Electronic Supplementary Material (ESI) for RSC Advances

For Supporting Information

Carbosilane Cationic Dendrimers Synthesized by Thiol-Ene Click Chemistry and Their Use as Antibacterial Agents

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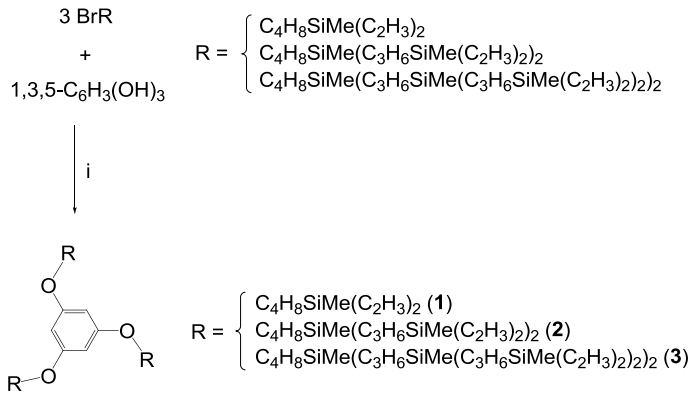
S1. Synthesis of vinyl dendrimers.



Scheme S1. Synthesis of vinyl dendrimers $G_nO_3V_m$ **1-3**; i) K_2CO_3, 18C6, 90 ºC.

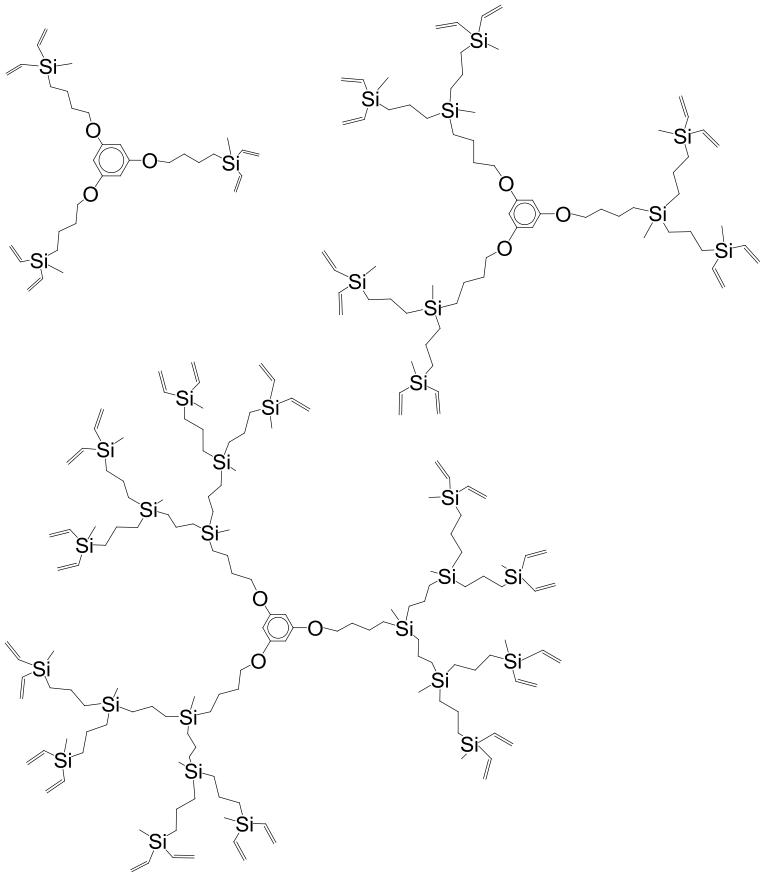


Figure S1. Drawing of vinyl terminated dendrimers **1-3**.

S2. pH titration of dendrimer 4.

We have performed a potentiometric titration in order to calculate the acid constant of the primary amines, as well as the pH at which this dendrimer precipitates. From this study, we have found that the pK_a of this compound is 9.36 represented by a small peak that could be detected in the first derivative, but that

had a very low intensity due to the coincidence of this point with the precipitation of the compound due to deprotonation of the first amines. This value is coherent with the theoretical approach in which six different values of pK_a oscillating from 9.29 to 10.47 can be calculated and is coherent with the fact that the deprotonation of the first amines will conduct to the precipitation of the whole skeleton.

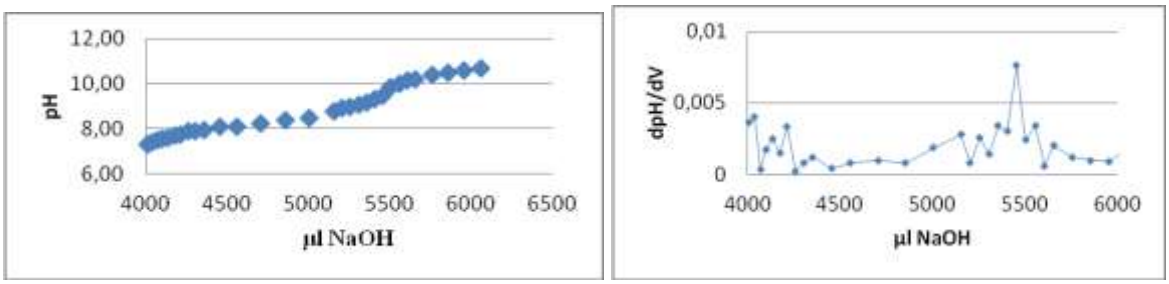


Figure S2. Potentiometric titration for **4** (left) and first derivative ot the titration curve (right).

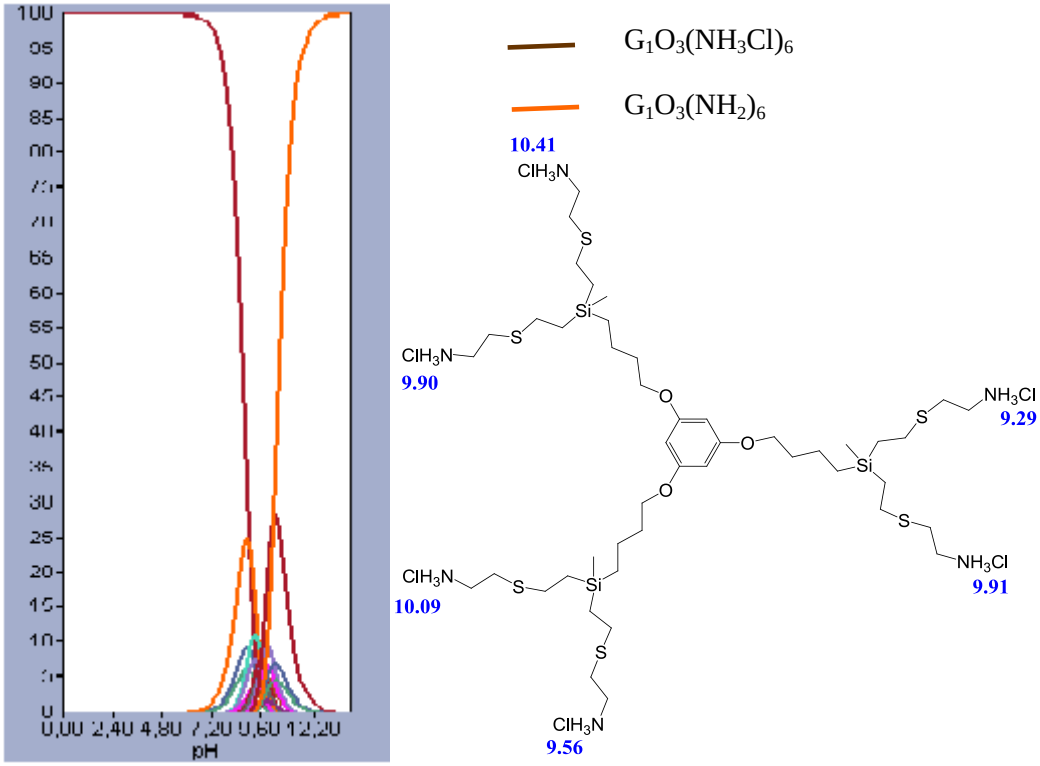


Figure S3. Theoretical peaks for the potentiometric titration of **4** (obtained with the chemical terms evaluator from Marvin).

S3. Experimental Section

S3.1. General Considerations. All reactions were carried out under inert atmosphere and solvents were purified from appropriate drying agents when necessary (THF). NMR spectra were recorded on a

Varian Unity VXR-300 (300.13 (^{1}H), 75.47 (^{13}C) MHz) or on a Bruker AV400 (400.13 (1H), 100.60 (^{13}C), 40.56 (^{15}N), 79.49 (^{29}Si) MHz). Chemical shifts (δ) are given in ppm. ^{1}H and ^{13}C resonances were measured relative to internal deuterated solvent peaks considering TMS = 0 ppm, meanwhile ^{15}N and ^{29}Si resonances were measured relative to external MeNO and TMS, respectively. When necessary, assignment of resonances was done from HSQC, HMBC, COSY, TOCSY and NOESY NMR experiments. Elemental analyses were performed on a LECO CHNS-932. Mass Spectra were obtained from a Bruker Ultraflex III and an Agilent 6210. Compounds, $HS(CH_2)_2NH_2{\cdot}HCl$, $HS(CH_2)_2NMe_2{\cdot}HCl$, 2,2'-dimethoxy-2-phenylacetophenone (DMPA), MeI (Aldrich) and K_2CO_3 (Panreac) were obtained from commercial sources. Compounds $G_nO_3(NMe_3I)_m$[1] were synthesized as published.

S3.2. Synthesis of compounds.

