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SUPPORTING INFORMATION

Title: A Topological View of Isomeric Dendrimers
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Ref. No.: O200800408

General synthetic procedures.

Persulfonylation of amines or sulfonamides with arylsulfonyl chlorides: A mixture of an amine, triethylamine (sixfold molar excess per amino group), and arylsulfonyl chloride (fourfold molar excess per amino group) was stirred in dichloromethane (50 ml per 1 g of the amine) at reflux for 12-24 hrs. Then the solvent was removed under reduced pressure and the residue was triturated with methanol. The solid precipitate was filtered through a glass filter and thoroughly washed with methanol. The resulting solid powders were dried in vacuum and then purified by either recrystallization from CH_2Cl_2/CH_3OH or chromatography on silica gel.

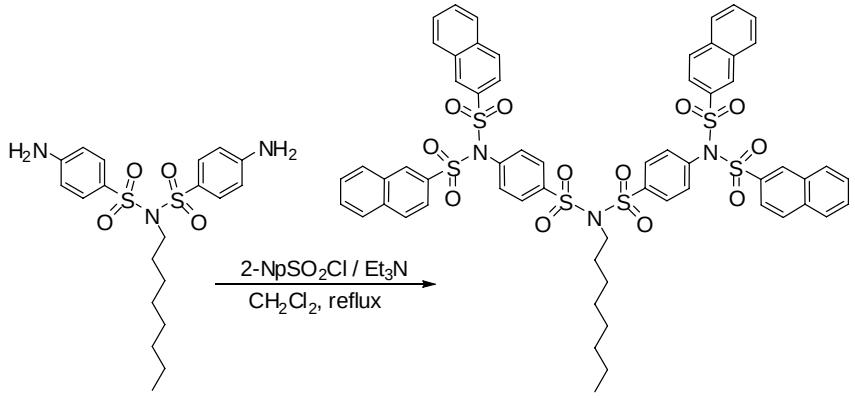
Reduction of nitroaromatic intermediates with tin (II) chloride dihydrate into amines: A mixture of 1 g of a nitro-compound and 8 g of $SnCl_2 \cdot 2H_2O$ was heated at 40 ^{0}C in 100-150 mL of a 1:1 mixture of ethanol and dichloromethane containing 2 mL of concentrated hydrochloric acid for 2 hrs. Then the reaction mixture was poured into 500 mL of deionized water and the amine was extracted with 200 mL of dichloromethane in a separation funnel. The organic layer was washed with water, with concentrated sodium hydrogen carbonate solution, dried over $MgSO_4$, and evaporated to give the corresponding amine.

Reductive cleavage of nitro-derivatives with tin (II) chloride dihydrate (preparation of aminosulfonamides): A mixture of a nitro-compound and $SnCl_2 \cdot 2H_2O$ (four equivalents per nitro group) was boiled in a mixture of ethanol and concentrated hydrochloric acid (5 mL per gram of nitro-compound) for 5 hrs, cooled, and then poured onto ice. The pH was adjusted to 10 with 2 M aqueous NaOH, and the released amine was extracted with dichloromethane, dried over $MgSO_4$, and then evaporated to give corresponding amines as colorless solids.

Catalytic reduction of nitro-derivatives with H_2: A nitro-compound was dissolved in a 2:1 mixture of benzene/ethanol. To this solution was added a catalytic amount of commercial 10% Pd/C that had been previously washed with ethanol. The resulting suspension was evacuated and the reaction flask was filled with H_2. This operation was repeated three times and the mixture was stirred for 24 hrs at room temperature under hydrogen pressure of 3 bar. Then the palladium catalyst was filtered off in a vacuum through a pad of Celite and rinsed with a 2:1 mixture of benzene/ethanol. The filtrates were combined and evaporated in vacuum to give a colorless solid. The yields of the catalytic hydrogenation are assumed quantitative.

Characterization data for the compounds

Compound 1. The compound was prepared from diamine **S1**[1] and 2-napthylsulfonyl chloride as shown in Scheme S1 according to the standard procedure. Recrystallized from methanol/dichloromethane; colorless solid; yield 81%; m.p. 190ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.29 (m, 10 H, CH_2), 1.74 (m. 2H, CH_2), 3.69 (m, 2 H, CH_2), 7.27 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.61- 7.79 (m, 8 H, ArH), 7.88- 8.08 (m, 22 H, ArH), 8.47 (m, 4 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.11, 22.63, 26.63, 28.96, 29.18, 30.07, 31.74, 49.99, 122.80, 127.94, 128.03, 129.24, 129.66, 129.77, 129.85, 130.78, 131.85, 132.57, 135.50, 135.60, 139.33, 141.01 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1222.18 [*M* + Na]$^+$, $C_{60}H_{53}N_3O_{12}S_6Na$ requires 1222.19; elemental analysis calcd (%) for $C_{60}H_{53}N_3O_{12}S_6$ (1200.47): C 60.03, H 4.45, N 3.50, S 16.03; found C 59.98, H 4.41, N 3.51, S 16.18.



