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Phenylurea-equipped *p-tert*-butylthiacalix[4]arenes as the synthetic receptors for monocharged anions

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***General procedure for the synthesis of compounds* 2-4.**

In a round bottom flask equipped with magnetic stirrer, reflux condenser and a calcium chloride tube, a mixture of 1.00 g (1.35 mmol) of *p-tert*-butylthiacalix[4]arene **1** and 2.98 g (10.80 mmol) of *N*-(3-bromopropyl)phthalimide was suspended in 60 ml of dry acetone (for the macrocycle **2**) or acetonitrile (for the macrocycles **3** and **4**) containing anhydrous alkali metal carbonate (1.20 g, 11.30 mmol Na_2CO_3 or 3.68 g, 11.3 mmol Cs_2CO_3), 1.70 g (11.30 mmol) of freshly dried sodium iodide (for the compound **3**) and then refluxed for 20 (compound **2**),[17] 60 (compound **4**) and 100 (compound **3**) hours. After cooling the reaction mixture, the solvent was evaporated under vacuum. Then 40 ml of 2 M HCl were added to the reaction mixture, the precipitate filtered and washed with water. The product was isolated from 100 ml of methanol by hot filtration.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(3-phtalimidopropoxy)thiacalix[4]arene *(cone)* 3. Yield: 1.22 g (60%). Mp: 254°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.18 (36H, s, $(CH_3)_3C$), 1.68 (8H, m, CH_2-$\underline{CH_2}$-CH_2), 3.64 (8H, t, $^3J_{HH}$ =6.6 Hz, N-CH_2), 3.94 (8H, t, $^3J_{HH}$ =8.0 Hz, O-CH_2), 7.32 (8H, s, Ar^1-H), 7.67-7.74 (8H, m, Ar^2-H), 7.78-7.85 (8H, m, Ar^2-H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 28.7, 31.1, 34.1, 35.2, 67.5, 123.2, 128.3, 129.0, 132.1, 133.8, 145.7, 157.2, 168.1. Spectrum ^{1}H-^{1}H NOESY: (the most important cross-peaks): H^{4b} / H^3, H^7 / H^8, H^8 / H^9. MS (MALDI-TOF): 1469.1 $[M+H]^+$, 1491.0 $[M+Na]^+$, 1507.0 $[M+K]^+$. Anal. Found (%): C, 68.25; H, 5.45; N, 3.74. $C_{84}H_{84}N_4O_{12}S_4$. Calculated (%): C, 68.59; H, 5.72; N, 3.81. IR spectrum (nujol, ν/cm^{-1}): 1266 (COC); 1715, 1772 (C=O).

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(3-phtalimidopropoxy)thiacalix[4]arene *(cone)* 4. Yield: 1.09 g (71%). Mp: 223 °C. ^{1}H NMR: ($CDCl_3$, δ, ppm., J/Hz): 0.77 (18H, s, $(CH_3)_3C$), 1.31 (18H, s, $(CH_3)_3C$), 2.50 (4H, m, CH_2-$\underline{CH_2}$-CH_2), 4.04 (4H, t, $^3J_{HH}$ =7.1 Hz, N-CH_2), 4.65 (4H, t, $^3J_{HH}$ =6.8 Hz O-CH_2), 6.89 (4H, s, Ar^1-H), 7.56-7.61 (4H, m, Ar^2-H), 7.59

(4H, s, Ar^3-H), 7.72 (2H, s, OH), 7.75-7.90 (4H, m, Ar^2-H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 30.7, 31.5, 34.0, 34.1, 35.5, 73.1, 122.1, 123.0, 128.8, 132.3, 132.7, 133.5, 134.2, 142.5, 147.8, 155.7, 156.1, 168.3. MS (MALDI-TOF): 1103.6 $[M+H]^+$, 1125.5, $[M+Na]^+$; 1141.5 $[M+K]^+$. Anal. Found (%): C, 62.52; H, 6.31; N, 3.40; S, 11.22 $C_{62}H_{66}N_2O_6S_4$. Calculated (%): C, 67.98; H, 6.07; N, 2.56; S, 11.71. IR spectrum (nujol, ν/cm^{-1}): 1245 (COC); 1708, 1768 (C=O); 3358 (OH).