$G_2O_3V_{12}$ (2). Following the procedure described for compound **4**, compound **2** was obtained as a colorless oil (1.03 g, 90 %) from the reaction of $1,3,5\text{-}(HO)_3C_6H_3$ (0.061 g, 0.49 mmol), BrG_2V_4 (1.25 g, 2.73 mmol), K_2CO_3 (2.26 g, 16.38 mmol) and 18-C-6 (0.22 g, 0.82 mmol) during 7 days. Data for **2**: NMR ($CDCl_3$):^{1}H-NMR: δ -0.09 (s, 9 H, Si*Me*), 0.13 (s, 18 H, Si*Me*C_2H_3), 0.52 (m, 18 H, $OCH_2CH_2CH_2C\mathit{H}_2Si$ and $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$), 0.69 (m, 12 H, $C\mathit{H}_2SiC_2H_3$), 1.46 (m, 18 H, $OCH_2CH_2C\mathit{H}_2CH_2Si$ and $SiCH_2C\mathit{H}_2CH_2Si$), 1.76 (m, 6 H, $OCH_2C\mathit{H}_2CH_2CH_2Si$), 3.88 (t, J = 6.6 Hz, 6 H, $OC\mathit{H}_2CH_2CH_2CH_2Si$), 5.70 and 6.06 (m, 39 H, $SiC\mathit{H}C\mathit{H}_2$ and $C_6\mathit{H}_3O_3$). ^{13}C-NMR: δ -5.2 y -5.1 (Si*Me*), 13.8 ($OCH_2CH_2CH_2\mathit{C}H_2Si$), 18.3 – 18.7 ($SiC\mathit{H}_2C\mathit{H}_2C\mathit{H}_2Si$), 20.5 ($OCH_2CH_2\mathit{C}H_2CH_2Si$), 33.2 ($OCH_2\mathit{C}H_2CH_2CH_2Si$), 67.6 ($OCH_2CH_2CH_2CH_2Si$), 93.6 ($C_6H_3O_3$; *C*-H), 132.6 ($SiCHCH_2$), 137.2 ($SiCHCH_2$), 160.9 ($C_6H_3O_3$; *C*-O). ^{29}Si-NMR: δ 1.8 (G_1–*Si*), -13.4 (G_2-*Si*CHCH2). Anal. Calc. $C_{69}H_{126}O_3Si_9$ (1256.51 g/mol): C, 65.69; H, 10.21; Exp.: C, 65.12; H, 9.64. MS: [M + H]+= 1255.80 uma (calcd. = 1255.77 uma).

$G_3O_3V_{24}$ (3). Following the procedure described for compound **4**, compound **3** was obtained as a colorless oil (1.84 g, 85 %) from the reaction of $1,3,5\text{-}(HO)_3C_6H_3$ (0.10 g, 0.85 mmol), BrG_3V_8 (2.31 g, 2.55 mmol), K_2CO_3 (2.11 g, 15.28 mmol) and 18-C-6 (0.20 g, 0.76 mmol) during 20 days. Data for **3**:

NMR ($CDCl_3$): ^{1}H-NMR: δ -0.12 y -0.09 (s, 24 H, Si*Me*), 0.10 (s, 36 H, Si*Me*C_2H_3), 0.52 (m, 54 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 0.68 (m, 24 H, $CH_2SiC_2H_3$), 1.33 (m, 42 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 1.75 (m, 6 H, $OCH_2CH_2CH_2CH_2Si$), 3.88 (t, J = 6.6 Hz, 6 H, $OCH_2CH_2CH_2CH_2Si$), 5.67 and 6.05 (m, 75 H, $SiCHCH_2$ and $C_6H_3O_3$). ^{13}C-NMR: δ -5.2 - -5.0 (Si*Me*), 13.9 ($OCH_2CH_2CH_2CH_2Si$), 17.7 – 18.9 ($SiCH_2CH_2CH_2Si$), 20.5 ($OCH_2CH_2CH_2CH_2Si$), 33.3 ($OCH_2CH_2CH_2CH_2Si$), 67.7 ($OCH_2CH_2CH_2CH_2Si$), 93.6 ($C_6H_3O_3$; *C*-H), 132.6 ($SiCHCH_2$), 137.2 ($SiCHCH_2$), 160.9 ($C_6H_3O_3$; *C*-O). ^{29}Si-NMR: δ 1.6 (G_1–*Si*), 1.0 (G_2–*Si*), -13.3 (G_3-*Si*$CHCH_2$). Anal. Calc. $C_{147}H_{270}O_3Si_{21}$ (2603.45 g/mol): C, 65.05; H, 10.45; Exp.: C, 63.52; H, 9.93. MS: [M + H]+= 2600.60 uma (calcd. = 2600.62 uma).

$G_2O_3(SNH_3Cl)_{12}$ (5). This compound was prepared from **2** (0.200 g, 0.16 mmol), cysteamine hydrochloride (0.240 g, 2.10 mmol), DMPA (0.053 g, 0.21 mmol), and a 1:2 THF/methanol solution (3 ml) using the preparative procedure for **4**, except the purification which was performed as a nanofiltration in which a MW = 1000 membrane was used. The pure product was dried in vacuo to afford **5** as a white solid (0.220 g, 54%). Data for **5**: NMR (DMSO): ^{1}H-NMR: δ -0.24 (s,9 H, Si*Me*), -0.10 (s, 18 H, $SiMe_2$), 0.41 (t, 12 H, $SiCH_2CH_2CH_2Si$), 0.43 (t, 12 H, $SiCH_2CH_2CH_2Si$), 0.50 (t, 6 H, $OCH_2CH_2CH_2CH_2SiMe$), 0.76 (t, 24 H, $-SiCH_2CH_2S$), 1.21 (m, 12 H, $SiCH_2CH_2CH_2Si$), 1.31 (m, 6 H, $OCH_2CH_2CH_2CH_2SiMe$), 1.58 (m, 6 H, $OCH_2CH_2CH_2CH_2SiMe$), 2.50 (t, 24 H, $SiCH_2CH_2S$), 2.70 (t, 24 H, $SCH_2CH_2NH_3^+$), 3.03 (t, 24 H, $SCH_2CH_2NH_3^+$), 3.97 (t, 6 H, $OCH_2CH_2CH_2CH_2SiMe$), 6.07 (s, 3 H, $C_6H_3O_3$), 8.10 (s, 3 H, $-NH_3^+$). ^{13}C-NMR: δ -5.2 (Si*Me*), 13.2 ($OCH_2CH_2CH_2CH_2SiMe$), 14.0 ($SiCH_2CH_2S$), 17.9 ($SiCH_2CH_2CH_2Si$), 19.9 ($OCH_2CH_2CH_2CH_2SiMe$), 26.3 ($SiCH_2CH_2S$), 27.7 ($SCH_2CH_2NH_3^+$), 32.5 ($OCH_2CH_2CH_2CH_2SiMe$), 38.4 ($SCH_2CH_2NH_3^+$), 67.0 ($OCH_2CH_2CH_2CH_2SiMe$), 93,6 ($C_6H_3O_3$, *C*-H), 160.4 ($C_6H_3O_3$, *C*-O). ^{15}N-NMR: δ -342.5 ($-NH_3^+$). ^{29}Si-NMR: 1.8 (G_1-SiMe), 2.2 (G_2-SiMe).). ESI: (2610.84 g/mol) q=2 (1090.57 $[M-10HCl-2Cl^-]^{2+}$), q=3 (727.39 $[M-9HCl-3Cl^-]^{3+}$), q=4 (545.80 $[M-4HCl-4Cl^-]^{4+}$). Anal. Calc.: $C_{93}H_{222}Cl_{12}N_{12}O_3S_{12}Si_9$ (2619.82 g/mol): C, 42.64; H, 8.54; N, 6.42; S, 14.69. *Exp.:* C, 41.03; H, 8.30; N, 6.25; S, 14.32.

$G_3O_3(SNH_3Cl)_{24}$ (6). This compound was prepared from **3** (0.200 g, 0.08 mmol), cysteamine hydrochloride (0.230 g, 2.00 mmol), DMPA (0.051 g, 0.20 mmol), and a 1:2 THF/methanol solution (3 ml) using the preparative procedure for **5**. The pure product was dried in vacuo to afford **6** as a white solid (0.170 g, 40%). Data for **6**: NMR (DMSO): ^{1}H-NMR: δ -0.18 (s, 9 H, Si*Me*), -0.15 (s, 18 H, Si*Me*), -0.07 (s, 36 H, Si*Me*), 0.48 and 0.55 (m, 54 H, $OCH_2CH_2CH_2C\mathit{H_2}Si$ and $SiC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.83 (m, 72 H, $SiC\mathit{H_2}CH_2S$), 1.26 (m, 48 H, $OCH_2C\mathit{H_2}C\mathit{H_2}CH_2Si$ and $SiCH_2C\mathit{H_2}CH_2Si$), 2.54 (t, 48 H, $SiCH_2C\mathit{H_2}S$), 2.73 (t, 48 H, $SC\mathit{H_2}CH_2NH_3^+$), 3.06 (t, 48 H, $SCH_2C\mathit{H_2}NH_3^+$), 3.88 (t, 6 H, $OC\mathit{H_2}CH_2CH_2CH_2SiMe$), 8.1 (s, 3 H, $-NH_3^+$). ^{13}C-NMR: -5.2 (Si*Me*), 13.2 ($OCH_2CH_2CH_2\mathit{C}H_2SiMe$), 13.5 ($SiCH_2CH_2S$), 17.7 ($SiCH_2CH_2CH_2Si$), 19.5 ($OCH_2CH_2CH_2CH_2SiMe$), 25.8 ($SiCH_2CH_2S$), 27.2 ($SCH_2CH_2NH_3^+$), 32.0 ($OCH_2CH_2CH_2CH_2SiMe$), 38.4 ($SCH_2CH_2NH_3^+$). ^{15}N-NMR: δ -342.5 ($-NH_3^+$). ^{29}Si-NMR*:* 1.8 (G_1-SiMe), 1.0 (G_2-SiMe) 2.2 G_3-SiMe). ESI: (5311.77 g/mol) q=5 (890.55 $[M-19HCl-5Cl^-]^{5+}$). Anal. Calc.*:* $C_{189}H_{462}Cl_{24}N_{24}O_3S_{24}Si_{21}$ (5330.08 g/mol): C, 42.59; H, 8.74; N, 6.31; S, 14.44. Exp.: C, 40.76; H, 8.67; N, 6.43; S, 13.34.