S1 **1**

Scheme S 1. Synthesis of compound **1**.

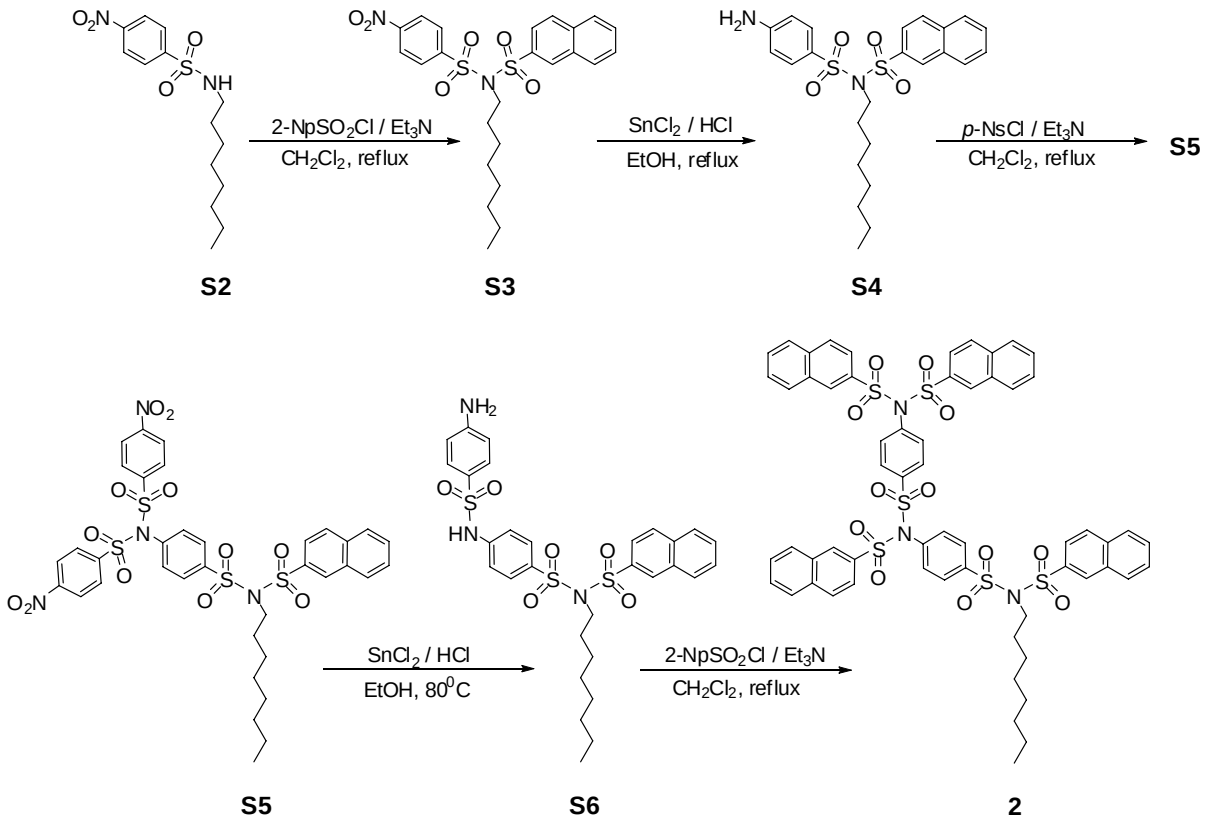
Compound 2. The synthesis of the compound is unfolded in Scheme S2. The starting sulfonamide **S2** was obtained by the published procedure.[1] Recrystalized from hot benzene; colorless solid; yield 79%; m.p. 250 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.19 (m, 10 H, CH_2), 1.71 (m. 2 H, CH_2), 3.73 (m, 2 H, CH_2), 7.21 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.31 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.58 – 7.80 (m, 8 H, ArH), 7.83 – 8.14 (m, 20 H, ArH), 8.46 (s, 1 H, ArH), 8.51 (s, 2 H, ArH), 8.59 (s, 1 H, ArH) ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1222.19 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{60}H_{53}N_3O_{12}S_6$ (1200.47): C 60.03, H 4.45, N 3.50, S 16.03; found C 60.21, H 4.53, N 3.60, S 16.24.

Compound S3. Recrystallized from ethanol; colorless solid; yield 49%; m.p. 76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.23 (m, 10 H, CH_2), 1.73 (m. 2 H, CH_2), 3.79 (m, 2 H, CH_2), 7.63 – 7.81 (m, 2 H, ArH), 7.93 – 8.12 (m, 4 H, ArH), 8.30 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 8.43 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 8.62 (s, 1 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.07, 22.58, 26.51, 28.91, 29.05, 29.95, 31.67, 50.10, 122.60, 124.29, 127.93, 128.02, 129.54, 129.64, 129.66, 129.79, 130.35, 131.90, 135.45, 136.10, 145.84, 150.55 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 527.13 [*M* + Na]$^+$, elemental analysis calcd (%) for $C_{24}H_{28}N_2O_6S_2$ (504.62): C 57.12, H 5.59, N 5.55, S 12.71; found C 57.19, H 5.64, N 5.59, S 12.62.