***General procedure for the synthesis of the compounds* 5, 7, 10, 13.**

In a round bottom flask equipped with magnetic stirrer and reflux condenser 1.00 g of the corresponding phthalimide derivative and 2 ml of hydrazine hydrate (40 mmol) in a mixture of 30 ml of ethanol and 20 ml of THF was refluxed for 4 hours. After cooling the reaction mixture, the solvent was evaporated under vacuum, and then 50 ml of $CHCl_3$ were 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.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(3-aminopropoxy)-2,8,14,20-tetrathiacalix[4]arene (*1,3-alternate*) 5. White powder, yield 0.58 g (90%). Mp: 258-260°C. ^1H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.24 (8H, m, CH_2-$\underline{CH_2}$-CH_2), 1.29 (36H, s, $(CH_3)_3C$), 2.46 (8H, t, $^3J_{HH}$ = 7.3 Hz, N-CH_2), 3.91 (8H, t, $^3J_{HH}$ = 6.8 Hz, O-CH_2),7.35 (8H, s, Ar-H). ^{13}C NMR ($CDCl_3$, δ, ppm.), δ: 31.3, 33.1, 34.2, 39.3, 67.0, 127.7, 128.1, 145.5, 157.0. Spectrum ^1H-^1H NOESY: H^{4b} / H^7, H^{4b} / H^8, H^{4b} / H^9, H^3 / H^7, H^3/ H^8, H^3 / H^9. MS ESI: 949.5 $[M+H]^+$. Anal. Found (%): C, 65.51; H, 8.30; N, 5.91; S, 13.70. $C_{52}H_{76}N_4O_4S_4$. Calculated (%): C, 65.78; H, 8.07; N, 5.90; S, 13.51. IR spectrum (nujol, ν/cm^{-1}): 1265 (COC); 3385 (NH_2).

5,11,1723-Tetra-*tert*-butyl-25,26,27,28-tetrakis(3-aminopropoxy)tetrathiacalix[4]arene (*cone*) 7. Yield: 0.60 g (90%) ^1H NMR ($CDCl_3$, δ, ppm., J/Hz): 1.10 (36H, s, $(CH_3)_3C$), 2.10 (8H, m, CH_2-$\underline{CH_2}$-CH_2), 3.00 (8H, t, $^3J_{HH}$=6.8 Hz N-CH_2), 4.25 (8H, t, $^3J_{HH}$ =6.8 Hz, O-CH_2), 7.30 (8H, s, Ar^1-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 31.2, 33.9, 34.1, 39.3, 73.6, 129.9, 134.0, 146.0, 157.0, 158.9. Spectrum ^1H-^1H NOESY: (the most important cross-peaks): H^{4b} / H^3, H^7 / H^8, H^8 / H^9. MS ESI: 949.5 (M^+). Anal. Found (%): C, 65.64; H, 8.17; N, 5.64; S, 13.30. $C_{52}H_{76}N_4O_4S_4$. Calculated (%): C, 65.78; H, 8.07; N, 5.90; S, 13.51. IR spectrum (nujol, ν/cm^1): 1265 (COC); 3397 (NH_2).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis(3-aminopropoxy)thiacalix[4]arene (*1,3-alternate*) 10. Yield 0.67 g (93%) Mp: 215-217°C. ^1H NMR ($CDCl_3$, δ, ppm., J/Hz): 1.27 (18H, s, $(CH_3)_3C$), 1.30 (18H, s, $(CH_3)_3C$), 0.85-1.45 (38H, m, $(CH_2)_8CH_3$, CH_2-CH_2-CH_2), 2.45 (4H, t, $^3J_{HH}$ =7.0 Hz, N-CH_2), 3.80 (4H, t, $^3J_{HH}$ =8.1 Hz, O-$\underline{CH_2}$-$(CH_2)_8CH_3$), 3.94 (4H, t, $^3J_{HH}$ =6.9 Hz, O-CH_2),