$G_2O_3(SNMe_2HCl)_{12}$ (**8**). This compound was prepared from **2** (0.503 g, 0.40 mmol), 2-(Dimethylamino)ethanethiol hydrochloride (0.788 g, 5.56 mmol), DMPA (0.123 g, 0.48 mmol), and a 1:2 THF/methanol solution (3 ml) using the preparative procedure for **5**. The pure product was dried in vacuo to afford **8** as a white solid (0.827 g, 70%). Data for **8**: NMR (DMSO): ^{1}H-NMR: δ -0.07 (s, 9 H, Si*Me*), 0.02 (s, 18 H, Si*Me*), 0.58 (m, 30 H $SiC\mathit{H_2}CH_2C\mathit{H_2}Si$ and $OCH_2CH_2CH_2C\mathit{H_2}Si$), 0.86 (t, J = 8.1 Hz, 24 H, $SiC\mathit{H_2}CH_2S$), 1.30 (m, 18 H $SiCH_2C\mathit{H_2}CH_2Si$ and $OCH_2CH_2C\mathit{H_2}CH_2Si$), 1.65 (m, 6 H, $OCH_2C\mathit{H_2}CH_2CH_2Si$), 2.62 (t, 8.3 Hz, 24 H, $SiCH_2C\mathit{H_2}S$), 2.74 (s, 72 H, $SCH_2CH_2N\mathit{Me_2}H^+$), 2.85 (m, 24 H, $SC\mathit{H_2}CH_2NMe_2H^+$), 3.21 (m, 24 H, $SCH_2C\mathit{H_2}NMe_2H^+$), 3.89 (m, 6 H, -O-$C\mathit{H_2}$), 6.01 (s, 3 H, $C_6\mathit{H}_3O_3$), 10.68 (bs, 12 H, $-NMe_2\mathit{H}^+$). ^{13}C-NMR: δ -5.7 y -5.4 (Si*Me*), 12.8 ($OCH_2CH_2CH_2\mathit{C}H_2Si$), 13.5 ($SiCH_2CH_2S$), 17.2 – 17.6 ($SiCH_2CH_2CH_2Si$), 19.5 ($OCH_2CH_2CH_2CH_2Si$), 24.1 ($SCH_2CH_2NMe_2H^+$), 26.0 ($SiCH_2CH_2S$), 32.1 ($OCH_2CH_2CH_2CH_2Si$), 41.3 ($SiCH_2CH_2N\mathit{Me_2}H^+$), 55.2 ($SCH_2CH_2NMe_2H^+$), 66.5 ($OCH_2$), 93.1 ($C_6H_3O_3$; *C*-H), 160.0 ($C_6H_3O_3$; *C*-O). ^{15}N-NMR: δ -338.3 ($-NMe_2H^+$). ^{29}Si-NMR: δ 1.7 (G_1–

*Si*Me), 2.4 (G_2–*Si*Me). Anal. Calcd. $C_{117}H_{270}Cl_{12}N_{12}O_3S_{12}Si_9$ (2956.46 g/mol): C, 47.53; H, 9.21; N, 5.69; S, 13.01; Found: C, 47.29; H, 5.69; N, 5.20; S, 12.21.

$G_3O_3(SNMe_2HCl)_{24}$ (**9**). This dendrimer was prepared from **3** (0.252 g, 0.10 mmol), 2-(Dimethylamino)ethanethiol hydrochloride (0.381 g, 2.69 mmol), DMPA (0.060 g, 0.23 mmol), and a 1:2 THF/methanol solution (3 ml) using the preparative procedure for **5**. The pure product was dried in vacuo to afford **9** as a pale yellow solid (0.414 g, 71%). Data for **9**: NMR (DMSO): ^{1}H-NMR: δ -0.09 (s, 27 H, Si*Me*), 0.02 (s, 36 H, Si*Me*), 0.57 (m, 78 H Si$CH_2CH_2CH_2$Si and O$CH_2CH_2CH_2CH_2$Si), 0.86 (m, 48 H, SiCH_2CH_2S), 1.30 (m, 42 H Si$CH_2CH_2CH_2$Si and O$CH_2CH_2CH_2CH_2$Si), 1.65 (m, 6 H, O$CH_2CH_2CH_2CH_2$Si), 2.60 (t, J = 8.3 Hz, 48 H, SiCH_2CH_2S), 2.74 (s, 144 H, SCH_2CH_2N*Me*$_2H^+$), 2.88 (m, 48 H, S$CH_2CH_2NMe_2H^+$), 3.22 (m, 48 H, S$CH_2CH_2NMe_2H^+$), 3.89 (m, 6 H, OCH_2), 6.01 (s, 3 H, $C_6H_3O_3$), 10.68 (bs, 24 H, -NMe_2H^+). ^{13}C-NMR: δ -5.7 - -5.2 (Si*Me*), 12.8 (O$CH_2CH_2CH_2CH_2$Si), 13.6 (SiCH_2CH_2S), 17.3 – 17.8 (Si$CH_2CH_2CH_2$Si), 19.5 (O$CH_2CH_2CH_2CH_2$Si), 24.2 (S$CH_2CH_2NMe_2H^+$), 26.0 (SiCH_2CH_2S), 41.3 (SiCH_2CH_2N*Me*$_2H^+$), 55.2 (S$CH_2CH_2NMe_2H^+$). ^{15}N-NMR: -339.1 (-*N*Me_2H^+). ^{29}Si-NMR: δ 1.0 (G_2–*Si*Me), 2.4 (G_3–*Si*Me). Anal. Calcd. $C_{237}H_{558}Cl_{24}N_{24}O_3S_{24}Si_{21}$ (6003.35 g/mol): C, 47.42; H, 9.37; N, 5.60; S, 12.82; Found: C, 46.64; H, 9.03; N, 5.20; S, 11.96.

$G_2O_3(SNMe_2)_{12}$ (**11**) Compound **11** was prepared from **8** (0.827 g, 0.28 mmol), NaOH (0.168 g, 4.20 mmol), and a 1:2 H_2O/$CHCl_3$ (1:1, 20 ml) mixture using the preparative procedure for **10** to get **11** a pale yellow oil (0.705, 100%). Data for **11**: NMR ($CDCl_3$): ^{1}H-NMR: δ -0.08 (s, 9 H, Si*Me*), -0.01 (s, 18 H, Si*Me*), 0.56 (m, 30 H Si$CH_2CH_2CH_2$Si and O$CH_2CH_2CH_2CH_2$Si), 0.88 (t, J = 8.6 Hz, 24 H, SiCH_2CH_2S), 1.27 (m, 12 H Si$CH_2CH_2CH_2$Si), 1.39 (m, 6 H, O$CH_2CH_2CH_2CH_2$Si), 1.65 (m, 6 H, O$CH_2CH_2CH_2CH_2$Si), 2.23 (s, 72 H, SCH_2CH_2N*Me*$_2$), 2.48 (m, 24 H, S$CH_2CH_2NMe_2$), 2.52 (m, 24 H, SiCH_2CH_2S), 2.57 (m, 24 H, S$CH_2CH_2NMe_2$), 3.85 (t, J = 6.3 Hz, 6H, OCH_2), 6.03 (s, 3 H, $C_6H_3O_3$). ^{13}C-NMR: δ -5.3 (Si*Me*), -5.1 (Si*Me*), 13.3 (O$CH_2CH_2CH_2CH_2$Si), 14.6 (SiCH_2CH_2S), 18.3 – 18.7 (Si$CH_2CH_2CH_2$Si), 20.5 (O$CH_2CH_2CH_2CH_2$Si), 27.7 (S$CH_2CH_2NMe_2$), 29.6 (SiCH_2CH_2S), 33.0 (O$CH_2CH_2CH_2CH_2$Si), 45.2 (SiCH_2CH_2N*Me*$_2$), 59.1 (S$CH_2CH_2NMe_2$), 68.0 (OCH_2), 93.7 ($C_6H_3O_3$; *C*-H), 160.8 ($C_6H_3O_3$; *C*-O). ^{15}N-

NMR: δ -352.1 (-*N*Me$_2$). ^{29}Si-NMR: δ 1.6 (G$_1$–*Si*Me), 2.0 (G$_2$–*Si*Me). Anal. Calcd. $C_{117}H_{258}N_{12}O_3S_{12}Si_9$ (2518.93 g/mol): C, 55.79; H, 10.32; N, 6.67; S, 15.28; Found: C, 54.79; H, 9.62; N, 6.56; S, 14.58.

G$_3$O$_3$(SNMe$_2$)$_{24}$ (**12**). Dendrimer **12** was prepared from **9** (0.414 g, 0.07 mmol), NaOH (0.083 g, 2.07 mmol), and a 1:2 $H_2O/CHCl_3$ (1:1, 20 ml) mixture using the preparative procedure for **8** to get **12** a pale yellow oil (0.354, 100%). Data for **12**: NMR ($CDCl_3$): ^{1}H-NMR: δ -0.10 (s, 27 H, Si*Me*), 0.00 (s, 36 H, Si*Me*), 0.53 (m, 78 H SiC*H*$_2$CH$_2$C*H*$_2$Si and OCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.88 (t, J = 8.6 Hz, 48 H, SiC*H*$_2$CH$_2$S), 1.27 (m, 36 H SiCH$_2$C*H*$_2$CH$_2$Si), 1.39 (m, 6 H, OCH$_2$CH$_2$C*H*$_2$CH$_2$Si), 1.70 (m, 6 H, OCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.23 (s, 144 H, SCH$_2$CH$_2$N*Me*$_2$), 2.48 (m, 48 H, SCH$_2$C*H*$_2$NMe$_2$), 2.54 (m, 48 H, SiCH$_2$C*H*$_2$S), 2.60 (m, 48 H, SC*H*$_2$CH$_2$NMe$_2$), 3.85 (t, J = 6.3 Hz, 6 H, OC*H*$_2$), 6.03 (s, 3 H, C$_6$*H*$_3$O$_3$). ^{13}C-NMR: δ -5.3 (Si*Me*), -5.2 (Si*Me*), 13.3 (OCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 14.6 (Si*C*H$_2$CH$_2$S), 18.5 – 18.8 (Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 20.5 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si), 27.7 (S*C*H$_2$CH$_2$NMe$_2$), 29.8 (SiCH$_2$*C*H$_2$S), 33.0 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 45.4 (SiCH$_2$CH$_2$N*Me*$_2$), 59.3 (SCH$_2$*C*H$_2$NMe$_2$), 68.0 (O*C*H$_2$), 93.7 (C$_6$H$_3$O$_3$; *C*-H), 160.8 (C$_6$H$_3$O$_3$; *C*-O). ^{15}N-NMR: δ -352.1 (-*N*Me$_2$). ^{29}Si-NMR: δ 0.9 (G$_2$-*Si*Me), 2.0 (G$_3$–*Si*Me). Anal. Calcd. $C_{237}H_{534}N_{24}O_3S_{24}Si_{21}$ (5128.29 g/mol): C, 55.51; H, 10.50; N, 6.56; S, 15.01; Found: C, 55.06; H, 9.90; N, 6.55; S, 14.31.

