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Pentakis-thiacalix[4]arenes with nitrile fragments: receptor properties toward cations of some *s*- and *d*-metals and self-assembly of nanoscale aggregates

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Procedure for the synthesis of compounds **2, 3** *and* **4a.**

*5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(3-cyanopropoxy)-28-(2-phthalimidoethoxy)-2,8,14,20-tetrathiacalix[4]arene (*1,3-alternate*)* **2**. In a round bottom flask equipped with magnetic stirrer, reflux condenser and a calcium chloride tube, a mixture of 1.00 g (1.12 mmol) of compound **1,** 3.1 g (20.2 mmol) of potassium carbonate, 0.84 ml (8.96 mmol) of 4-chlorobutyronitrile and 60 ml of dry acetone was refluxed for 40 h. After cooling the solvent was evaporated *in vacuo*. Then 40 ml of 2 M HCl was added to the residue, the precipitate was filtered off and washed with water. The product was isolated from 100 ml of methanol by hot filtration. Yield 86%. Mp 225−227 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.10-1.26 (2H, m, CH_2-$\underline{CH_2}$-CH_2), 1.32 (9H, s, $(CH_3)_3C$), 1.33 (9H, s $(CH_3)_3C$), 1.35 (18H, s, $(CH_3)_3C$), 1.40-1.54 (4H, m, CH_2-$\underline{CH_2}$-CH_2), 1.80 (2H, t, $^3J_{HH}$ =7.6 Hz, $\underline{CH_2}$-CN), 1.96 (4H, t, $^3J_{HH}$ = 7.6 Hz, $\underline{CH_2}$-CN), 3.54 (2H, m, $\underline{CH_2\text{-}Pht}$), 3.86-4.13 (8H, m, O-$CH_2$), 7.33 (2H, s, Ar^1-H), 7.39 (2H, d, $^3J_{HH}$ = 2.4 Hz, Ar^2-H), 7.40 (2H, s, Ar^3-H), 7.70 (2H, d, $^3J_{HH}$ = 2.4 Hz, Ar^3-H), 7.68-7.73 (2H, m, Ar^{Pht}-H), 7.81-7.86 (2H, m, Ar^{Pht}-H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 13.6, 13.7, 24.3, 25.3, 31.26, 31.28, 31.29, 34.38, 34.42, 34.49, 36.5, 65.1, 65.5, 66.5, 119.0, 119.3, 123.2, 126.2, 127.5, 127.5, 127.9, 128.47, 128.51, 128.57, 128.58, 132.0, 133.9, 146.8, 147.0, 147.3, 155.2, 156.1, 156.8, 167.5. ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / $H^{7'}$, $H^{4'b}$ / H^8, H^{4+b} / $H^{7'}$. MS (MALDI-TOF): calculated [M^+] m/z = 1094.4; found $[M+Na]^+$ m/z = 1117.8, $[M+K]^+$ m/z = 1133.7. Found (%): C, 67.67; H, 6.35; N, 5.45; S, 11.59. Calc. for $C_{62}H_{70}N_4O_6S_4$ (%): C, 67.98; H, 6.44; N, 5.11; S, 11.71. IR (nujol, ν/cm^{-1}): 1265 (COC); 1716, 1774 (C=O), 2247 (CN).

