Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2012

Novel Capsular Aggregates from Flexible Tripodal Triureas with $C_3$ Symmetry


chem_201102246_sm_m miscellaneous_information.pdf
**General:** $^1$H and $^{13}$C NMR spectra were measured on Bruker AC 200 ($^1$H: 200 MHz, $^{13}$C: 50 MHz), Varian Unity-300 ($^1$H: 300 MHz, $^{13}$C: 75 MHz), Bruker AVANCE 300 ($^1$H: 300 MHz, $^{13}$C: 75 MHz) and Bruker AVANCE 400 ($^1$H: 400 MHz, $^{13}$C: 101 MHz) spectrometers with TMS ($\delta$ 0.00 ppm) or the solvent residual peak as internal standards. IR spectra were recorded on a FT-IR Nicolet Impact 400 infrared spectrometer and melting points were taken on a Reichert apparatus and are not corrected.

**CAUTION:** Azido compounds may represent an explosion hazard when being concentrated under vacuum or stored neat. A safety shield and appropriate handling procedures are recommended.

**Synthesis of triazides 7a-c.** The synthesis of triazides 7a-b has been previously reported.[1]

**Bis(2-azidobenzyl)(2-azido-5-chlorobenzyl)amine (7c).** A solution of 2-azido-5-chlorobenzyl iodide[1] (0.75 g, 2.6 mmol) in dry dioxane (15 mL) was slowly added to a solution of bis(2-azidobenzyl)amine[1] (0.71 g, 2.6 mmol) in the same solvent (30 mL). Then, the reaction mixture was stirred under reflux for 5 h. After cooling, a solution of triethylamine (0.52 g, 3.1 mmol) in dry dioxane (2 mL) was added and the stirring was maintained for 2 h more. The solvent was removed under reduced pressure and the residue purified by silica-gel chromatography eluting with 13:1 hexanes/Et$_2$O ($R_f$ = 0.82) to afford 7c (68% yield) as colorless prisms (an analytical sample was obtained by recrystallization from 1:1 Et$_2$O/n-hexane). M.p. 83-85 °C; $^1$H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 3.51$ (s, 2H), 3.56 (s, 4H), 7.00 (d, $^3$J(H,H) = 8.4 Hz, 1H), 7.07-7.19 (m, 4H), 7.22-7.31 (m, 3H), 7.48-7.56 (m, 2H), 7.65 ppm (d, $^4$J(H,H) = 2.6 Hz, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$, 20 °C): $\delta = 52.6$ (t), 53.2 (2×t), 118.1 (2×d), 119.1 (d), 124.7 (2×d), 127.9 (d), 128.3 (2×d), 130.2 (s), 130.3 (d), 130.4 (2×s), 130.6 (2×d), 132.7 (s), 136.7 (s), 138.5 ppm (2×s); IR (Nujol): $\tilde{\nu} = 2126$ (vs), 2090 (vs), 1581 (m), 1487 (vs), 1407 (w), 1284 (s), 1151 (m), 1114 (m), 980 (w), 900 (w), 816 (w), 800 (w), 756 (m) cm$^{-1}$; MS (70 eV, EI): $m/z$ (%): 446 (1) [$M^+2$], 444 (3) [$M^+$], 256 (21), 241 (11), 222 (23), 221 (32), 220 (27), 206 (13), 205 (13), 193 (17), 165 (14), 137 (15), 118 (16), 106 (30), 104 (80), 102 (55), 91 (22), 89 (37), 77 (100); elemental analysis calcd (%) for C$_{21}$H$_{17}$ClN$_{10}$ (444.9): C 56.70, H 3.85, N 31.48; found: C 56.38, H 3.92, N 31.08.
General procedure for the synthesis of triamines 8a-c. The corresponding triazide 7a-c (2.3 mmol) was dissolved in freshly distilled Et₂O (30 mL) and slowly added to a suspension of LiAlH₄ (0.26 g, 6.9 mmol) in the same solvent (40 mL) at 0 °C under N₂. The mixture was stirred at this temperature for 1 h, warmed to 20 °C, and further stirred for 5 h. Then, the reaction mixture was cooled to 0 °C and treated with 10% aqueous NaOH (10 mL). After filtration over a pad of celite, which was subsequently washed with Et₂O (3×20 mL), the ethereal phase was separated and the aqueous phase extracted with CH₂Cl₂ (3×20 mL). The combined extracts were dried over MgSO₄, the solvent evaporated under reduced pressure and the residue was purified by silica-gel chromatography.