Compound S4. Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.24 (m, 10 H, CH_2), 1.73 (m. 2 H, CH_2), 3.70 (m, 2 H, CH_2), 4.51 (br, 2H, NH), 6.70 (m, 2 H, ArH), 7.58 – 7.73 (m, 2 H, ArH), 7.78 – 7.89 (m, 2 H, ArH), 7.90 – 8.08 (m, 4 H, ArH), 8.54 (s, 1 H, ArH) ppm; MS (HiRes MALDI-FT, DCTB mix): *m/z* = 497.1532 [*M*+Na]$^+$, calcd monoisotopic peak ($^{12}C_{24}{}^1H_{30}{}^{14}N_2{}^{16}O_4{}^{32}S_2Na$) 497.1545.

Compound S5. Recrystallized from dichloromethane/methanol; yellowish solid; m.p. 196 – 198 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^{3}J_{H,\,H}$ = 6.3 Hz, 3 H, CH_3), 1.23 (m, 10 H, CH_2), 1.73 (m. 2H, CH_2), 3.78 (m, 2 H, CH_2), 7.29 (m, 2 H, ArH), 7.63 – 7.79 (m, 2 H, ArH), 7.92 – 8.11 (m, 4 H, ArH), 8.12 – 8.25 (m, 6 H, ArH), 8.43 – 8.55 (m, 4 H, ArH), 8.64 (s, 1 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.07, 22.58, 26.55, 28.94, 29.06, 29.93, 31.69, 50.01, 122.59, 124.63, 127.91, 128.03, 129.63, 129.66, 129.67, 129.75, 130.15, 130.33, 131.93, 131.96, 135.45, 136.22, 137.58, 142.96, 143.76, 151.18 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 867.11 $[M + Na]^+$;elemental analysis calcd (%) for $C_{36}H_{36}N_4O_{12}S_4$ (844.95): C 51.17, H 4.29, N 6.63, S 15.18; found C 51.14, H 4.37, N 6.66, S 15.33.

Compound S6. Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^{3}J_{H,\,H}$ = 6.4 Hz, 3 H, CH_3), 1.23 (br. s, 10 H, CH_2), 1.70 (m. 2H, CH_2), 3.70 (m, 2 H, CH_2), 4.22 (s, 2 H, NH_2), 6.65 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 7.15 (s, 1 H, NH), 7.67 (m, 4 H, ArH), 7.91-8.03 (m, 6 H, ArH), 8.55 (s, 1 H, ArH) ppm; MS (HiRes MALDI-FT, DCTB mix): *m/z* = 652.1584 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{30}{}^{1}H_{35}{}^{14}N_3{}^{16}O_6{}^{32}S_3Na$) 652.1586.



Scheme S 2. Synthesis of compound **2**.

Compound 3. The synthesis of the compound is shown in Scheme S3. Purified by column chromatography (silica gel, dichloromethane, R_f = 0.75); colorless solid; yield 69%; m.p. 237 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, $^{3}J_{H,\,H}$ = 6.6 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.71 (m. 2 H, CH_2), 3.68 (m, 2 H, CH_2), 7.14 – 7.38 (m, 6 H, ArH), 7.58 – 8.13 (m, 36 H, ArH), 8.42 (s, 1 H, ArH), 8.46 (s, 2 H, ArH), 8.51 (s, 2 H, ArH), ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1567.20 $[M+Na]^+$; elemental analysis calcd (%) for $C_{76}H_{64}N_4O_{16}S_8$ (1545.86): C 59.05, H 4.17, N 3.62, S 16.59; found C 59.18, H 4.33, N 3.69, S 16.66.