*5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(3-cyanopropoxy)-28-(2-aminoethoxy)-2,8,14,20-tetrathiacalix[4]arene (*1,3-alternate*)* **3**. In a round bottom flask equipped with magnetic stirrer and reflux condenser mixture of 1.00 g of compound **2**, 2 ml of hydrazine hydrate (40 mmol), 30 ml of ethanol and 20 ml of THF was refluxed for 4 h. After cooling the solvent was evaporated *in vacuo,* and then 50 ml of $CHCl_3$ was added. The organic layer was washed with 20 ml of 20% NH_3. The organic phase was separated and dried over 3Å molecular sieves. The solvent was distilled off under reduced pressure. Yield 95%. Mp 277–279 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.31 (18H, s, $(CH_3)_3C$), 1.33 (18H, s, $(CH_3)_3C$), 1.42 (6H, m, CH_2-$\underline{CH_2}$-CH_2), 1.90 (2H, t, $^3J_{HH}$ =7.6 Hz, $\underline{CH_2}$-CN), 1.98 (4H, t, $^3J_{HH}$ =7.6 Hz, $\underline{CH_2}$-CN), 2.34 (2H, t, $^3J_{HH}$ = 5.6 Hz, $\underline{CH_2}$-NH_2), 3.90 (4H, t, $^3J_{HH}$ = 5.7 Hz, $\underline{CH_2}$-CN), 3.96 (6H, m, O-CH_2), 7.36 (2H, d, $^3J_{HH}$ = 2.5 Hz, Ar^1-H), 7.38 (2H, d, $^3J_{HH}$ = 2.5 Hz, Ar^3-H), 7.38 (2H, s, Ar^1-H), 7.39 (2H, s, Ar^3-H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 13.9, 14.1, 25.2, 25.4, 31.4, 31.50, 31.51, 34.58, 34.60, 34.63, 41.8, 66.8, 71.4, 119.5, 119.7, 127.6, 127.7, 128.0, 128.3, 128.4, 128.59, 128.63, 146.7, 147.1, 147.2, 156.2, 156.3, 156.8. ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / $H^{7'}$, $H^{7'}$ / H^3, $H^{7'}$ / H^5, H^{4+b} / $H^{7'}$, $H^{7'}$ / H^{3+}, $H^{7'}$ / H^{5+}. MS (MALDI-TOF): calculated [M^+] m/z = 964.4; found $[M+K]^+$ m/z = 1003.4. Found (%): C, 67.39; H, 6.76; N, 5.98; S, 14.76. Calc. for $C_{54}H_{68}N_4O_4S_4$ (%): C, 67.18; H, 7.10; N, 5.80; S, 13.29. IR (nujol, ν/cm^{-1}): 1265 (COC); 2247 (CN); 3385 (NH_2).

5,11,17,23-Tetra-tert-*butyl-25,26,27-tris(3-cyanopropoxy)-28-[2-(4-hydroxy-1,3-dioxobutylamino)ethoxy]-2,8,14,20-tetrathiacalix[4]arene (*1,3-alternate*)* **4a**. In a round bottom flask equipped with magnetic stirrer, a mixture of 1.00 g (1.04 mmol) compound **3**, 0.21 g (2.08 mmol) succinic anhydride in CH_2Cl_2 was stirred for 24 h. The solvent was distilled off under reduced pressure. Yield 92%. Mp 251–252 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.31 (18H, s, $(CH_3)_3C$), 1.32 (9H, s, $(CH_3)_3C$), 1.33 (9H, s, $(CH_3)_3C$), 1.38-1.54 (6H, m, CH_2-$\underline{CH_2}$-CH_2), 1.81 (2H, t, $^3J_{HH}$ =7.7 Hz, $\underline{CH_2}$-CN), 1.99 (4H, t, $^3J_{HH}$ =7.6 Hz, $\underline{CH_2}$-CN), 2.50 (2H, m, $\underline{CH_2}$-CONH), 2.66 (2H, m, $\underline{CH_2}$-COOH), 3.27 (2H, m, $\underline{CH_2}$-NH), 3.89 (2H, t, $^3J_{HH}$ =6.1 Hz, O-$\underline{CH_2}$), 4.00 (4H, m, O-$\underline{CH_2}$), 4.07 (2H, t, $^3J_{HH}$ =6.6 Hz, O-$\underline{CH_2}$), 6.53 (1H, t, $^3J_{HH}$ =6.2 Hz, CH_2-$\underline{NH}$), 7.33 (2H, s, Ar^1-H), 7.36 (2H, d, $^4J_{HH}$ = 2.4 Hz, Ar^1-H), 7.42 (2H, d, $^4J_{HH}$ = 2.4 Hz, Ar^3-H), 7.43 (2H, s, Ar^1-H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 12.6, 13.8, 24.6, 25.3, 29.8, 30.6, 31.3, 31.34, 31.36, 34.45, 39.6, 65.2, 66.7, 69.8, 119.3, 120.2, 126.6, 127.6, 127.7, 127.96, 128.04, 128.2, 128.3, 128.6, 146.5, 147.2, 155.3, 156.2, 157. ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / $H^{7'}$, $H^{7'}$ / H^3, $H^{7'}$ / H^5, H^9 / $H^{4'b}$, H^9 / $H^{3'}$, H^{4+b} / $H^{7'}$, $H^{7'}$ / H^{3+}, $H^{7'}$ / H^{5+}. MS (MALDI-TOF): calculated [M^+] m/z = 1064.4; found $[M+K]^+$ m/z = 1103.5. Found (%): C, 65.19; H, 6.66; N, 5.03, S, 11.76. Calc. for $C_{58}H_{72}N_4O_7S_4$ (%): C, 65.38; H, 6.81; N, 5.26; S, 12.04. IR (nujol, ν/cm^{-1}): 1263 (COC); 1677, 1711 (C=O), 2246 (CN).