Bis(2-amino-5-methylbenzyl)(2-aminobenzyl)amine (8a). The crude product was eluted with 1:2 AcOEt/hexanes ($R_f$ = 0.24) to afford 8a (92% yield) as colorless prisms (an analytical sample was obtained by recrystallization from 1:1 Et₂O/n-pentane). M.p. 187-189 °C; ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): δ = 2.20 (s, 6H), 3.42 (s, 4H), 3.45 (s, 2H), 3.79 (br s, 6H), 6.46-6.49 (m, 2H), 6.55 (dd, 3J(H,H) = 8.4 Hz, 4J(H,H) = 0.9 Hz, 1H), 6.66 (td, 3J(H,H) = 7.4 Hz, 4J(H,H) = 1.0 Hz, 1H), 6.86-6.88 (m, 4H), 7.03-7.08 ppm (m, 2H); ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ = 20.4 (2×q), 57.1 (3×t), 115.5 (2×d), 115.7 (d), 117.8 (2×d), 121.98 (s), 122.03 (2×s), 126.9 (2×s), 128.9 (d), 129.4 (2×d), 130.2 (d), 132.6 (2×d), 143.1 (2×s), 145.7 ppm (s); IR (Nujol): $\tilde{\nu} = 3456$ (vs), 3368 (vs), 1620 (s), 1582 (m), 1504 (vs), 1315 (s), 1293 (s), 1249 (w), 1155 (m), 1098 (s), 1007 (w), 963 (m), 825 (s), 750 (s) cm⁻¹; MS (70 eV, EI): m/z (%): 360 (3) $[M⁺]$, 254 (12), 241 (5), 240 (29), 238 (7), 237 (10), 224 (5), 223 (15), 135 (17), 134 (5), 121 (17), 120 (100), 106 (10), 106 (48), 91 (11), 79 (5), 77 (13); elemental analysis calcd (%) for C$_{23}$H$_{28}$N$_4$·0.25H$_2$O (360.5): C 75.68, H 7.87, N 15.35; found: C 75.82, H 7.98, N 15.46.

