouro, Assembling triazolated calix[4]semitubes by means of copper(I)-catalyzed azide–alkyne cycloaddition, *Org. Chem. Front.*, 2021, **8**, 3853–3866.

S2. M. Malakhova, A. Gorbunov, N. Ozerov, I. Korniltsev, K. Ermolov, S. Bezzubov, V. Kovalev and I. Vatsouro, Triazolated calix[4]semitubes: assembling strategies towards long multicalixarene architectures, *Org. Chem. Front.*, 2022, **9**, 3084–3092.

S3. K.-C. Chang, I.-H. Su, A. Senthilvelan and W.-S. Chung, Triazole-modified calix[4]crown as a novel fluorescent on-off switchable chemosensor, *Org. Lett.*, 2007, **9**, 3363–3366.

S4. Calculations were performed using the ORCA 4.2.1 program package at the DFT BLYP/def2-SVP/SDD (for Ag) level: (*a*) F. Neese, The ORCA program system, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73–78; (*b*) F. Neese, Software update: the ORCA program system, version 4.0, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, e1327; (*c*) F. Neese, F. Wennmohs, A. Hansen and U. Becker, Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange, *Chem. Phys.*, 2009, **356**, 98–109; (*d*) F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305; (*e*) F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065; (*f*) D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, Energy-adjusted ab initio pseudopotentials for the second and third row transition elements, *Theor. Chim. Acta*, 1990, **77**, 123–141.