7.32 (4H, s, Ar^1-H), 7.34 (4H, s, Ar^3-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.2, 22.9, 26.0, 28.8, 29.5, 29.8, 29.9, 30.2, 31.4, 31.5, 32.1, 34.4, 39.6, 67.6, 68.8, 127.3, 128.0, 128.3, 128.6, 145.7, 157.0, 157.5. Spectrum ^{1}H-^{1}H NOESY: (the most important cross-peaks): H^{4b} / $H^{7'}$, H^3 / $H^{7'}$, $H^{4'b}$ / H^7, $H^{3'}$ / H^7. MS (MALDI-TOF): 1115.9 $[M+H]^+$, 1138.9 $[M+Na]^+$, 1154.9 $[M+K]^+$. Anal. Found (%): C, 65.64; H, 8.17; N, 5.64; S, 13.30. $C_{66}H_{102}N_2O_4S_4$. Calculated (%): C, 65.78; H, 8.07; N, 5.90; S, 13.51. IR spectrum (nujol, ν/см$^{-1}$): 1266 (COC); 3362 (NH_2).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis[3-*N*,*N*-bis(3-aminopropyl)aminopropoxy]-tetrathiacalix[4]arene (*1,3-alternate*) 13. Yield 0.67 g (95%). Mp: 170°C. ^{1}H NMR ($CDCl_3$, δ,ppm, J/Hz): 1.23 (18H, s, $(CH_3)_3C$), 1.24 (18H, s, $(CH_3)_3C$), 0.87-1.48 (58H, m, $(CH_2)_8CH_3$, CH_2-$\underline{CH_2}$-CH_2), 1.42 (8H, b. s, NH_2), 2.75 (12H, t, $^3J_{HH}$ =6.1 Hz, N-CH_2), 3.86 (4H, b. t, OCH_2), 3.99 (4H, t, $^3J_{HH}$ =6.8 Hz, OCH_2), 7.34 (4H, s, Ar^1), 7.35 (4H, s Ar^2). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.2, 22.8, 26.0, 27.1, 29.4, 29.5, 29.8, 29.9, 30.0, 30.1, 30.8, 31.4, 34.5, 31.6, 32.0, 34.3, 40.8 51.3, 51.7, 69.1, 69.3, 39.9, 128.3, 128.7, 128.8, 129.3, 129.8, 145.3, 157.8. MS (MALDI-TOF): 1345.2 $[M+H]^+$, 1368.2 $[M+Na]^+$, 1384.2 $[M+K]^+$. Anal. Found (%): C, 69.64; H, 9.37; N, 6.14; S, 9.30. $C_{78}H_{130}N_6O_4S_4$. Calculated (%): C, 69.70; H, 9.75; N, 6.25; S, 9.54. IR spectrum (nujol, ν/см$^{-1}$): 1267 (COC); 3399 (NH_2).