Bis(2-aminobenzyl)(2-amino-5-methylbenzyl)amine (8b). The crude product was eluted with 1:1 AcOEt/hexanes ($R_f$ = 0.39) to afford 8b (61% yield) as colorless prisms (an analytical sample was obtained by recrystallization from 4:1 Et₂O/n-hexane). M.p. 191-195 °C; ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): δ = 2.21 (s, 3H), 3.43 (s, 2H), 3.46 (s, 4H), 3.92 (br s, 6H), 6.49 (d, 3J(H,H) = 8.4 Hz, 1H), 6.56 (dd, 3J(H,H) = 8.1 Hz, 4J(H,H) = 1.2 Hz, 2H), 6.67 (td, 3J(H,H) = 7.5 Hz, 4J(H,H) = 1.1 Hz, 2H), 6.86-6.88 (m, 2H), 7.03-7.09 ppm (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ = 20.4 (q), 57.1 (3×t), 115.5 (2×d), 115.7 (d), 117.8 (2×d), 121.9 (2×s), 122.0 (s), 126.9 (s), 128.9 (2×d), 129.4 (d), 132.0 (2×d), 132.6 (d), 143.0 (s), 145.6 ppm (2×s); IR (Nujol): $\tilde{\nu} = 3446$ (s), 3347 (s), 1618 (s), 1579 (m), 1506 (s), 1494 (vs), 1311 (s), 1285 (m), 1155 (m), 1098 (w), 958 (m), 750 (vs) cm⁻¹; MS (70 eV, EI): m/z (%): 360 (3) $[M⁺]$, 254 (12), 241 (5), 240 (29), 238 (7), 237 (10), 224 (5), 223 (15), 135 (17), 134 (5), 121 (17), 120 (100), 106 (10), 106 (48), 91 (11), 79 (5), 77 (13); elemental analysis calcd (%) for C$_{22}$H$_{26}$N$_4$·0.75H₂O (346.5): C 73.40, H 7.87, N 15.35; found: C 73.72, H 7.56, N 15.73.
Bis(2-aminobenzyl)(2-amino-5-chlorobenzyl)amine (8c). The crude product was eluted with 2:3 AcOEt/hexanes ($R_f = 0.59$) to afford 8c (76% yield) as colorless prisms (an analytical sample was obtained by recrystallization from 1:1 Et$_2$O/n-hexane). M.p. 128-135 °C; $^1$H NMR (300 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 3.39$ (s, 2H), 3.43 (s, 4H), 3.85 (br s, 6H), 6.46 (d, $^3$$J$(H,H) = 8.4 Hz, 1H), 6.56 (d, $^3$$J$(H,H) = 7.8 Hz, 2H), 6.67 (td, $^3$$J$(H,H) = 7.5 Hz, $^4$$J$(H,H) = 1.2 Hz, 2H), 6.99-7.09 ppm (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$, 20 °C): $\delta = 56.8$ (t), 57.1 (2x t), 115.6 (2x d), 116.5 (d), 118.0 (2x d), 121.6 (2x s), 122.1 (s), 123.4 (s), 128.6 (d), 129.0 (2x d), 131.3 (d), 132.0 (2x d), 144.3 (s), 145.5 ppm (2x s); IR (Nujol): $\nu = 3411$ (vs), 3335 (vs), 1622 (s), 1583 (m), 1495 (vs), 1421 (m), 1314 (m), 1293 (m), 1277 (m), 1098 (m), 1061 (w), 966 (w), 817 (w), 760 (s) cm$^{-1}$; MS (70 eV, EI): m/z (%): 366 (2) [$M^+$], 262 (8), 260 (27), 243 (15), 226 (20), 209 (12), 155 (11), 140 (30), 121 (54), 106 (100), 103 (18), 93 (6), 79 (17), 78 (11), 76 (43); elemental analysis calcd (%) for C$_{21}$H$_{23}$ClN$_4$ (366.9): C 68.75, H 6.32, N 15.27; found: C 68.32, H 6.83, N 15.35.
Preparation of tris(2-ureidobenzyl)amines 3c-e

**Bis{2-[N’-(4-methylphenyl)ureido]benzyl}{5-methyl-2-[N’-(4-methylphenyl)ureido]benzyl}amine (3c):** 81% yield; colorless prisms (from 1:1 CHCl₃/Et₂O). M.p. 235-237 °C; ¹H NMR (300 MHz, [D₆]DMSO, 20 °C): δ = 2.16 (s, 3H), 2.22 (s, 9H), 3.61 (s, 6H), 7.28-7.30 (m, 6H), 7.37 (d, 3J(H,H) = 8.1 Hz, 1H), 7.50 (d, 3J(H,H) = 7.8 Hz, 2H), 7.53-7.56 (m, 2H), 7.79 (s, 1H), 7.92 (s, 2H), 8.59 (s, 1H), 8.65 ppm (s, 2H); ¹³C NMR (75 MHz, [D₆]DMSO, 20 °C): δ = 54.5 (t), 54.6 (t), 118.3 (d), 123.5 (d), 123.6 (d), 124.4 (d), 127.0 (d), 127.7 (d), 128.8 (d), 129.0 (d), 129.6 (d), 129.8 (s), 129.9 (s), 130.3 (s), 130.4 (s), 130.5 (s), 130.7 (s), 131.7 (s), 153.0 (s), 153.4 ppm (s); IR (Nujol): ν = 3322 (vs), 1655 (vs), 1601 (vs), 15 64 (vs), 1313 (m), 1233 (m), 977 (w), 940 (w), 817 (m), 744 (m), 715 (m), 689 (m) cm⁻¹; elemental analysis calcd (%) for C₄₆H₄₇N₇O₃ (745.9): C 74.07, H 6.35, N 13.14; found: C 74.38, H 6.49, N 13.29.