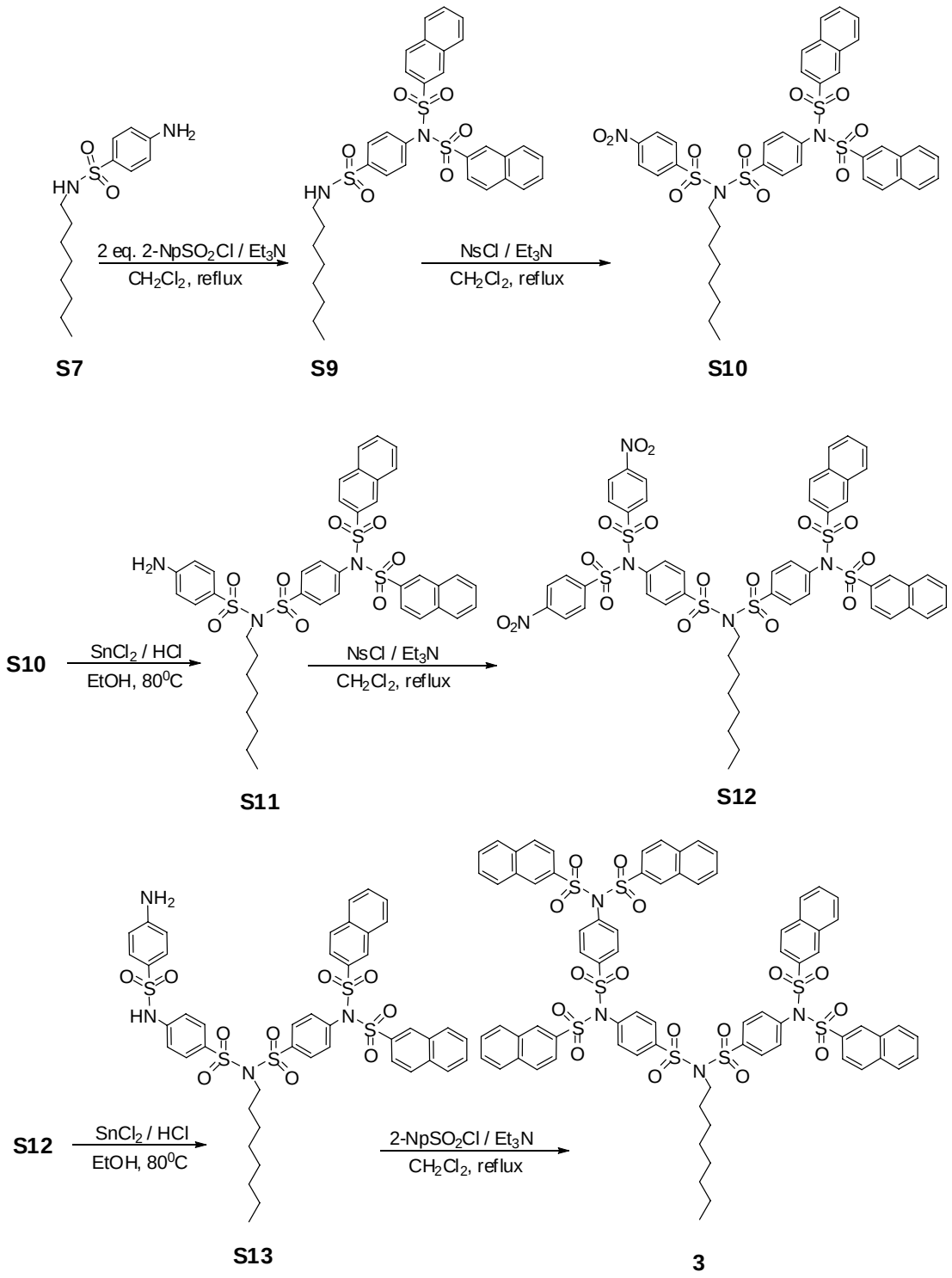
Compound S9. As illustrated in Scheme S3, a mixture of N-*n*-octyl-4-aminobenzenesulfonamide **S8**[1] (5 g, 18 mmol), triethylamine (10 mL), and 2-naphthalenesulfonyl chloride (8.1 g, 36 mmol) was stirred in 100 mL of dichloromethane at

reflux for 2 hrs. Then the solvent was removed under reduced pressure and the residue was triturated with methanol. The colorless amorphous solid was filtered and then recrystallized from dichloromethane/methanol. Yield 7.4 g (64%); m.p. 78 – 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^{3}J_{H, H}$ = 6.9 Hz, 3 H, CH_3), 1.25 (s, 10 H, CH_2), 1.50 (br, 2H, CH_2), 3.02 (m, 2 H, CH_2), 4.69 (t, $^{3}J_{H, H}$ = 6.0 Hz, 1 H, NH), 7.21 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 7.63-7.75 (m, 4 H, ArH), 7.90 – 8.03 (m, 8 H, ArH), 8.47 (d, $^{3}J_{H, H}$ = 1.5 Hz, 2 H, ArH) ppm; ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.19, 22.71, 26.63, 29.16, 29.22, 29.84, 31.83, 43.55, 122.94, 128.01, 128.04, 128.13, 129.67, 129.81, 129.93, 130.81, 131.97, 132.59, 135.58, 135.86, 138.09, 142.07 ppm. MS (EI, 80 eV): *m/z* = 664.17 $[M]^+$, 474.16 $[M - C_{10}H_7SO_2]^+$; elemental analysis calcd (%) for $C_{34}H_{36}N_2O_6S_3$ (664.85): C 61.42, H 5.46, N 4.21, S 14.47; found C 61.57, H 5.40, N 4.16, S 14.82.