G$_2$O$_3$(SNMe$_3$I)$_{12}$ (**14**). Dendrimer **14** was prepared using a similar method to that described for **13**, starting from **11** (0.148 g, 0.06 mmol) and MeI (0.04 ml, 0.70 mmol) to get **14** as a white solid (0.233 g, 94%). Data for **14**: NMR (DMSO): ^{1}H-NMR: δ -0.03 (s, 9 H, Si*Me*), 0.08 (s, 18 H, Si*Me*), 0.59 (m, 24 H, SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.68 (m, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.90 (m, 24 H, SiC*H*$_2$CH$_2$S), 1.36 (m, 18 H, OCH$_2$CH$_2$C*H*$_2$CH$_2$Si and SiCH$_2$C*H*$_2$CH$_2$Si), 1.71 (m, 6 H, OCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.67 (m, 24 H, SiCH$_2$C*H*$_2$S), 2.94 (m, 24 H, SC*H*$_2$CH$_2$NMe$_3^+$), 3.15 (s, 108 H, SCH$_2$CH$_2$N*Me*$_3^+$), 3.60 (m, 24 H, SCH$_2$C*H*$_2$NMe$_3^+$), 3.91 (t, 6 H, OC*H*$_2$), 6.02 (s, 3 H, C$_6$*H*$_3$O$_3$). ^{13}C-NMR: δ -5.6 (Si*Me*), 11.8 (OCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 13.6 (Si*C*H$_2$CH$_2$S), 17.2 – 19.6 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si and Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 23.1 (S*C*H$_2$CH$_2$NMe$_3^+$), 26.4 (SiCH$_2$*C*H$_2$S), 32.3 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 51.7 (SiCH$_2$CH$_2$N*Me*$_3^+$), 63.9 (SCH$_2$*C*H$_2$NMe$_3^+$), 66.9 (O*C*H$_2$), 93.4 (C$_6$H$_3$O$_3$; *C*-H), 160.7 (C$_6$H$_3$O$_3$; *C*-O). ^{15}N-NMR: δ -330.0 (-*N*Me$_3^+$). ^{29}Si-NMR: δ 1.8 (G$_1$–*Si*Me), 2.5 (G$_2$–*Si*Me). ESI: (4218.63 g/mol) q=2 (1982.54 [M-2I$^-$]$^{2+}$), q=3 (1279.40

[M-3I$^-$]$^{3+}$), q=4 (927.79 [M-4I$^-$]$^{4+}$), q=5 (716.86 [M-5I$^-$]$^{5+}$). Anal. Calcd. $C_{129}H_{294}I_{12}N_{12}O_3S_{12}Si_9$ (4222.20 g/mol): C, 36.70; H, 7.02; N, 3.98; S, 9.11; Found: C, 36.10; H, 6.80; N, 4.01; S, 7.31.

$G_3O_3(SNMe_3I)_{24}$ (15). Compound **15** was prepared using a similar method to that described for **13**, starting from **12** (0.186 g, 0.04 mmol) and MeI (0.05 ml, 0.87 mmol) to get **15** as a pale yellow solid (0.303 g, 98%). Data for **15**: NMR (DMSO): ^{1}H-NMR: δ -0.08 (s, 27 H, Si*Me*), 0.05 (s, 36 H, Si*Me*), 0.53 (m, 72 H, SiC*H*$_2$CH$_2$C*H*$_2$Si) 0.63 (m, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_2$Si), 0.86 (m, 48 H, SiC*H*$_2$CH$_2$S), 1.28 (m, 48 H, OCH$_2$CH$_2$C*H*$_2$CH$_2$Si and SiCH$_2$C*H*$_2$CH$_2$Si), 1.69 (m, 6 H, OCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.65 (m, 48 H, SiCH$_2$C*H*$_2$S), 2.91 (m, 48 H, SC*H*$_2$CH$_2$NMe$_3^+$), 3.14 (s, 216 H, SCH$_2$CH$_2$N*Me*$_3^+$), 3.59 (m, 48 H, SCH$_2$C*H*$_2$NMe$_3^+$), 3.89 (t, 6 H, OC*H*$_2$), 6.02 (s, 3 H, C$_6$*H*$_3$O$_3$). ^{13}C-NMR: δ -6.0 - -5.5 (Si*Me*), 11.8 (OCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 13.9 (Si*C*H$_2$CH$_2$S), 17.0 – 19.0 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si and Si*C*H$_2$*C*H$_2$*C*H$_2$Si), 23.3 (S*C*H$_2$CH$_2$NMe$_3^+$), 26.5 (SiCH$_2$*C*H$_2$S), 31.4 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 51.8 (SiCH$_2$CH$_2$N*Me*$_3^+$), 64.0 (SCH$_2$*C*H$_2$NMe$_3^+$), 66.1 (O*C*H$_2$), 92.0 (C$_6$H$_3$O$_3$; *C*-H), 160.7 (C$_6$H$_3$O$_3$; *C*-O). ^{15}N-NMR: δ -330.0 (-*N*Me$_3^+$). ^{29}Si-NMR: δ 0.9 (G$_2$–*Si*Me), 2.3 (G$_3$–*Si*Me$_2$). ESI: (8527.35 g/mol) q=6 (1295.48 [M-6I$^-$]$^{6+}$), q=7 (1092.29 [M-7I$^-$]$^{7+}$). Found. $C_{261}H_{606}I_{24}N_{24}O_3S_{24}Si_{21}$ (8534.83 g/mol): C, 36.73; H, 7.16; N, 3.94; S, 9.02; Exp.: C, 36.44; H, 7.10; N, 4.02; S, 8.52.

$G_2O_3(NMe_2(CH_2CH_2OH)I)_{12}$ (17). Dendrimer **17** was prepared using a similar method to that described for **16**, starting from **11** (0.211 g, 0.08 mmol) and I(CH$_2$)$_2$OH (0.09 ml, 1.20 mmol) to get **17** as a brownish solid (0.338 g, 86 %). Data for **17**: NMR (DMSO): ^{1}H-NMR: δ -0.05 (m, 9 H, Si*Me*), 0.03 (s, 18 H, Si*Me*), 0.63-0.58 (m, 30 H, OCH$_2$CH$_2$CH$_2$C*H*$_2$Si and SiC*H*$_2$CH$_2$C*H*$_2$Si), 0.88 (t, 24 H, SiC*H*$_2$CH$_2$S); 1.37 (m, 18 H, OCH$_2$CH$_2$C*H*$_2$CH$_2$Si and SiCH$_2$C*H*$_2$CH$_2$Si), 1.65 (m, 6 H, OCH$_2$C*H*$_2$CH$_2$CH$_2$Si), 2.60 (t, 24 H, SiCH$_2$C*H*$_2$S), 2.96 (m, 24 H, SC*H*$_2$CH$_2$N$^+$), 3.11 (s, 72 H, -N*Me*$_2$CH$_2$CH$_2$OHI), 3.43 (m, 24 H, -NMe$_2$CH$_2$C*H*$_2$OHI), 3.58 (m, 24 H, SCH$_2$C*H*$_2$N$^+$), 3.85 (m, 30 H, OC*H*$_2$ and N$^+$C*H*$_2$CH$_2$OHI), 5.29 (s, 12 H, O*H*), 6,03 (s, 3 H, C$_6$*H*$_3$O$_3$). ^{13}C-NMR: δ -4.7 (Si*Me*), 14.6 (OCH$_2$CH$_2$CH$_2$*C*H$_2$Si), 18.4 (Si*C*H$_2$CH$_2$S), 20.5 (OCH$_2$CH$_2$*C*H$_2$CH$_2$Si and Si*C*H$_2$**C**H$_2$**C**H$_2$Si), 23.9 (S*C*H$_2$CH$_2$N$^+$), 27.2 (SiCH$_2$*C*H$_2$S), 31.1 (OCH$_2$*C*H$_2$CH$_2$CH$_2$Si), 51.2 (-N*Me*$_2$CH$_2$CH$_2$OHI), 55.4 (-NMe$_2$*C*H$_2$CH$_2$OHI), 64.1 (SCH$_2$*C*H$_2$N$^+$), 65.0 (-

$NMe_2CH_2CH_2OHI$), 67.5 (OCH_2), 93.7 ($C_6H_3O_3$; *C*-H), 160.9 ($C_6H_3O_3$; *C*-O). ^{15}N-NMR: δ -324.2 (-*N*$Me_2CH_2CH_2OH$).). ESI: (4682.92 g/mol) q=6 (636.93 $[M\text{-}6I^-]^{6+}$), q=8 (445.98 $[M\text{-}8I^-]^{8+}$). Anal. Calcd. $C_{148}H_{338}I_{12}N_{12}O_{15}S_{12}Si_9$ (4686.74 g/mol): C, 36.96; H, 6.99; N, 3.67; S, 8.40; Found: C, 36.68; H, 6.75; N, 3.60; S, 8.72.

$G_3O_3(NMe_2(CH_2CH_2OH)I)_{24}$ (18). Dendrimer **18** was prepared using a similar method to that described for **16**, starting from **11** (0.217 g, 0.09 mmol) and $I(CH_2)_2OH$ (0.10 ml, 1.22 mmol) to get **18** as a brownish solid (0.678 g, 85 %). Data for **18**: NMR (DMSO): ^{1}H-NMR: δ -0.08 (m, 9 H, Si*Me*), 0.03 (s, 54 H, Si*Me*), 0.61-0.54 (m, 78 H, $OCH_2CH_2CH_2CH_2Si$ and $OCH_2CH_2CH_2CH_2Si$), 0.84 (t, 48 H, $SiCH_2CH_2S$), 1.28 (m, 42 H, $OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$), 1.74 (m, 6 H, $OCH_2CH_2CH_2CH_2Si$), 2.63 (t, 48 H, $SiCH_2CH_2S$), 2.93 (m, 48 H, $SCH_2CH_2N^+$), 3.31 (s, 144 H, -$NMe_2CH_2CH_2OHI$), 3.46 (m, 48H, -$NMe_2CH_2CH_2OHI$), 3.58 (m, 48 H, $SCH_2CH_2N^+$), 3.84 (m, 54 H, OCH_2 and $N^+CH_2CH_2OHI$), 5.30 (s, 24 H, O*H*), 6.00 (s, 3 H, $C_6H_3O_3$). ^{13}C-NMR: δ -5.6 (Si*Me*), 13.8 ($OCH_2CH_2CH_2CH_2Si$), 17.7 ($OCH_2CH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2CH_2Si$), 23.1 ($SCH_2CH_2N^+$), 26.4 ($SiCH_2CH_2S$), 50.3 (-$NMe_2CH_2CH_2OHI$), 54.5 (-$NMe_2CH_2CH_2OHI$), 63.1 ($SCH_2CH_2N^+$), 64.1 (-$NMe_2CH_2CH_2OHI$), 67.5 (OCH_2). ^{15}N-NMR: δ -324.2 (-*N*$Me_2CH_2CH_2OH$). Anal. Calcd. $C_{285}H_{654}I_{24}N_{24}O_{27}S_{24}Si_{21}$ (9255.45 g/mol): C, 37.05; H, 7.12; N, 3.64; S, 8.33; Found: C, 37.53; H, 6.98; N, 3.54; S, 7.80.