**Bis{2-[N’-(4-methylphenyl)ureido]benzyl}{5-chloro-2-[N’-(4-methylphenyl)ureido]benzyl}amine (3d):** 71% yield; colorless prisms (from 1:1 CHCl₃/Et₂O). M.p. 226 -230 °C; ¹H NMR (300 MHz, [D₆]DMSO, 20 °C): δ = 2.21 (s, 9H), 3.62 (s, 2H), 3.65 (s, 4H), 7.02 -7.06 (m, 8H), 7.13-7.21 (m, 3H), 7.26-7.30 (m, 6H), 7.53-7.61 (m, 6H), 7.92 (s, 2H), 7.94 (s, 1H), 8.67 ppm (s, 3H); ¹³C NMR (50 MHz, [D₆]DMSO, 20 °C): δ = 54.1 (t), 54.4 (t), 118.3 (d), 118.4 (d), 123.7 (d), 123.8 (d), 124.8 (d), 126.9 (d), 127.1 (d), 127.4 (s), 127.6 (d), 128.0 (d), 129.2 (d), 129.8 (s), 130.6 (s), 130.8 (s), 131.9 (s), 136.0 (s), 137.0 (s), 137.2 (s), 152.7 (s), 153.1 ppm (s); IR (Nujol): ν = 3328 (s), 1660 (vs), 1604 (vs), 1563 (vs), 1514 (s), 1313 (m), 1113 (w), 973 (w), 914 (w), 817 (m), 744 (m), 689 (m) cm⁻¹; elemental analysis calcd (%) for C₄₅H₄₄ClN₇O₃ (766.3): C 70.53, H 5.79, N 12.79; found: C 70.36, H 6.12, N 12.83.

**Bis{2-[N’-(4-trifluoromethylphenyl)ureido]benzyl}{5-chloro-2-[N’-(4-trifluoromethylphenyl)ureido]benzyl}amine (3e):** 73% yield; colorless prisms (from 1:1 CHCl₃/Et₂O). M.p. 248-251 °C; ¹H NMR (300 MHz, [D₆]DMSO, 20 °C): δ = 3.62 (s, 2H), 3.66 (s, 4H), 7.05 (td, 3J(H,H) = 7.5 Hz, 1J(H,H) = 0.9 Hz, 2H), 7.12-7.19 (m, 3H), 7.51-7.61 (m, 6H), 7.92 (s, 2H), 7.94 (s, 1H), 8.67 ppm (s, 3H); ¹³C NMR (50 MHz, [D₆]DMSO, 20 °C): δ = 54.1 (t), 54.4 (t), 118.3 (d), 118.4 (d), 123.7 (d), 123.8 (d), 124.8 (d), 126.9 (d), 127.1 (d), 127.4 (s), 127.6 (d), 128.0 (d), 129.2 (d), 129.8 (s), 130.6 (s), 130.8 (s), 131.9 (s), 136.0 (s), 137.0 (s), 137.2 (s), 152.7 (s), 153.1 ppm (s); IR (Nujol): ν = 3328 (s), 1660 (vs), 1604 (vs), 1563 (vs), 1514 (s), 1313 (m), 1239 (m), 1113 (w), 973 (w), 818 (m), 749 (m) cm⁻¹; elemental analysis calcd (%) for C₄₅H₄₄ClF₉N₇O₃ (928.2): C 58.23, H 3.80, N 10.56; found: C 58.41, H 4.15, N 10.72.
3-Nitrobenzyl iodide. NaI (9.61 g, 64.2 mmol) was added to a solution of 3-nitrobenzyl chloride (5.50 g, 32.1 mmol) in dry acetone (50 mL) and the reaction mixture was stirred at 20 °C for 20 h. The solid was filtered and washed with cold acetone (5×20 mL). The solvent was removed under reduced pressure and the residue purified by silica-gel chromatography eluting with 1:9 AcOEt/hexanes (RF = 0.45) to afford 3-nitrobenzyl iodide (99% yield) as yellow prisms. M.p. 84-85 °C (lit. 84-86 °C);