***General procedure for the synthesis of the compounds* 6, 8, 11, 14.**

Into a round bottom flask equipped with a magnetic stirrer, 0.50 g of the corresponding amine was introduced. Phenylisocyanate in a two-fold excess per each amino group (the calixarene: phenylisocyanate mole ratio was 1:8 for compounds **6**, **8** and **14**, and 1:4 for compound **11**), and 20 ml of tetrahydrofuran were added. The reaction mixture was left for one day. The solvent was distilled off under reduced pressure and the residue was recrystallized from chloroform/methanol.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(3-phenylureido)propoxy]tetrathiacalix[4]arene (*1,3-alternate*) 6. Yield 84%. Mp: >330°C. ^{1}H NMR (DMSO-d_6, δ, ppm, J/Hz): 1.20 (36H, s, $(CH_3)_3C$), 1.20-1.24 (8H, m, CH_2-$\underline{CH_2}$-CH_2), 2.94 (8H, m, NH-$\underline{CH_2}$-CH_2-CH_2), 3.85 (8H, t, $^3J_{HH}$ =7.1 Hz, O-CH_2), 6.01 (4H, t, $^3J_{HH}$ =5.7 Hz, $\underline{NH}$-CH_2-CH_2-CH_2), 6.85-7.4 (28H, m, Ar, Ph-) 8.50 (4H, m, Ph-$\underline{NH}$). ^{13}C NMR (125 MHz, DMSO-d_6), δ: 29.4, 30.8, 33.9, 36.0, 66.7, 117.7, 121.1, 127.4, 127.5, 128.6, 140.4, 145.7, 155.2, 156.4. Spectrum ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / H^7, H^{4b} / H^8, H^{4b} / H^9, H^3 / H^7, H^3/ H^8, H^3 / H^9. MS (MALDI-TOF): 1442.2 $[M+Na]^+$. Anal. Found (%): C, 67.64; H, 6.67; N, 7.54; S, 8.70. $C_{80}H_{96}N_8O_8S_4$. Calculated (%): C, 67.38; H, 6.79; N, 7.86; S, 8.99. IR spectrum (nujol, ν/cm^{-1}): 1552, 1643, (CO); 3322 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(3-phenylureido)propoxy]tetrathia-calix[4]arene (*cone*) 8. Yield 70%. Mp: 253°C. ^{1}H NMR (DMSO-d_6, δ, ppm, J/Hz): 1.06 (36H, s, $(CH_3)_3C$), 2.10 (8H, m, CH_2-$\underline{CH_2}$-CH_2), 3.41 (8H, m, NH-$\underline{CH_2}$-CH_2-CH_2), 4.15 (8H, t, $^{3}J_{HH}$ =7.1 Hz, O-CH_2), 6.28 (4H, t, $^{3}J_{HH}$ =5.62 Hz, $\underline{NH}$-CH_2-CH_2-CH_2), 6.85-7.4 (28H, m, Ar, Ph-) 8.41 (4H, m, Ph-$\underline{NH}$). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 30.5, 30.8, 33.7, 36.4, 73.8, 117.8, 120.9, 128.6. 129.4, 133.9, 140.4, 154.8, 155.3, 158.7. Spectrum ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / H^{3}, H^{7} / H^{8}, H^{8} / H^{9}. MS (MALDI-TOF): 1442.2 $[M+Na]^{+}$. Anal. Found (%): C, 67.57; H, 6.62; N, 7.58; S, 8.64. $C_{80}H_{96}N_8O_8S_4$. Calculated (%): C, 67.38; H, 6.79; N, 7.86; S, 8.99. IR spectrum (nujol, ν/cm^{-1}): 1553, 1647, (CO); 3330 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis[(3-phenylureido)propoxy]thiacalix[4]arene (*1,3-alternate*) 11. Yield 81%. Mp: 115°C. ^{1}H NMR ($CDCl_3$, δ, ppm., J/Hz): 1.22 (18H, s, $(CH_3)_3C$), 1.31 (18H, s, $(CH_3)_3C$), 0.80-1.69 (38H, m, $(CH_2)_8CH_3$, CH_2-$\underline{CH_2}$-CH_2), 2.80-3.00 (4H, b. t, N-CH_2), 3.71-3.99 (8H, m, O-$\underline{CH_2}$-$(CH_2)_8CH_3$, O-$\underline{CH_2}$), 5.70-5.80 (2H, m, $\underline{NH}$-Ph), 6.94-7.04 (2H, m, $\underline{NH}$-CH_2), 7.15-7.28, 7.67 (10H, m, N-$\underline{Ph}$), 7.30 (4H, s, Ar^{1}-H), 7.35 (4H, s, Ar^{3}-H). ^{13}C NMR (100 Hz, $CDCl_3$), δ:14.3, 22.8, 26.0, 28.7, 29.5, 29.7, 29.9 30.2, 30.8, 31.4, 31.5 32.1, 34.4, 38.0, 66.8 ,38.6, 120.2, 123.1, 126.7, 127.7, 127.8, 128.4, 129.2, 139.9, 145.9, 146.0, 156.5, 156.7, 157.0. MS (MALDI-TOF): 1377.03 $[M+Na]^{+}$. Anal. Found (%): C, 70.98; H, 8.85; N, 4.16; S, 9.96. $C_{80}H_{122}N_4O_6S_4$. Calculated (%):C, 70.96; H, 8.34; N, 4.14; S, 9.47. IR spectrum (nujol, ν/cm^{-1}): 1551, 1642, (CO); 3324 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis{3-*N*,*N*-bis[(3-phenylureido)propoxy]-aminopropoxy}tetrathiacalix[4]arene (*1,3-alternate*) 14. Yield 79%. Mp: 126°C. ^{1}H NMR ($CDCl_3$, δ,ppm, J/Hz): 1.23 (18H, s, $(CH_3)_3C$), 1.27 (18H, s, $(CH_3)_3C$), 0.80-1.80 (58H, m, $(CH_2)_8CH_3$, CH_2-$\underline{CH_2}$-CH_2), 2.31 (4H, br. t. N$\underline{CH_2}CH_2CH_2O$) 2.41(16H, br. t. N$\underline{CH_2}$CH2$\underline{CH_2}$N) 3.26 (4H, br.t, OCH_2), 3.82 (4H, br. t, OCH_2), 6.63 (8H, m, $CH_2CH_2CH_2\underline{NH}$), 6.94 (8H, br. t. Ph$\underline{NH}$) 7.07-7.23, 7.83 (40H, m, Ph), 7.31 (4H, s, Ar^{1}), 7.39 (4H, s, Ar^{2}). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 22.7, 24.5, 25.7, 28.4, 29.3, 29.6, 29.7, 30.0, 31.2, 31.4, 31.9, 34.2, 34.3, 36.8, 51.0, 119.1, 122.3, 126.0, 127.7, 128.9, 129.8, 130.2, 139.3, 146.5, 156.8. Anal. Found (%): C, 69.78; H, 8.25; N, 7.46; S, 6.96. $C_{106}H_{150}N_{10}O_8S_4$. Calculated (%):C, 69.93; H, 8.30; N, 7.69; S, 7.04. IR spectrum (nujol, ν/cm^{-1}): 1555, 1647, (CO); 3322 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis(3-phalimidopropoxy)thiacalix[4]arene 9. In a round bottom flask equipped with a magnetic stirrer, reflux condenser and a calcium chloride tube, a