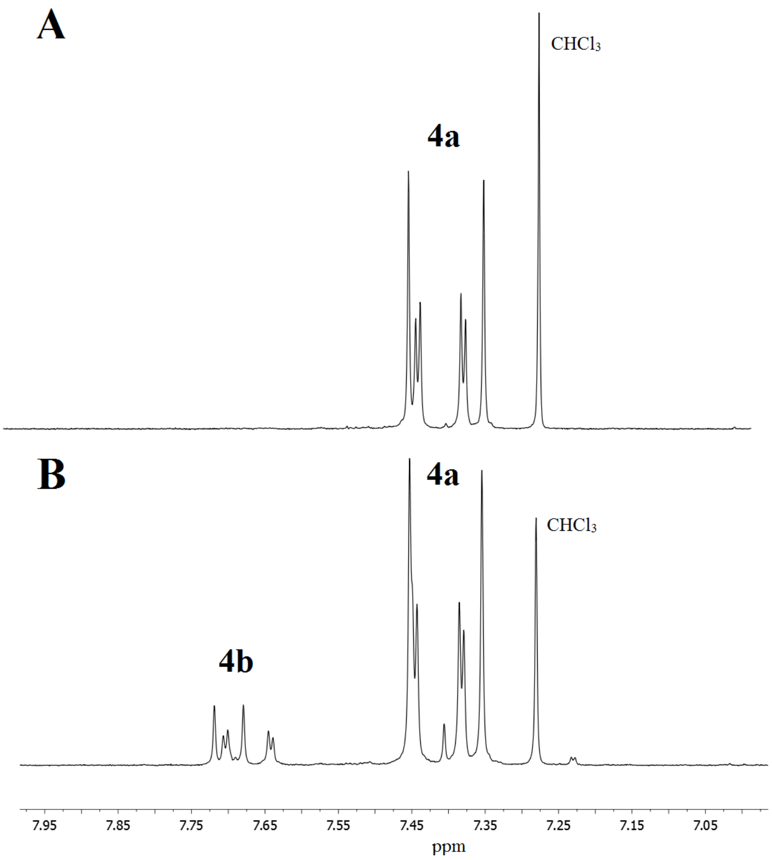

Figure S1 Fragments of ^{1}H NMR spectra of the reaction mixtures after acylation of the compound **3** by succinic anhydride at 0°C (A) and 35°C (B).

General procedure for the synthesis of compounds **8-10.**

In a round bottom flask equipped with magnetic stirrer, a mixture of 100 mg (0.089 mmol) of the corresponding compounds **5-7**, 379 mg (0.356 mmol) compound **4a**, 74 mg (0.358 mmol) DCC, catalytic amount of DMAP in 10 ml of CH_2Cl_2 was stirred for 48−125 h. The precipitate of dicyclohexylurea was filtered off, the solvent was distilled off *in vacuo*. The product was isolated from 20 ml of methanol by filtration.