Compound S10. **S9** (3 g, 4.5 mmol), triethylamine (8 mL), and 4-nitrobenzenesulfonyl chloride (2.7 g, 12 mmol) were used in the standard persulfonylation reaction Recrystallized from dichloromethane/methanol to give yellowish crystalline powder. Yield 2.8 g (75%); m.p. 94 – 96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^{3}J_{H, H}$ = 6.9 Hz, 3 H, CH_3), 1.25 (s, 10 H, CH_2), 1.69 (br. 2H, CH_2), 3.72 (m, 2 H, CH_2), 7.28 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 7.63 – 7.76 (m, 4 H, ArH), 7.92 – 8.05 (m, 10 H, ArH), 8.22 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 8.41 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 8.49 (d, $^{3}J_{H, H}$ = 1.5 Hz, 2 H, ArH) ppm; ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.18, 22.70, 26.61, 29.00, 29.21, 30.07, 31.79, 50.29, 122.93, 124.48 128.07, 128.14, 129.38, 129.68, 129.75, 129.88, 130.00, 130.91, 131.99, 132.73, 135.64, 135.73, 139.62, 140.98, 145.50, 150.76 ppm; MS (EI, 80 eV): *m/z* = 849.20 $[M]^+$, 664.20 $[M - p\text{-}NO_2C_6H_4SO_2]^+$, 473.10 $[M - p\text{-}NO_2C_6H_4SO_2 - C_{10}H_7SO_2]^+$; elemental analysis calcd (%) for $C_{40}H_{39}N_3O_{10}S_4$ (850.01): C 56.52, H 4.62, N 4.94, S 15.09; found C 56.99, H 4.78, N 4.68, S 14.89.

Compound S11. Standard reduction of **S10**. Colorless solid; M.p. 89 – 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^{3}J_{H, H}$ = 6.9 Hz, 3 H, CH_3), 1.25 (s, 10 H, CH_2), 1.70 (br, 2H, CH_2), 3.65 (m, 2 H, CH_2), 6.99 (d, $^{3}J_{H, H}$ = 8.4 Hz, 2 H, ArH), 7.25 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 7.63-7.76 (m, 4 H, ArH), 7.82 (d, $^{3}J_{H, H}$ = 8.4 Hz, 2 H, ArH), 7.92-8.04 (m, 10 H, ArH), 8.48 (d, $^{3}J_{H, H}$ = 1.5 Hz, 2 H, ArH) ppm; ^{13}C NMR (75.47 MHz, $(CD_3)_2SO$): δ = 13.93, 22.03, 25.84, 28.33, 28.49, 29.32, 31.13, 50.19, 112.55, 122.08, 122.34, 128.00, 128.12, 128.30, 129.04, 129.75, 129.93, 130.14, 130.36, 131.40, 132.51, 134.85, 135.09, 137.90, 141.63, 154.51 ppm; MS (EI, 80 eV): *m/z* = 819.24 $[M]^+$, 664.20 $[M - p\text{-}NH_2C_6H_4SO_2]^+$, 473.13 $[M - p\text{-}NH_2C_6H_4SO_2 - C_{10}H_7SO_2]^+$.

Compound S12. **S10** (1 g, 1.2 mmol), triethylamine (3 mL), and 4-nitrophenylsulfonyl chloride (1.05 g, 4.7 mmol) were used in the reaction. Recrystallized from dichloromethane/methanol to give colorless crystals; yield 0.84 g (58%); m.p. 217-218 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^{3}J_{H, H}$ = 6.9 Hz, 3 H, CH_3), 1.27 (s, 10 H, CH_2), 1.73 (br. 2H, CH_2), 3.70 (m, 2 H, CH_2), 7.23 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 7.28 (d, $^{3}J_{H, H}$ = 8.7 Hz, 2 H, ArH), 7.64-7.76 (m, 4 H, ArH), 7.90-8.04 (m, 12 H, ArH), 8.13 (d, $^{3}J_{H, H}$ = 8.7 Hz, 4 H, ArH), 8.42 (d, $^{3}J_{H, H}$ = 8.7 Hz, 4 H, ArH), 8.48 (d, $^{3}J_{H, H}$ = 1.5 Hz, 2 H, ArH) ppm; ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.18, 22.69, 26.67, 29.05, 29.23, 30.21, 31.80, 50.21, 122.87, 124.69 128.12, 128.14, 129.35, 129.76, 129.87, 130.01, 130.16, 130.89, 131.95, 132.15, 132.52, 132.68, 135.60, 135.68, 137.98, 139.58, 140.86, 142.26, 143.71, 151.19 ppm; MS (ESI pos., CH_3OH/CH_2Cl_2): *m/z* = 1229.09 $[M+K]^+$ calcd monoisotopic peak ($^{12}C_{52}{}^{1}H_{47}{}^{14}N_5{}^{16}O_{16}{}^{32}S_6K$) 1228.10; 1212.12 $[M+Na]^+$ calcd monoisotopic peak ($^{12}C_{52}{}^{1}H_{47}{}^{14}N_5{}^{16}O_{16}{}^{32}S_6Na$) 1212.12; elemental analysis calcd (%) for $C_{52}H_{47}N_5O_{16}S_6$ (1190.34): C 52.47, H 3.98, N 5.88, S 16.16; found C 52.56, H 4.13, N 5.81, S 16.26.