mixture of 1.50 g (1.37 mmol) diphthalimide **4**, 1.21 g (5.48 mmol) 1-bromodecane, 1.80 g (5.48 mmol) of freshly powdered cesium carbonate and 60 ml of acetonitrile was refluxed for 10 hours. After cooling the reaction mixture, the precipitate was filtered, the solvent from the filtrate was distilled off under reduced pressure and the residue recrystallized from methanol. Yield 1.60 g (85%). Mp. 215-217°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.20 (18H, s, $(CH_3)_3C$), 1.25 (18H, s, $(CH_3)_3C$), 0.80-1.60 (38H, m, $(CH_2)_8CH_3$), 1.64 (4H, m, CH_2-$\underline{CH_2}$-CH_2), 3.62 (4H, t, $^{3}J_{HH}$ =6.8 Hz, N-CH_2), 3.79 (4H, t, $^{3}J_{HH}$ =7.6 Hz, O-$\underline{CH_2}$-$(CH_2)_8CH_3$), 4.00 (4H, t, $^{3}J_{HH}$ =7.9 Hz, O-CH_2), 7.31 (4H, s, Ar^1-H), 7.33 (4H, s, Ar^3-H), 7.67-7.85 (8H, m, Ar^2-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.3, 26.0, 28.9, 29.5, 29.8, 29.9, 30.1, 31.3, 31.5, 32.0, 34.3, 35.5, 67.5, 69.1, 123.3, 128.1, 128.2, 128.4, 128.5, 132.3, 134.0, 145.5, 145.8, 157.2, 157.3, 168.2. Spectrum ^{1}H-^{1}H NOESY (the most important cross-peaks): H^{4b} / $H^{7'}$, H^{3} / $H^{7'}$, $H^{4'b}$ / H^{7}, $H^{3'}$ / H^{7}. MS (MALDI-TOF): 1375.3, $[M+H]^+$; 1398.2, $[M+Na]^+$; 1415.2, $[M+K]^+$. Anal. Found (%): C, 71.78; H, 7.65; N, 2.06; S, 9.12. $C_{82}H_{106}N_2O_8S_4$. Calculated (%):C, 71.58; H, 7.76; N, 2.04; S, 9.32. IR spectrum (nujol, ν/cm^{-1}): 1267 (COC); 1715, 1775 (C=O).

5,11,17,23-Tetra-*tert*-butyl-25,27-didecyl-26,28-bis[3-*N*,*N*-bis(3-phtalimidopropyl)amino-propoxy]tetrathiacalix[4]arene 12. In a round bottom flask equipped with a magnetic stirrer, a reflux condenser and a calcium chloride tube, a mixture of 0.60 g (0.54 mmol) of diamine **10**, 1.20 g (4.32 mmol) *N*-(3-bromopropyl)phthalimide, 0.60 g (4.32 mmol) of freshly powdered potassium carbonate and 40 ml of freshly distilled acetonitrile was refluxed for 60 hours. After cooling the reaction mixture, the carbonate was filtered off, washed with 2x20 ml of chloroform. The solvent was distilled off under reduced pressure and the residue recrystallized from acetonitrile. Yield 0.87 g (60%). Mp: 68°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.22 (36H, s, $(CH_3)_3C$), 1.82 (24H, m, CH_2-$\underline{CH_2}$-CH_2), 2.52 (24H, m, N-CH_2), 3.73 (16H, t, $^{3}J_{HH}$ =7.4 Hz, CH_2-Pht), 3.95 (8H, t, $^{3}J_{HH}$ =7.6 Hz, O-CH_2), 7.40 (8H, s, Ar^1-H), 7.63-7.70 (8H, m, Ar^2-H), 7.75-7.82 (8H, m, Ar^2-H). ^{13}C NMR (100 Hz, $CDCl_3$): 14.1, 22.7, 25.8, 26.2, 26.7, 29.3, 29.4, 29.6, 29.7, 29.9, 31.3, 31.4, 31.9, 34.1, 34.2, 36.4, 50.6, 50.8, 69.0, 69.8, 123.1, 128.3, 128.4, 129.4, 129.6, 132.3, 144.8, 145.1, 153.7, 157.7, 157.9, 168.2. MS (MALDI-TOF): 1879.56, $[M+H]^+$; 1903.56, $[M+Na]^+$; 1918.56, $[M+K]^+$. Anal. Found (%): C, 70.48; H, 7.35; N, 4.46; S, 6.62. $C_{110}H_{138}N_6O_{12}S_4$. Calculated (%):C, 70.86; H, 7.46; N, 4.51; S, 6.88. IR spectrum (nujol, ν/cm^{-1}): 1265 (COC); 1709, 1771 (C=O).