\[ \text{[\text{1}H NMR (200 MHz, CDCl}_3, 20 °C, TMS):} \]

\[ \delta = 4.50 (s, 2H), 7.49 (t, 3J(H,H) = 8.0 Hz, 1H), 7.71 (dt, 3J(H,H) = 7.7 Hz, 4J(H,H) = 1.3 Hz, 1H), 8.11 (ddd, 3J(H,H) = 8.2 Hz, 4J(H,H) = 2.2 Hz, 4J(H,H) = 1.0 Hz, 1H), 8.23 ppm (t, 3J(H,H) = 2.0 Hz, 1H) ; \]

\[ \text{IR (Nujol): } n~\text{= 1516 (vs), 1352 (vs), 1313 (s), 1097 (w), 1070 (w),} \]

906 (w), 816 (m), 739 (m), 685 (s), 672 (m) cm\(^{-1}\).

Bis(3-nitrobenzyl)(3-azidobenzyl)amine (9). To a suspension of Na\(_2\)CO\(_3\) (1.77 g, 16.7 mmol) in dry acetonitrile (10 mL) 3-azidobenzylamine\(^{[3]}\) (0.43 g, 2.9 mmol) and 3-nitrobenzyl iodide (1.53 g, 5.8 mmol) were subsequently added in the same solvent (2 and 5 mL respectively) and the reaction mixture stirred under reflux for 24 h and under N\(_2\). After cooling, the inorganic salts were filtered and washed with cold acetonitrile (4×10 mL). The filtrate was collected, the solvent removed and the residue purified by silica-gel chromatography eluting with 1:13 EtOAc/hexanes (RF = 0.11) to afford 9 (57% yield) as colorless prisms (an analytical sample was obtained by recrystallization from 1:3 CH\(_2\)Cl\(_2\)/Et\(_2\)O). M.p. 105-108 °C; \[ \text{[\text{1}H NMR (200 MHz, CDCl}_3, 20 °C, TMS):} \]

\[ \delta = 3.60 (s, 2H), 3.69 (s, 4H), 6.93 (ddd, 3J(H,H) = 7.8 Hz, 4J(H,H) = 2.2 Hz, 4J(H,H) = 1.0 Hz, 1H), 7.03 (s, 1H), 7.17 (d, 2J(H,H) = 7.7 Hz, 1H), 7.34 (t, 3J(H,H) = 7.7 Hz, 1H), 7.52 (t, 3J(H,H) = 7.9 Hz, 2H), 7.74 (d, 3J(H,H) = 7.6 Hz, 2H), 8.11 (ddd, 3J(H,H) = 8.1 Hz, 4J(H,H) = 2.2 Hz, 4J(H,H) = 1.0 Hz, 2H), 8.22 ppm (s, 2H) ; \]

\[ \text{[\text{13}C NMR (50 MHz, CDCl}_3, 20 °C):} \]

\[ \delta = 57.5 (2\times t), 58.0 (t), 118.1 (d), 119.2 (d), 122.5 (2\times d), 123.5 (2\times d), 125.2 (d), 129.6 (2\times d), 130.1 (d), 134.7 (2\times d), 140.36 (s), 140.38 (s), 141.0 (2\times s), 148.4 ppm (2\times s); \]

\[ \text{IR (Nujol): } \nu = 2110 (vs), 1586 (w), 1531 (vs), 1348 (vs), 1282 (s), 1245 (w), 1199 (w), 1163 (w), 1126 (w), 1080 (w), 974 (w), 877 (w), 820 (w), 809 (m), 791 (w), 740 (s); \]

\[ \text{MS (70 eV, EI): } m/z (%): 418 (28) [M+], 391 (30), 390 (72), 373 (42), 284 (54), 268 (43), 254 (53), 165 (24), 163 (25), 151 (27), 121 (24), 120 (51), 107 (89), 105 (38), 104 (53), 89 (93), 77 (56); \]

\[ \text{elemental analysis calcd (% for } C_{21}H_{18}N_6O_4(418.4): C 60.28, H 4.34, N 20.09; found: C 60.22, H 4.47, N 20.18.} \]