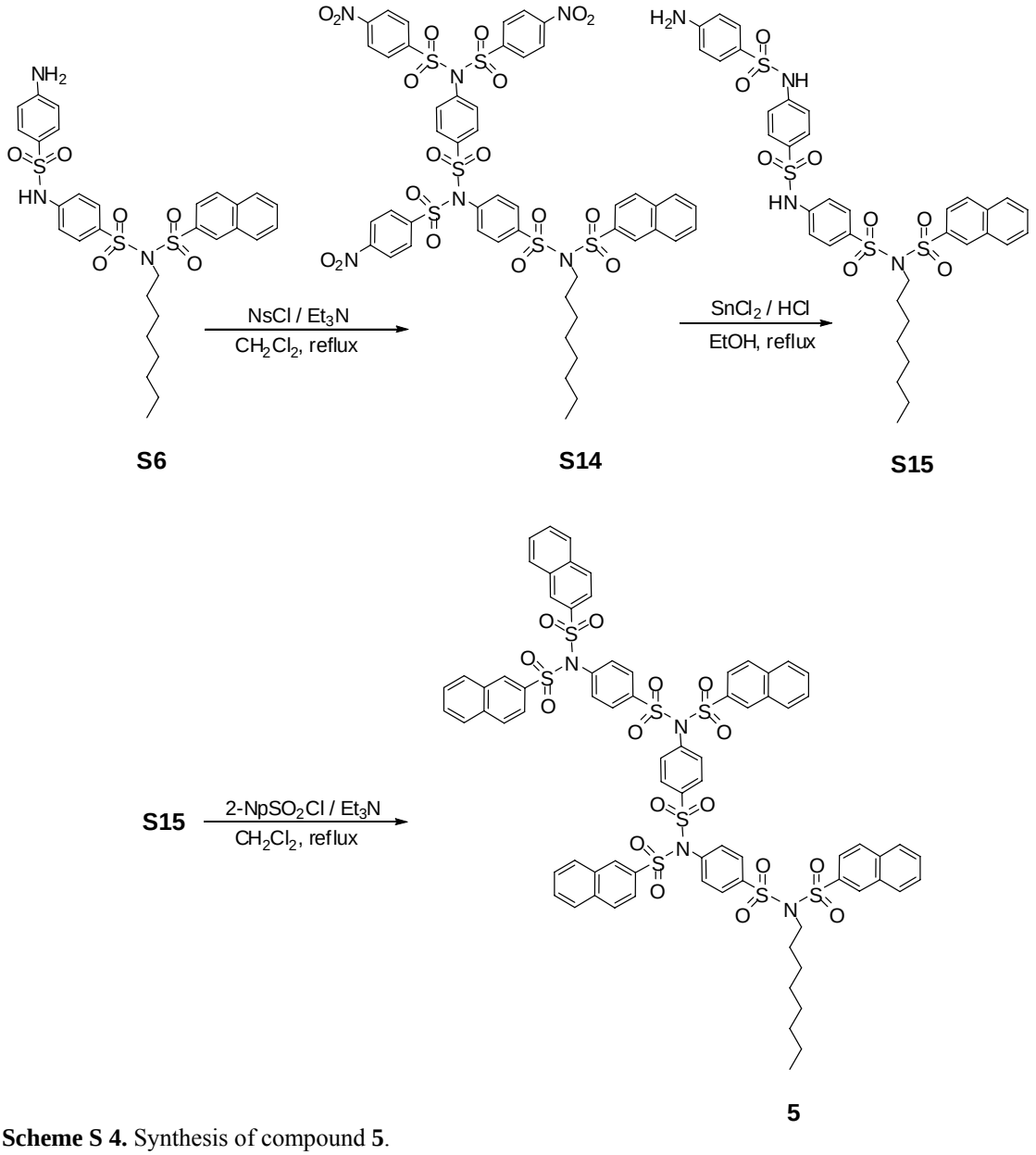


Scheme S 3. Synthesis of compound **3**.

Compound S13. ^{1}H NMR (300 MHz, DMSO): δ = 0.84 (t, $^{3}J_{H,\,H}$ = 6.9 Hz, 3 H, CH_3), 1.17 (m, 10 H, CH_2), 1.51 (m, 2H, CH_2), 3.67 (m, 2 H, CH_2), 6.09 (s, 2H, NH_2), 6.58 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 7.29 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 7.48 (m, 4 H, ArH), 7.68 – 7.92 (m, 8 H, ArH), 8.03 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 8.15 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 8.24 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 8.50 (s, 2H, ArH), 10.80 (br, 1H, $NHSO_2$) ppm; MS (HiRes ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 997.1706 $[M+Na]^{+}$, calcd monoisotopic peak ($^{12}C_{46}H_{46}{}^{14}N_4{}^{16}O_{10}{}^{32}S_5Na$) 997.1715.