Compound **8**. Yield 82%. Mp 198−199 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.31 (36H, s, $(CH_3)_3C$), 1.33 (72H, s, $(CH_3)_3C$), 1.34 (36H, s, $(CH_3)_3C$), 1.35 (36H, s, $(CH_3)_3C$), 1.40-1.55 (24H, m, CH_2-$\underline{CH_2}$-CH_2), 1.99 (24H, m, $\underline{CH_2}$-CN), 2.42 (8H, m, $\underline{CH_2}$-CONH), 2.63 (8H, m, $\underline{CH_2}$-COO), 3.22 (8H, m, $\underline{CH_2}$-NH), 3.62 (8H, m, $\underline{CH_2}$-NH), 3.89 (8H, t, $^3J_{HH}$ = 6.3 Hz, $\underline{CH_2}$-O), 3.92-4.30 (32H, m, O-$\underline{CH_2}$), 4.87 (8H, s, O-$\underline{CH_2}$), 6.33 (4H, m, CH_2-$\underline{NH}$), 7.35 (8H, s, Ar^1-H), 7.36 (8H, s, Ar^1-H), 7.38 (8H, d, $^4J_{HH}$ = 2.4 Hz, Ar^1-H), 7.44 (8H, s, Ar^1-H), 7.42 (8H, d, $^4J_{HH}$ = 2.4 Hz, Ar^3-H), 8.40 (4H, m, CH_2-$\underline{NH}$). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 12.8, 13.8, 14.2, 24.5, 24.7, 24.9, 25.3, 25.6, 29.5, 31.1, 31.27, 31.32, 33.9, 34.3, 34.4, 34.5, 38.2, 39.2, 39.4, 49.1, 55.7, 65.3, 66.7, 119.4, 123.1, 126.0, 126.6, 127.7, 127.8, 128.2, 129.5, 132.2, 133.9, 146.4, 147.2, 155.4, 156.3, 157.0, 157.8, 168.7, 171.3, 172.6. MS (MALDI-TOF): calculated [M$^+$] m/z = 5315.1; found [M+K]$^+$ m/z = 5354.4. Anal. Found (%): C, 64.89; H, 6.56; N, 5.18; S, 11.76. $C_{288}H_{356}N_{20}O_{36}S_{20}$. Calculated (%): C, 65.08; H, 6.75; N, 5.27; S, 12.07. IR (nujol, ν/cm^{-1}): 1264 (COC); 1678, 1716, 1711, 1736 (C=O), 2247 (CN).

Compound **9**. Yield 70%. Mp 158−160 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.25 (36H, s, $(CH_3)_3C$), 1.32 (36H, s, $(CH_3)_3C$), 1.34 (72H, s, $(CH_3)_3C$), 1.35 (36H, s, $(CH_3)_3C$), 1.40-1.60 (24H, m, CH_2-$\underline{CH}_2$-CH_2), 1.96 (8H, m, $\underline{CH}_2$-CN), 1.98 (16H, t, $^3J_{HH}$ = 7.5 Hz, $\underline{CH}_2$-CN), 2.43 (8H, m, $\underline{CH}_2$-CONH), 2.63 (8H, m, $\underline{CH}_2$-COO), 3.21 (8H, m, $\underline{CH}_2$-NH), 3.74 (8H, m, $\underline{CH}_2$-NH), 3.80-4.30 (40H, m, O-$\underline{CH}_2$), 4.22 (8H, s, O-$\underline{CH}_2$), 6.36 (4H, m, CH_2-$\underline{NH}$), 7.31-7.51 (40H, m, Ar-H), 7.60 (4H, m, CH_2-$\underline{NH}$). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 12.6, 13.8, 14.2, 24.6, 24.9, 25.3, 25.5, 26.1, 28.8, 29.0, 29.3, 29.5, 30.6, 30.7, 31.1, 31.3, 32.4, 33.7, 34.5, 38.1, 39.4, 40.2, 42.7, 47.5, 49.5, 54.6, 58.9, 60.8, 62.2, 65.2, 66.7, 70.1, 70.9, 119.4, 120.1, 126.6, 127.3, 127.6, 127.9, 128.1, 128.3, 128.4. MS (MALDI-TOF): calculated [M$^+$] m/z = 5315.1; found [M+K]$^+$ m/z = 5354.4. Found (%): C, 64.88; H, 6.44; N, 5.14; S, 11.87. Calc. for $C_{288}H_{356}N_{20}O_{36}S_{20}$ (%): C, 65.08; H, 6.75; N, 5.27; S, 12.07. IR (nujol, ν/cm^{-1}): 1263 (COC); 1677, 1711, 1774 (C=O), 2246 (CN).