Bis(3-nitrobenzyl)(3-aminobenzyl)amine (10): PMe\(_3\) in toluene (1.0 M; 3.6 mL; 3.6 mmol) was slowly added at 0 °C to a solution of 9 (1.00 g, 2.4 mmol) in freshly distilled THF (30 mL) under N\(_2\). The reaction mixture was then stirred at this temperature for 30 min. Then, H\(_2\)O (15 mL) was added and the reaction mixture stirred at 20 °C for 16 h. After removal of the organic solvent, H\(_2\)O (20 mL) was added and the aqueous phase extracted with CH\(_2\)Cl\(_2\) (3×20 mL). The combined extracts were dried over MgSO\(_4\), the solvent evaporated under reduced pressure and the residue purified by silica-gel chromatography eluting with 1:1
AcOEt/hexanes (Rf = 0.39); 96% yield (yellow oil); 1H NMR (200 MHz, CDCl3, 20 °C, TMS): δ = 3.50 (s, 2H), 3.67 (s, 4H), 3.74 (br s, 2H), 6.59 (d, 3J(H,H) = 7.2 Hz, 1H), 6.72 (s, 1H), 6.76 (d, 3J(H,H) = 8.6 Hz, 1H), 7.14 (t, 3J(H,H) = 7.6 Hz, 1H), 7.49 (t, 3J(H,H) = 8.0 Hz, 2H), 7.73 (d, 3J(H,H) = 7.6 Hz, 2H), 8.08 (d, 3J(H,H) = 7.2 Hz, 2H), 8.24 ppm (br s, 2H); 13C NMR (50 MHz, CDCl3, 20 °C): δ = 57.4 (2×t), 58.4 (t), 114.3 (d), 115.3 (d), 119.0 (d), 122.3 (2×d), 123.5 (2×d), 129.4 (2×d), 134.7 (2×d), 139.4 (s), 141.4 (2×s), 146.8 (s), 148.3 ppm (2×s); IR (Neat): ν~ = 3465 (s), 3387 (s), 1622 (s), 1533 (vs), 1351 (vs), 1320 (m), 1297 (m), 1245 (w), 1162 (w), 1124 (w), 981 (w), 873 (w), 806 (m), 790 (w), 735 (s), 697 (s), 674 (s) cm⁻¹; MS (70 eV, EI): m/z (%): 393 (36) [M⁺+1], 392 (47) [M⁺], 136 (79), 120 (28), 108 (71), 107 (96), 106 (100), 90 (83), 89 (57), 79 (53), 78 (40), 77 (49); elemental analysis calcd (%) for C21H20N4O4 (392.4): C 64.28, H 5.14, N 14.28; found: C 64.63, H 5.50, N 14.44.