S3.3. Computational methods.

3D atomistic models of dendrimer structures were created using Materials Studio software package from Accelrys Inc. The RESP technique[2] was used for calculation of partial charges. For this charge parametrization the R.E.D.-III.5 tools[3] was used. The necessary QM calculations (QM structure minimisations, molecular electrostatic potential (MEP) calculations) were done using GAMESS.[4] The default, HF/6-31G*, level of theory was used for all charge-related QM calculations and the MEP potential was fitted on Connolly molecular surface. The GAFF (Generalized Amber Force Field)[5] force field was used for simulated dendrimers. Missing force field parameters were fitted by minimizing the differences

between QM and force field based relative energies of properly chosen molecular fragments. 100 conformations of each molecular fragment were used for the force field parameters fitting. QM energies were calculated at MP2/HF/6-31G** level of theory using GAMESS and fitting was accomplished using *paramfit* routine from AMBER12 software[6]. Van der Waals parameters for Si atoms were taken from the MM3 force field[7]. The dendrimer structures were solvated in explicit water (TIP3P model) with proper number of counterions and additional salt to preserve neutrality of the whole system and to ensure proper ionic strength (0.15 M). This molecular system was subsequently minimized (5000 steps with 2 kcal/(mol Å2) restraint applied to dendrimers + 5000 without restraint), heated (200 ps of Molecular dynamics in NVT ensemble) to 310K and then simulated using molecular dynamics in NPT ensemble (T = 310 K and P = 0.1 MPa) for 65 ns. AMBER12 software was used for all the simulations. Hydrogens were constrained with the SHAKE algorithm[8] to allow 2 fs time step. Langevin thermostat with collision frequency 2 ps was used for all molecular dynamics runs[9]. The pressure relaxation time for weak-coupling barostat was 2 ps. Particle mesh Ewald method (PME)[10] was used to treat long range electrostatic interactions under periodic conditions with a direct space cutoff of 10 angstroms. The same cutoff was used for van der Waals interactions. The pmemd.cuda module from Amber12 was used for all the above described simulation steps.[11] For the structural analyses (Rg, RDF) the last 3050 frames (which span the final 30 ns of whole simulation) were used. Amber module cpptraj was used to accomplish these analyses. The same module was used to find the most representative conformations of the dendrimers (RMSD based cluster analysis). Calculation and visualization of electrostatic potential on dendrimer molecular surface was done using Adaptive Poisson-Boltzmann Solver as implemented in APBS[12] plugin of VMD[13]. The visualizations of dendrimer structures were performed using UCSF Chimera software.[14]

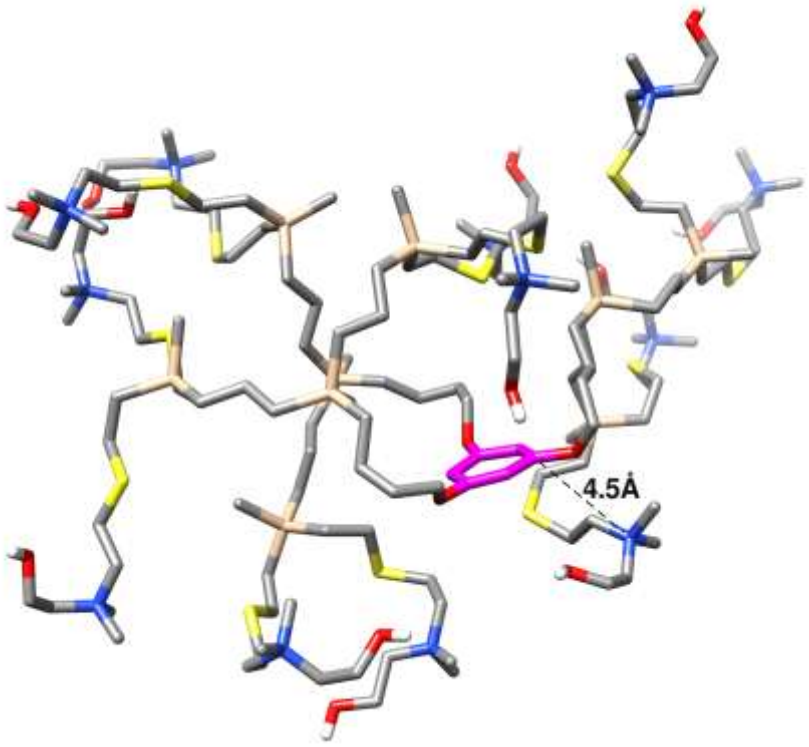


Figure S4. Backfolding in case of dendrimer **17**. Atom colors are the same as in figure 3.

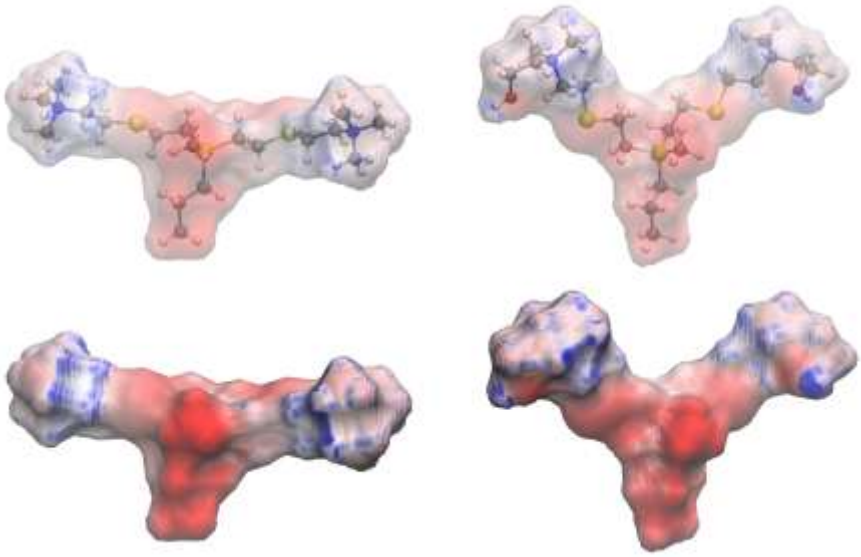


Figure S5. Detail view of terminal dendrimer fragment consisting of two end residues attached to repetitive unit (dendrimer **14** – left, dendrimer **17** - right). Molecular surface is colored according to electrostatic potential. Red color denotes low values (0 kT/e and lower) and the blue color means high potential values (+10 kT/e (0.256 V) and higher). The effect of water was implicitly taken into account in

this electrostatic calculation. Atom colors are: C – grey, H – white, O – red, S – yellow and Si atom (branching point) in yellow too.

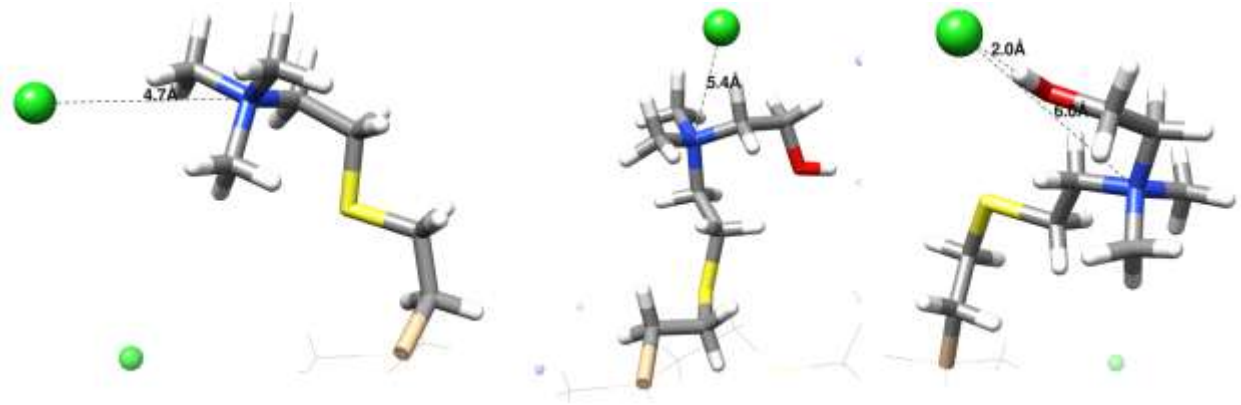


Figure S6. Interaction of Cl^- anions (green) with terminal unit of dendrimer **14** (left) and **17** (middle and right). In case of dendrimer **17** two interaction modes are visualized. Optimal interaction of Cl^- just with cationic charge centered arround given N atom (middle) and second mode where anion interacts with the given cationic group and also with OH dipole.

S3.4. pH titration.

A solution of NaOH (1.8 µM) was carefully added to a solution of **4** (38.5 mg) in water. The pH was measured using a pH-Meter Basic 20+ of Crison.

S4. References

1. E. Pedziwiatr-Werbicka, E. Fuentes-Paniagua, V. Dzmitruk, J. Sánchez-Nieves, M. Sudas, E. Drozd, A. Shakhbazau, D. Shcharbin, F. J. d. l. Mata, R. Gómez-Ramírez, M. Á. Muñoz-Fernández and M. Bryszewska, *Colloids Surf. B: Biointerfaces*, 2013, **109**, 183– 189.
2. C. I. Bayly, P. Cieplak, W. D. Cornell and P. A. Kollman, *J. Phys. Chem.*, 1993, **97**, 10269.
3. F.-Y. Dupradeau, A. Pigache, T. Zaffran, C. Savineau, R. Lelong, N. Grivel, D. Lelong, W. Rosanski and P. Cieplak, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7821.
4. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347-1363.
5. J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollamn and D. A. Case, *J. Comput. Chem.*, 2004, **25**, 1157–1174.
6. D. A. Case, T. A. Darden, T. E. C. III, C. L. Simmerling, J. Wang, R. E. Duke, R. Luo, R. C. Walker, W. Zhang, K. M. Merz, B. Roberts, S. Hayik, A. Roitberg, G. Seabra, J. Swails, A. W. Goetz, I. Kolossváry, K. F.Wong, F. Paesani, J. Vanicek, R. M. Wolf, J. Liu, X. Wu, S. R. Brozell, T. Steinbrecher, H. Gohlke, Q. Cai, X. Ye, J. Wang, M.-J. Hsieh, G. Cui, D. R. Roe, D. H. Mathews, M. G. Seetin, R. Salomon-Ferrer, C. Sagui, V. Babin, T. Luchko, S. Gusarov, A. Kovalenko and P. A. Kollman, *University of California, San Francisco*, 2012, AMBER 12.
7. J.-H. Lii, A. Norman and L. Allinger, *J. Comput. Chem.*, 1991, **12**, 186-199.