Compound 4. The synthesis and characterization were reported.[1]

Compound 5. The synthesis is shown in Scheme S4. Chromatographic separation (silica gel, CH_2Cl_2, R_f = 0.75);colorless solid; yield 61%; m.p. 311 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.71 (m. 2 H, CH_2), 3.74 (m, 2 H, CH_2), 7.13 – 7.41 (m, 6 H, ArH), 7.56 – 8.19 (m, 36 H, ArH), 8.44 (s, 1 H, ArH), 8.49 (s, 1 H, ArH), 8.53 (s, 2 H, ArH), 8.60 (s, 1 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.05, 22.55, 26.53, 28.89, 29.04, 29.91, 31.65, 49.91, 122.49, 122.57, 122.67, 122.71, 122.74, 122.83, 127.82, 127.98, 128.04, 129.26, 129.39, 129.63, 129.69, 129.80, 129.85, 129.88, 130.04, 130.14, 130.25, 130.32, 130.80, 130.83, 130.99, 131.83, 131.87, 132.12, 132.26, 132.44, 132.49, 132.59, 132.66, 135.09, 135.36, 135.52, 135.54, 135.59, 136.31, 136.38, 138.11, 138.54, 139.65, 140.22, 140.49, 140.81, 142.03 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1567.19 $[M+Na]^+$; elemental analysis calcd (%) for $C_{76}H_{64}N_4O_{16}S_8$ (1545.86): C 59.05, H 4.17, N 3.62, S 16.59; found C 59.34, H 4.29, N 3.59, S 16.72.



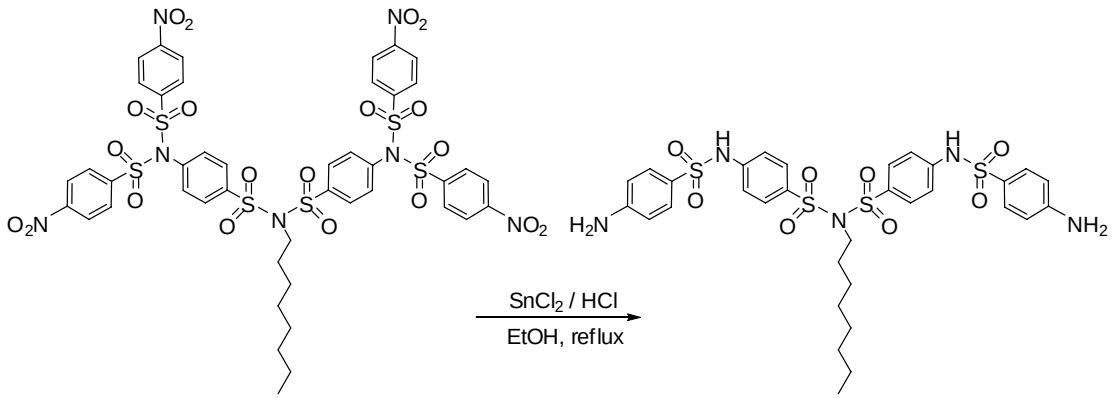
Scheme S 4. Synthesis of compound **5**.

Compound S14. Recrystallized from THF/methanol; yellowish solid; yield 75%; m.p. 245°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.18 (br. s, 10 H,

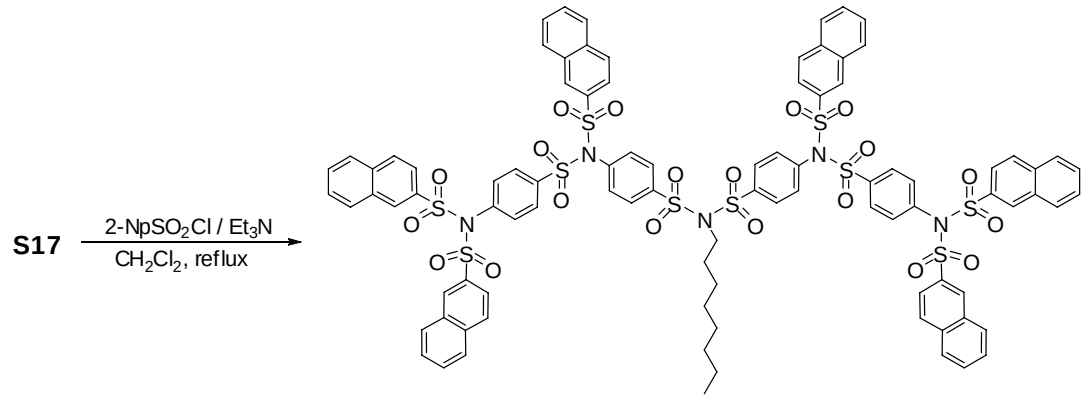
CH_2), 1.68 (m, 2H, CH_2), 3.74 (m, 2 H, CH_2), 7.25 (m, 4 H, ArH); 7.68 (m, 2 H, ArH), 7.94-8.02 (m, 6 H, ArH), 8.11-8.19 (m, 8 H, ArH), 8.45 (d, $^3J_{H,\,H}$ = 8.7 Hz, 6 H, ArH), 8.60 (s, 1 H, ArH) ppm; elemental analysis calcd (%) for $C_{48}H_{44}N_6O_{18}S_6$ (1185.28): C 48.64, H 3.74, N 7.09, S 16.23; found C 48.49, H 3.79, N 7.08, S 16.15.