Bis(3-nitrobenzyl){3-['N'-(4-butylphenyl)ureido]benzyl}amine (11). To a solution of 10 (0.66 g, 1.67 mmol) in dry CH2Cl2 (20 mL) 4-n-butylphenyl isocyanate (0.30 g, 1.67 mmol) was added under N2. After stirring at 20 °C for 24 h the solvent was removed under reduced pressure and the residue purified by silica-gel chromatography eluting with 3:7 AcOEt/hexanes (Rf = 0.11); 97% yield; colorless prisms (an analytical sample was obtained by recrystallization from 1:1 CH2Cl2/Et2O). M.p. 132-133 °C; 1H NMR (401 MHz, CDCl3, 20 °C, TMS): δ = 0.87 (t, 3J(H,H) = 7.3 Hz, 3H), 1.27 (sext, 3J(H,H) = 7.3 Hz, 2H), 1.46 (quint, 3J(H,H) = 7.2 Hz, 2H), 2.44 (t, 3J(H,H) = 7.6 Hz, 2H), 3.39 (s, 2H), 3.52 (s, 4H), 6.95-6.99 (m, 4H), 7.09-7.13 (m, 3H), 7.40 (t, 3J(H,H) = 7.9 Hz, 2H), 7.44 (s, 1H), 7.55 (s, 1H), 7.63 (d, 3J(H,H) = 7.6 Hz, 2H), 7.68 (s, 1H), 8.00 (dd, 3J(H,H) = 8.0 Hz, 4J(H,H) = 1.4 Hz, 2H), 8.13 ppm (s, 2H); 13C NMR (101 MHz, CDCl3, 20 °C): δ = 14.0 (q), 22.3 (t), 33.6 (t), 35.0 (t), 57.2 (2×t), 58.2 (t), 119.1 (d), 120.6 (d), 121.1 (2×d), 122.3 (2×d), 123.4 (2×d), 123.6 (d), 129.0 (2×d), 129.2 (d), 129.4 (2×d), 134.8 (2×d), 135.5 (s), 138.70 (s), 138.74 (s), 139.2 (s), 141.3 (2×s), 148.3 (2×s), 154.2 ppm (s); IR (Nujol): ν~ = 3323 (s), 1656 (s), 1596 (s), 1530 (vs), 1351 (vs), 1311 (s), 1242 (s), 1218 (s), 1165 (m), 1126 (m), 1082 (m), 973 (w), 893 (w), 804 (w), 741 (s) cm⁻¹; MS (FAB⁺): m/z (%): 568 (100) [M⁺+1], 567 (46) [M⁺], 566 (65), 550 (44), 281 (43), 221 (31), 149 (46), 147 (80), 133 (45), 132 (95), 120 (47), 109 (63); elemental analysis calcd (%) for C32H30N4O4 (567.7): C 67.71, H 5.86, N 12.34; found: C 67.76, H 5.94, N 12.46.