8. J.-P. Ryckaert, G. Ciccotti and H. J. C. Berendsen, *J. Comput. Phys.*, 1977, **23**, 327-341.
9. X. Wu and B. R. Brooks, *Chem. Phys. Lett.*, 2003, **381**, 512-518.
10. T. Darden, L. Perera, L. Li and L. Pedersen, *J. Chem. Phys.*, 1999, **7**, R55.
11. A. W. Goetz, M. J. Williamson, D. Xu, D. Poole, S. L. Grand and R. C. Walker, *J. Chem. Theory Comput*, 2012, **8**, 1542.
12. N. A. Baker, D. Sept, S. Joseph, M. J. Holst and J. A. McCammon, *Proc. Natl. Acad. Sci. USA 98*, 2001, 10037-10041.
13. W. Humphrey, A. Dalki and K. Schulten, *J. Molec. Graphics*, 1996, **14**, 33-38.
14. E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng and T. E. Ferrin, *J. Comput. Chem.*, 2004, **25**, 1605-1612.

S5. Selected NMR spectra

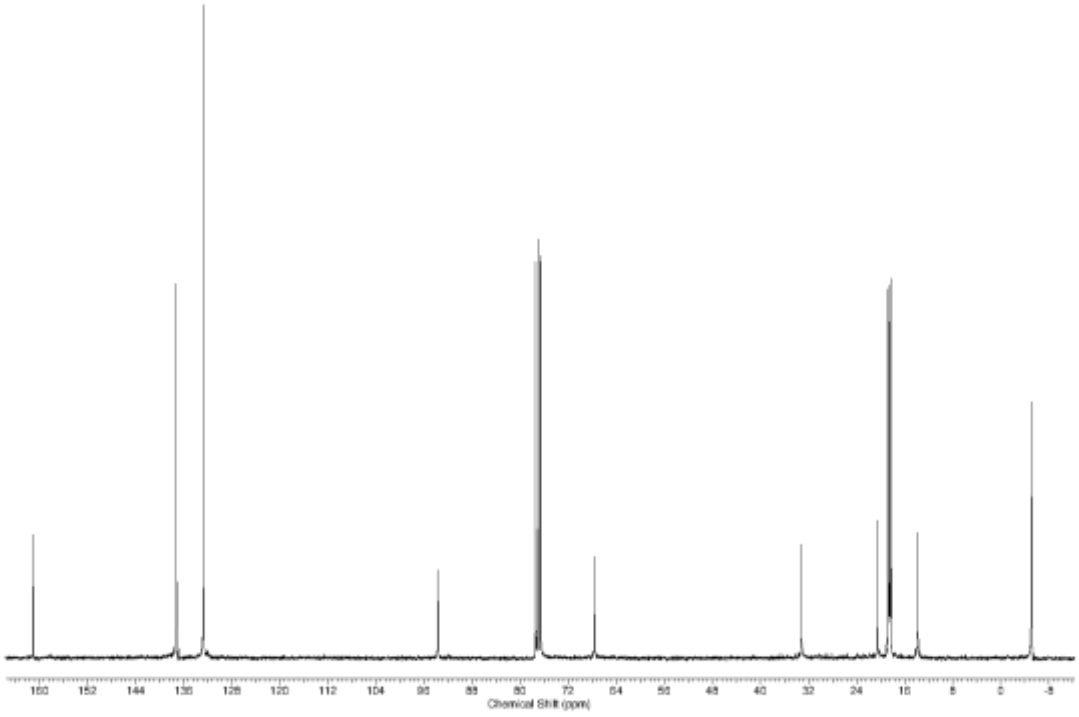


Figure S7. ^{13}C-NMR ($CDCl_3$) spectra of **2**.

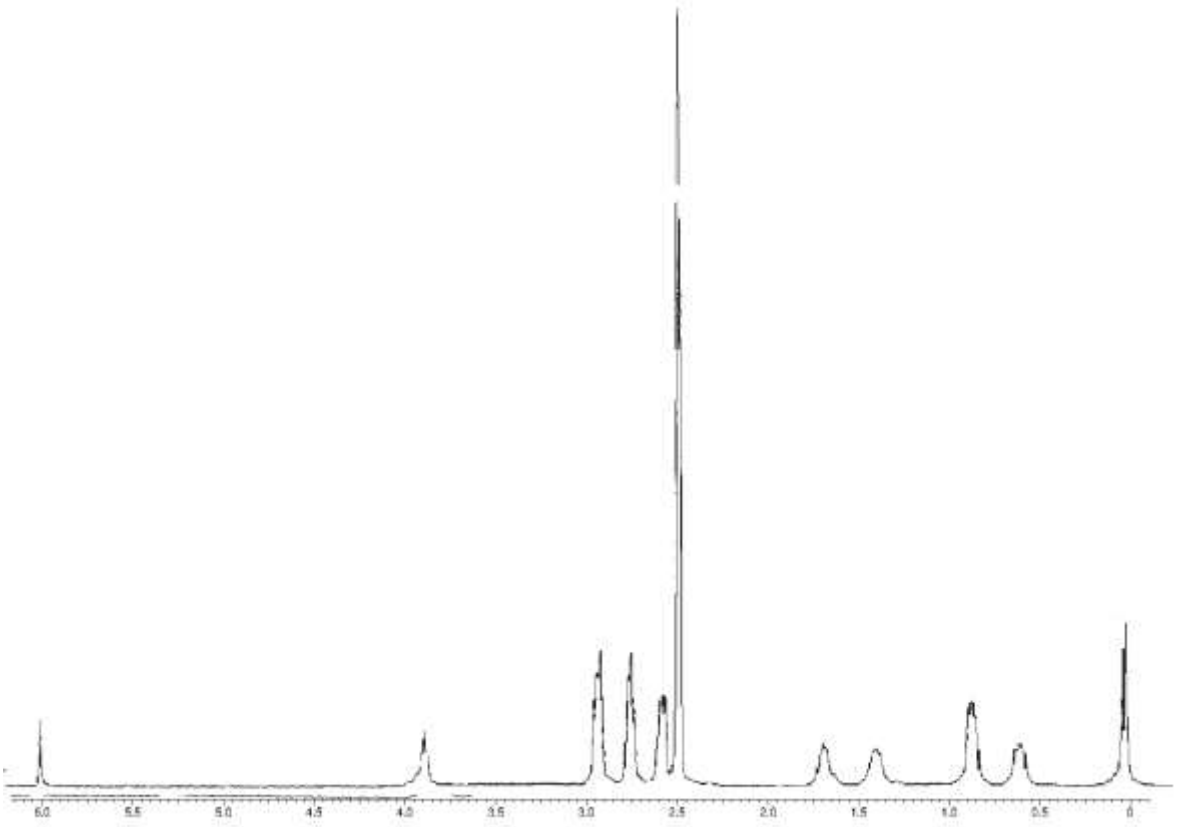


Figure S8. ^{1}H-NMR spectra (DMSO) of **4**.