Compound **10**. Yield 73%. Mp 153−154 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.05 (36H, s, $(CH_3)_3C$), 1.32 (36H, s, $(CH_3)_3C$), 1.34 (72H, s, $(CH_3)_3C$), 1.35 (36H, s, $(CH_3)_3C$), 1.40-1.75 (24H, m, CH_2-$\underline{CH}_2$-CH_2), 1.93 (8H, m, $\underline{CH}_2$-CN), 1.98 (16H, t, $^3J_{HH}$ = 7.5 Hz, $\underline{CH}_2$-CN), 2.43 (8H, m, $\underline{CH}_2$-CONH), 2.61 (8H, m, $\underline{CH}_2$-COO), 3.10-3.70 (16H, m, $\underline{CH}_2$-NH), 3.80-4.36 (40H, m, O-$\underline{CH}_2$), 4.27 (6H, m, O-$\underline{CH}_2$), 4.27 (2H, s, O-$\underline{CH}_2$), 6.34 (4H, m, CH_2-$\underline{NH}$), 7.17-7.58 (40H, m, Ar-H), 7.81 (4H, m, CH_2-$\underline{NH}$). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 12.7, 13.8, 14.2, 22.9, 24.6, 25.3, 25.6, 29.5, 31.0, 31.27, 31.32, 34.18, 34.4, 34.8, 38.2, 39.2, 55.7, 65.3, 90.0, 92.0, 96.5, 102.9, 104.5, 106.9, 109.3, 115.4, 116.2, 118.6, 119.3, 120.0, 122.5, 125.0, 125.8, 126.6, 127.7, 127.9, 128.3, 133.2, 134.3, 135.1, 136.6, 137.7, 139.5, 140.4, 146.4, 147.2, 155.4, 156.3, 157.1, 159.1, 161.1, 165.1, 168.4, 171.3, 172.5. MS (MALDI-TOF): calculated [M$^+$] m/z = 5315.1; found [M+K]$^+$ m/z = 5354.4. Found (%): C, 65.03; H, 6.62 N, 5.12; S, 11.76. Calc. for $C_{288}H_{356}N_{20}O_{36}S_{20}$ (%): C, 65.08; H, 6.75; N, 5.27; S, 12.07. IR (nujol, ν/cm^{-1}): 1264 (COC); 1676, 1735 (C=O), 2246 (CN).

Determination of the stability constant and stoichiometry of the complex by UV titration.

UV measurements were performed with a Shimadzu UV-3600 instrument. A 10^{-2} M solution of lithium, silver(I), copper(II), nickel(II), iron(III) and cobalt(III) nitrates (0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 μl) in methanol was added to 1 ml solution of receptor [**4a** (9·10^{-6} M), **8-10**

($3\cdot10^{-6}$ M)] in dichloromethane. The volume was brought to 3 ml with methanol. The UV spectra of the obtained solutions were then recorded. The stability constant and stoichiometry of complexes were measured in accordance with the literature.[32] Three independent experiments were carried out for each series. Student's *t*-test was used in statistical data processing.

Determination of the hydrodynamic particle size by DLS.

The particle sizes were determined using a Zetasizer Nano ZS instrument at 20 °C. The instrument contains a 4 mW He-Ne laser operating at a wavelength of 633 nm. The measurements were performed using quartz cuvettes. The solutions of the investigated systems were prepared by addition of 1000 excess of lithium, silver(I), copper(II), nickel(II), iron(III) and cobalt(III) nitrates to 10 ml of 10^{-6} M solution of thiacalixarene derivatives **4a, 8-10** in CH_2Cl_2 (HPLC). The mixture was mechanically shaken for 3 h and then filtered to remove unreacted substrates. Three independent experiments were carried out for each combination of a ligand and metal nitrate. Student's *t*-test was used in statistical data processing.