Bis(3-aminobenzyl){3-['N'-(4-butylphenyl)ureido]benzyl}amine (12): To a solution of 11 (0.82 g, 1.5 mmol) in freshly distilled THF (25 mL), PtO2 (0.40 g, 1.8 mmol) was added and the reaction mixture stirred at 20 °C for 16 h under H2. After filtration over a pad of celite, which was further washed with THF (2×5 mL), the solvent was removed under reduced pressure and the residue was purified by silica-gel chromatography eluting with 4:1 AcOEt/hexanes (Rf = 0.34); 75% yield; colorless prisms (an analytical sample was obtained
by recrystallization from 1:3 CHCl₃/n-pentane). M.p. 150-151 °C; ¹H NMR (401 MHz, CDCl₃, 20 °C, TMS): δ = 0.88 (t, ³J(H,H) = 7.3 Hz, 3H), 1.27 (sext, ³J(H,H) = 7.4 Hz, 2H), 1.48 (quint, ³J(H,H) = 7.7 Hz, 2H), 2.45 (t, ³J(H,H) = 7.4 Hz, 2H), 3.37 (s, 6H), 3.51 (br s, 4H), 6.47 (d, ³J(H,H) = 7.5 Hz, 2H), 6.71 (d, ³J(H,H) = 7.5 Hz, 2H), 6.75 (s, 2H), 6.94-7.10 (m, 9H), 7.40-7.47 (m, 2H), 7.54 ppm (br s, 1H); ¹³C NMR (101 MHz, CDCl₃, 20 °C): δ = 14.0 (q), 22.4 (t), 33.7 (t), 35.0 (t), 57.6 (t), 57.8 (2×t), 113.9 (2×d), 115.7 (2×d), 118.8 (d), 119.3 (2×d), 120.7 (d), 120.9 (2×d), 123.8 (d), 128.7 (d), 128.9 (2×d), 129.0 (2×d), 135.8 (s), 138.4 (2×s), 140.8 (s), 140.9 (2×s), 146.4 (2×s), 154.2 ppm (s); IR (Nujol): ν = 3350 (vs), 3204 (vs), 1665 (s), 1599 (vs), 1550 (vs), 1515 (vs), 1314 (s), 1248 (s), 1167 (m), 1123 (w), 873 (w), 784 (m), 701 (m) cm⁻¹; MS (FAB⁺): m/z (%): 508 (97) [M⁺+1], 506 (59), 401 (84), 281 (33), 221 (40), 211 (59), 207 (44), 147 (100), 133 (55), 132 (68), 121 (47), 120 (48), 109 (61); elemental analysis calcd (%) for C₃₂H₃₇N₅O (507.7): C 75.71, H 7.35, N 13.79; found: C 75.45, H 7.70, N 13.88.
Preparation of bis(2-amino-5-chlorobenzyl)(3-aminopropyl)amine (14). PMe₃ in THF (1.0 M; 3.5 mL; 3.5 mmol) was slowly added at 0 °C to a solution of 13[3] (0.23 g, 0.5 mmol) in freshly distilled THF (20 mL) under N₂. The reaction mixture was then stirred at this temperature for 5 h. Then, H₂O (18 mL) was added and the reaction mixture was stirred at 20 °C for 18 h. After that, more H₂O (50 mL) was added and the aqueous phase extracted with CH₂Cl₂ (3×50 mL). The combined extracts were dried over MgSO₄, the solvent evaporated under reduced pressure, and the residue purified by silica-gel chromatography eluting with 9:1 EtOH/NH₃(aq) (R_f = 0.40); 98% yield. Colorless oil; ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): δ = 1.67 (quint, ³J(H,H) = 6.7 Hz, 2H), 2.44 (t, ³J(H,H) = 6.9 Hz, 2H), 2.61 (t, ³J(H,H) = 6.7 Hz, 2H), 3.41 (s, 4H), 4.20 (br s, 6H), 6.52 (d, ³J(H,H) = 8.3 Hz, 2H), 6.98-7.03 ppm (m, 4H); ¹³C NMR (101 MHz, CDCl₃, 20 °C): δ = 29.8 (t), 40.3 (t), 51.7 (t), 57.3 (t), 116.7 (d), 122.3 (s), 123.8 (s), 128.5 (d), 130.9 (d), 144.5 (s); IR (Neat): ν= 3449 (s), 3341 (s), 3206 (s), 1622 (vs), 1425 (s), 1293 (s), 1211 (m), 1152 (m), 1118 (m), 911 (m), 882 (m), 821 (m), 738 (s) cm⁻¹.
Figure S1. $^1$H NMR spectra (25 °C) of: a) triurea 3a in [D$_6$]DMSO (300 MHz), b) triurea 1a in [D$_6$]DMSO (400 MHz), c) triurea 3a in CDCl$_3$ (300 MHz) and d) triurea 1a in CDCl$_3$ (400 MHz). Residual peaks of water and solvent have been labelled by an asterisk (*) or a circle (o), respectively.
Figure S2. $^1$H NMR spectra (25 °C) of: a) triurea 4a in [D$_6$]DMSO (400 MHz), b) triurea 1b in [D$_6$]DMSO (300 MHz), c) triurea 4a in CDCl$_3$ (400 MHz) and d) triurea 1b in CDCl$_3$ (300 MHz). Residual peaks of water and solvent have been labelled by an asterisk (*) or a circle (o), respectively.
Figure S3. High-frequency regions of the $^1$H NMR spectra (400 MHz, CDCl$_3$, 25 °C) of the triureas: a) 4a, b) 4b and c) 4c, where the NH’s bearing the pendant R$^1$ and R$^2$ groups resonate.
Figure S4. $^1$H NMR spectra (25 °C) of: a) triurea 5a in [D$_6$]DMSO (400 MHz), b) triurea 2 in [D$_6$]DMSO (300 MHz), c) triurea 5a in CDCl$_3$ (400 MHz) and d) triurea 2 in CDCl$_3$ (400 MHz). Residual peaks of water and solvent have been labelled by an asterisk (*) or a circle (o), respectively.
Figure S5. High-frequency region of the $^1$H NMR spectrum of 5a (400 MHz, CD$_2$Cl$_2$, 25 °C), where the NH’s bearing the pendant aryl groups resonate. In CD$_2$Cl$_2$, 5a·5a@CD$_2$Cl$_2$ is the only species.
Figure S6. ESI-MS (CHCl$_3$; 1% AcOH) of triurea 5a.
Figure S7. ESI-MS (CHCl₃; 1% AcOH) of triurea 6.
References