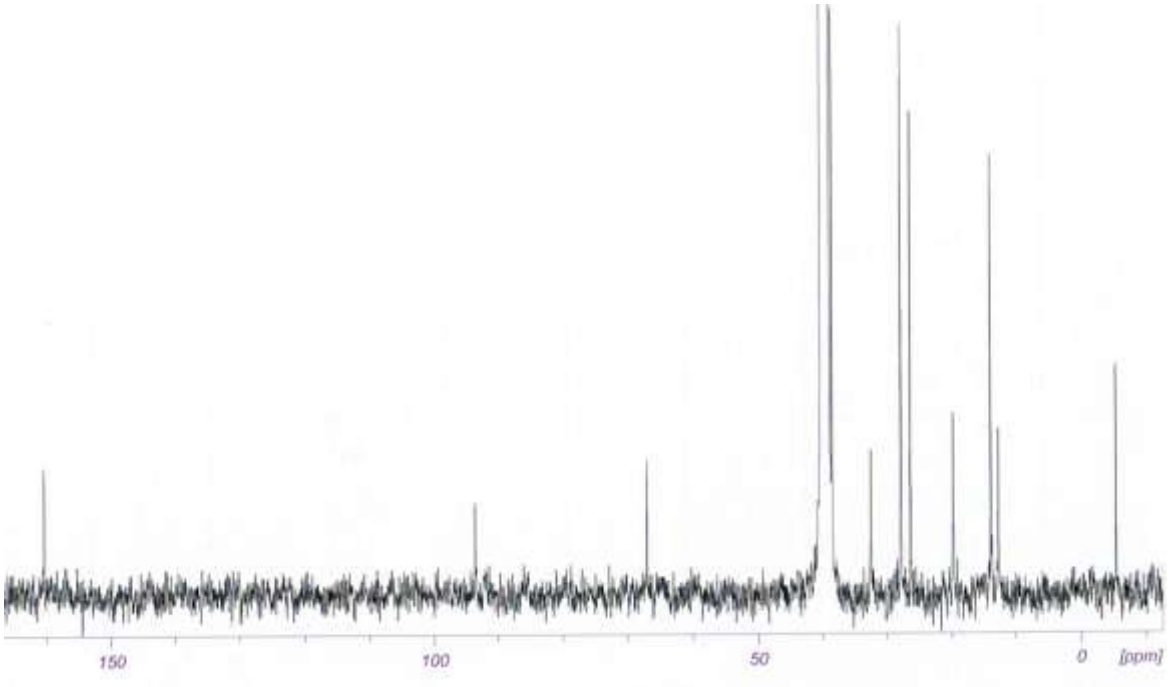


Figure S9. ^{13}C-NMR spectra (DMSO) of **4**

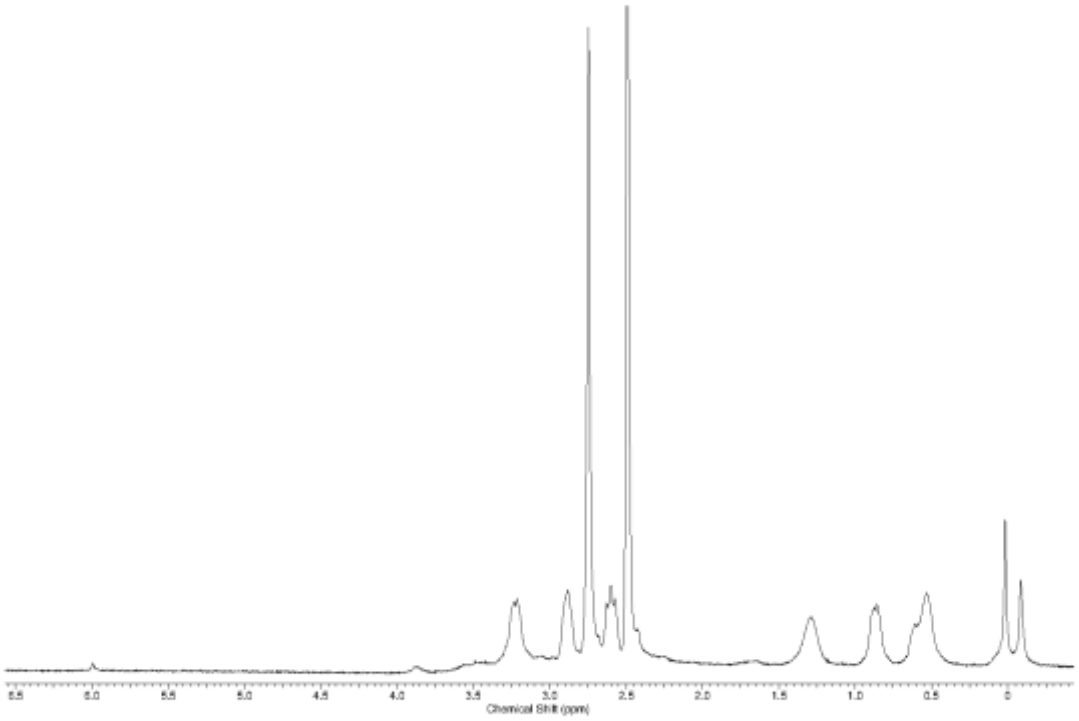


Figure S10. ^{1}H-NMR spectra (DMSO) of **9**.

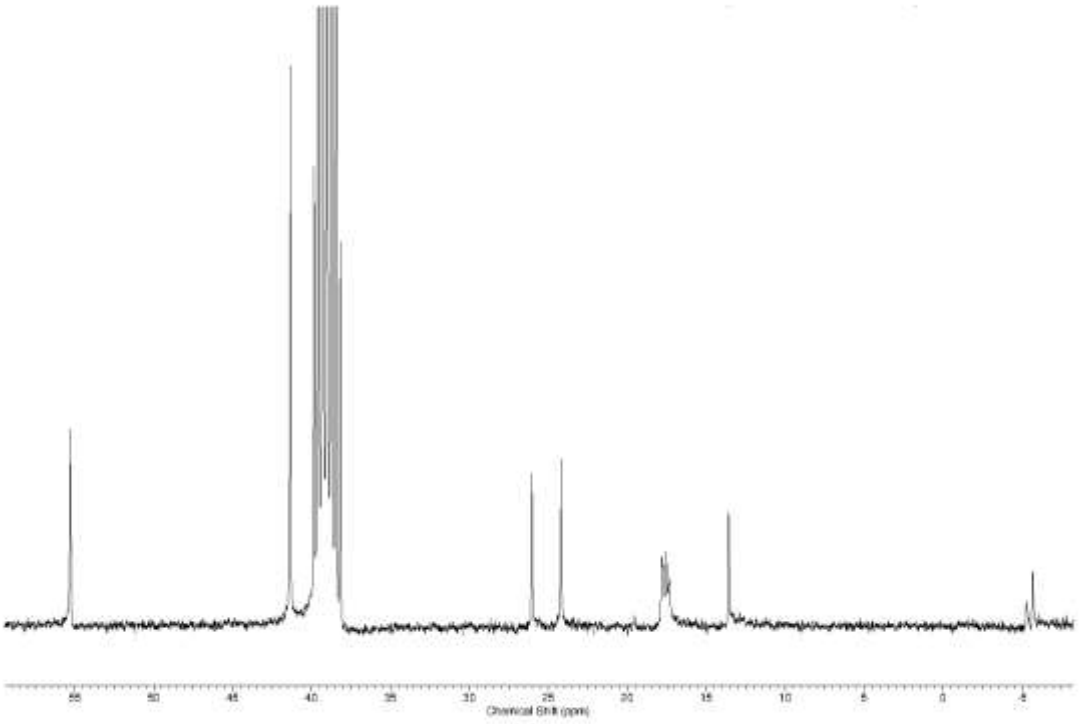


Figure S11. ^{13}C-NMR spectra (DMSO) of **9**.

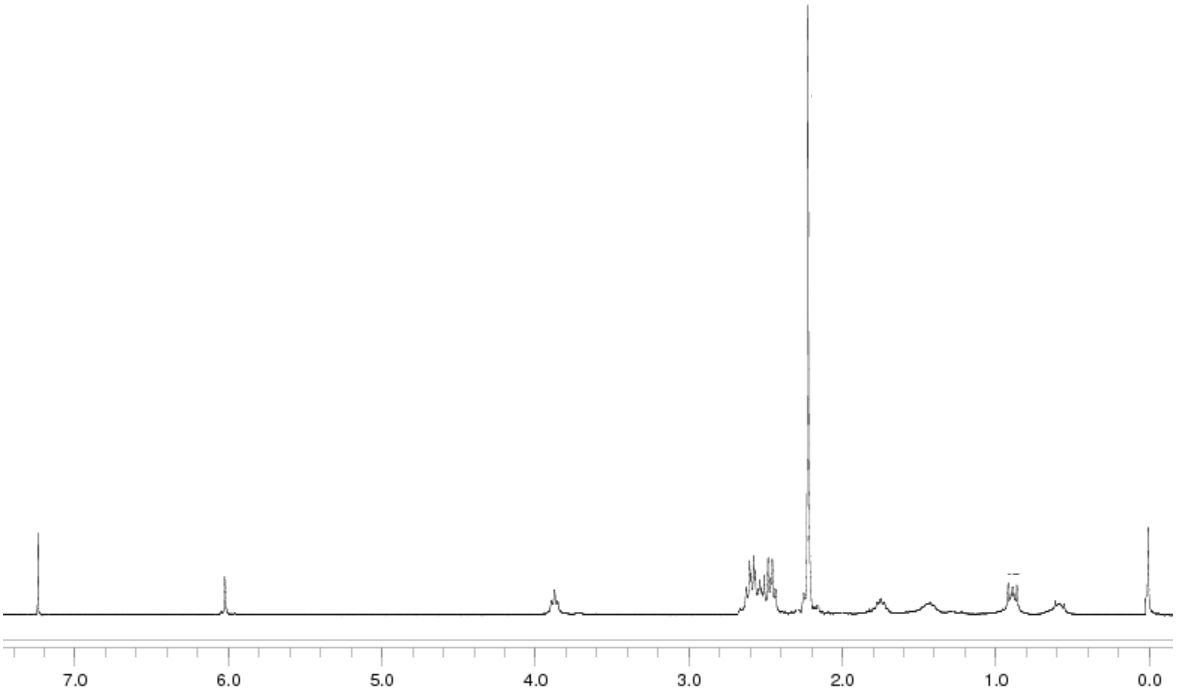


Figure S12. ^{1}H-NMR spectra ($CDCl_3$) of **10**

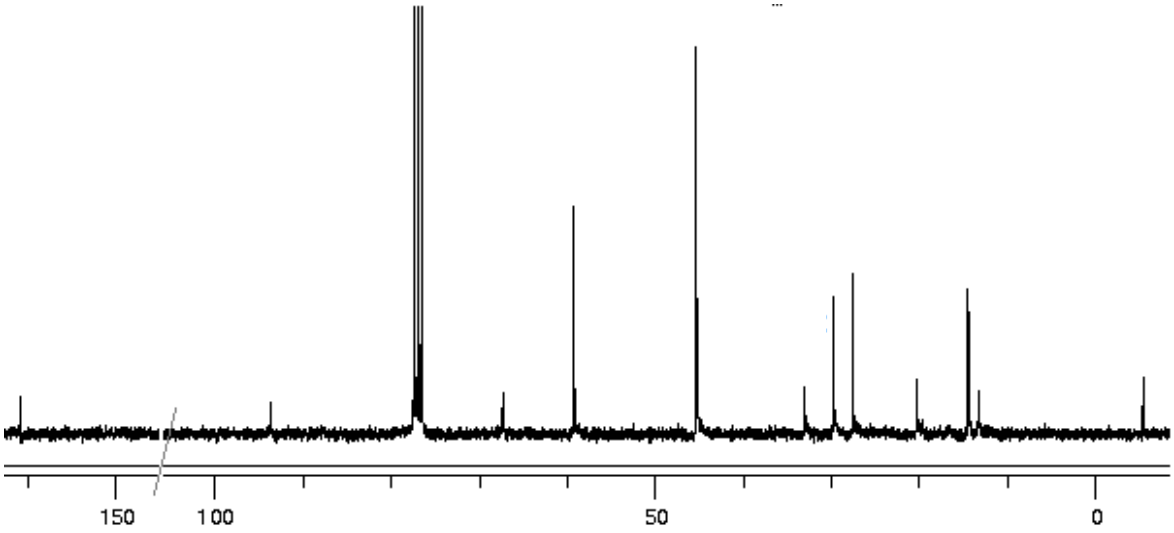


Figure S13. ^{13}C-NMR spectra ($CDCl_3$) of **10**.

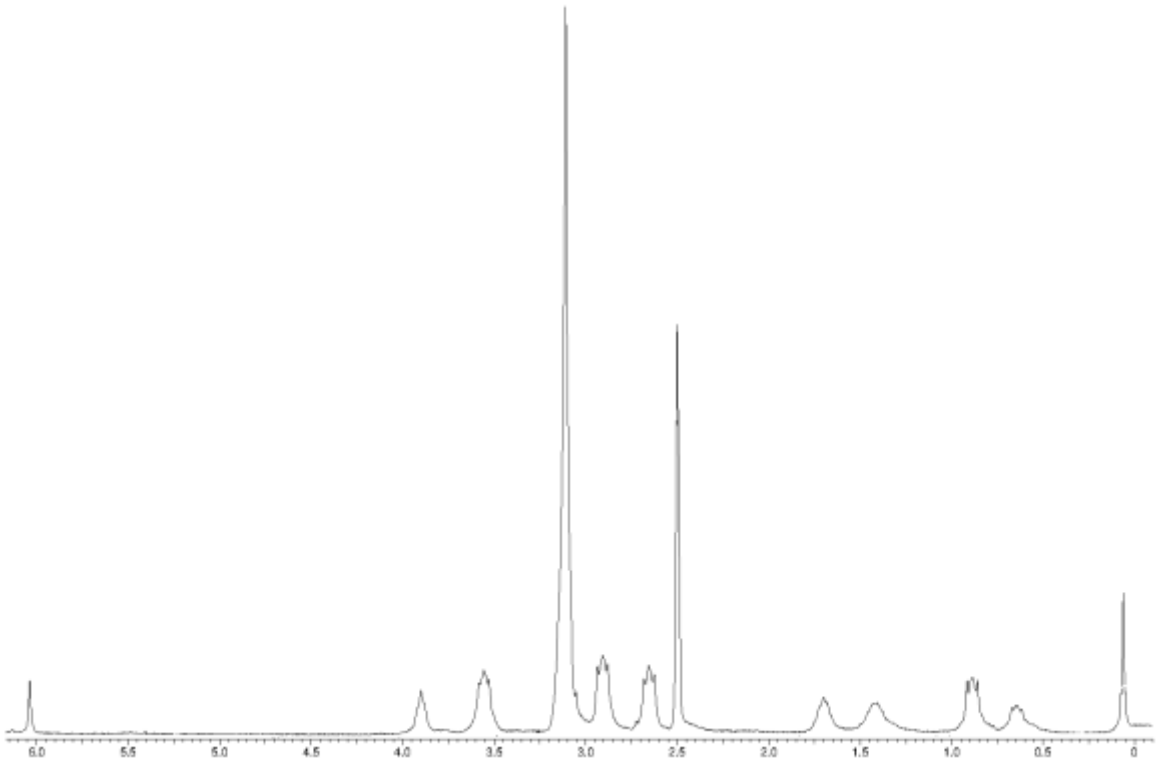


Figure S14. ^{1}H-NMR spectra (DMSO) of **13**.

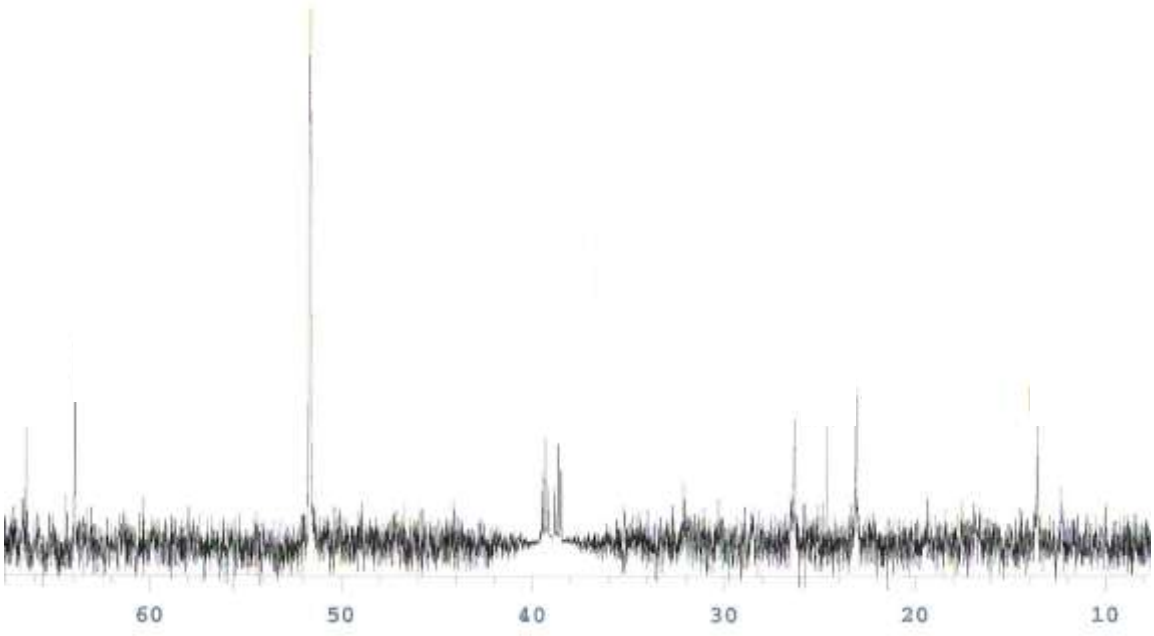


Figure S15. ^{13}C-NMR spectra (DMSO) of **13**.

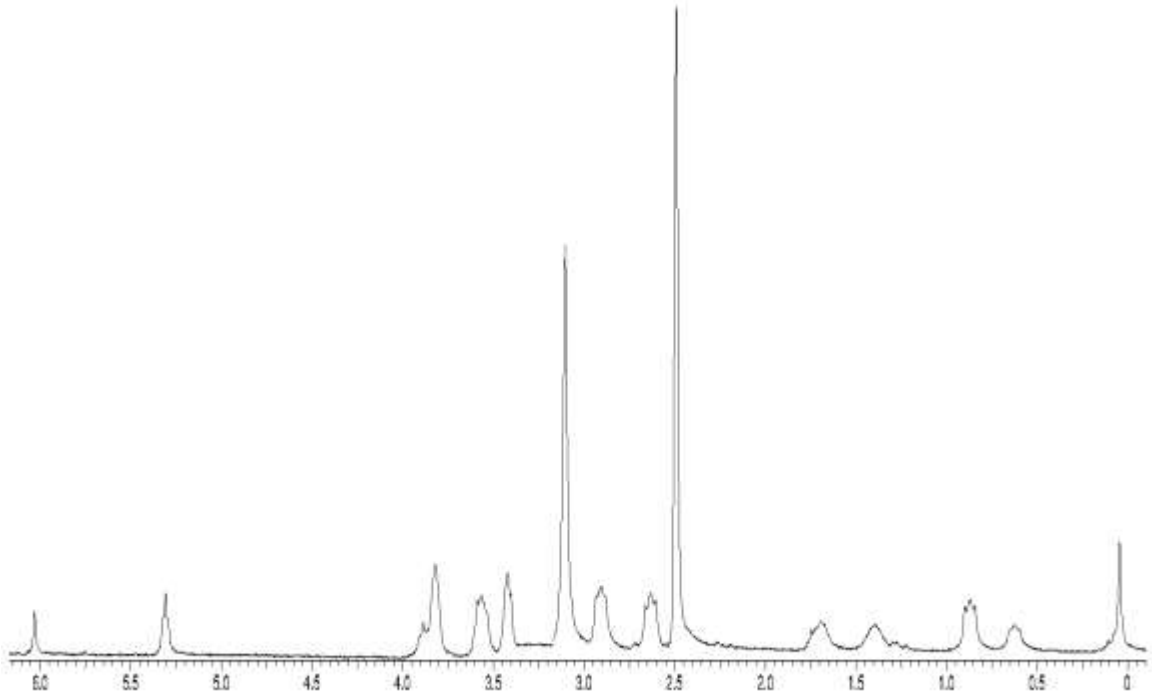


Figure S16. ^{1}H-NMR spectra (DMSO) of **16**.

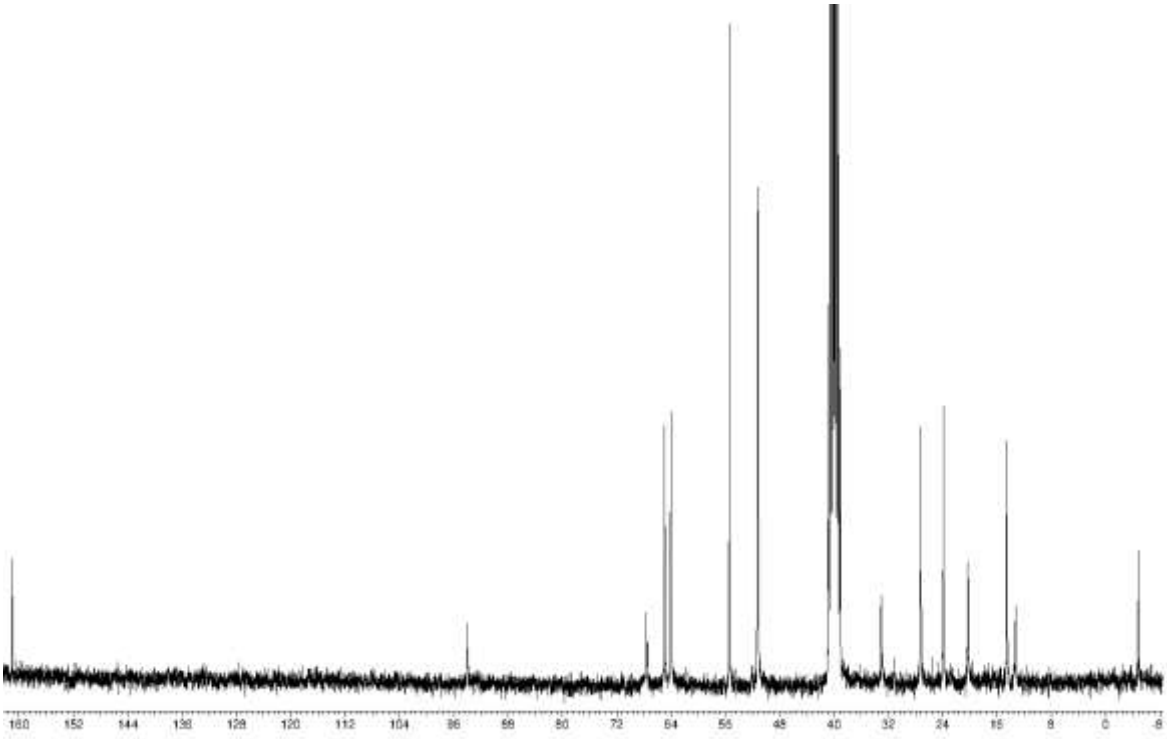


Figure S17. ^{13}C-NMR spectra (DMSO) of **16**.