Compound S15. Colorless solid; ^{1}H NMR (300 MHz, DMSO-d_6/DMF-d_7): δ = 0.83 (t, $^3J_{H,\,H}$ = 6.6 Hz, 3 H, CH_3), 1.12 (m, 10 H, CH_2), 1.53 (m. 2 H, CH_2), 3.70 (m, 2 H, CH_2), 6.05 (s, 2 H, NH_2), 6.55 (d, $^3J_{H,\,H}$ = 8.7 Hz, 2 H, ArH), 7.13 – 8.24 (m, 16 H, ArH), 8.55 (s, 1 H, ArH), 10.61 (br, 1 H, NH), 11.04 (br, 1 H, NH) ppm; MS (HiRes MALDI-FT, 3-HPA): *m/z* = 807.1629 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{36}{}^1H_{40}{}^{14}N_4{}^{16}O_8{}^{32}S_4Na$) 807.1627.

Compound 6. The synthesis of the compound is depicted in Scheme S5. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.60); colorless solid, yield 67%; m.p. 190 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H,\,H}$ = 6.6 Hz, 3 H, CH_3), 1.27 (m, 10 H, CH_2), 1.74 (m. 2 H, CH_2), 3.72 (m, 2 H, CH_2), 7.23 (d, $^3J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 7.33 (d, $^3J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 7.59 – 7.80 (m, 12 H, ArH), 7.80 – 8.11 (m, 32 H, ArH), 8.45 (s, 2 H, ArH), 8.53 (s, 4 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.57, 26.56, 28.92, 29.06, 29.98, 31.66, 49.99, 122.58, 127.75, 127.87, 128.01, 128.05, 129.43, 129.65, 129.75, 129.78, 129.89, 130.31, 130.83, 131.86, 131.91, 132.18, 132.69, 135.39, 135.53, 136.39, 138.19, 139.79, 139.99, 142.27 ppm; MS (MALDI-TOF., DCTB Mix 1:10): *m/z* = 1912.19 $[M+Na]^+$, 1928.16 $[M+K]^+$; elemental analysis calcd (%) for $C_{92}H_{75}N_5O_{20}S_{10}$ (1891.25): C 58.43, H 4.00, N 3.70, S 16.95; found C 58.72, H 4.10, N 3.74, S 16.71.



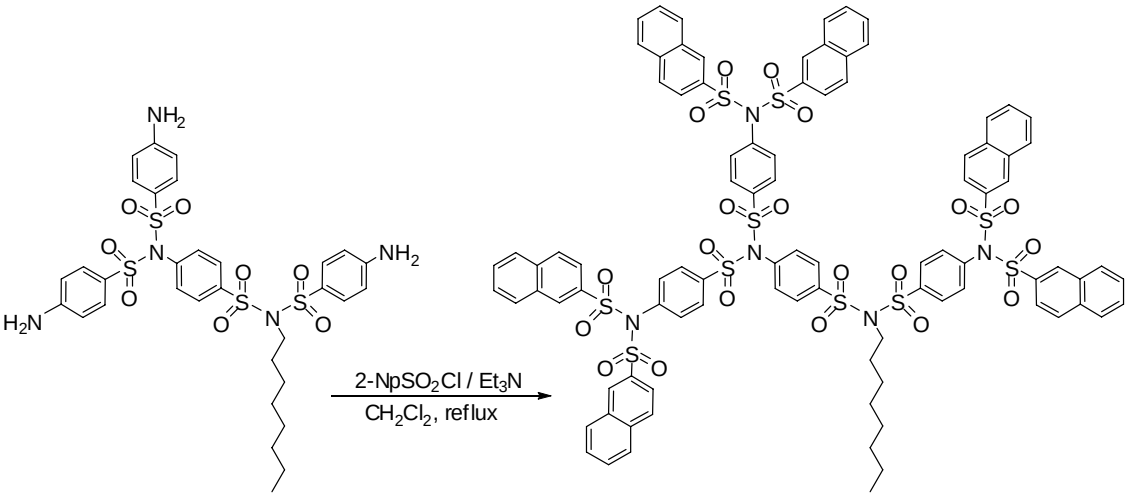
S16 **S17**



6

Scheme S 5. Synthesis of compound **6**.

Compound S17. Obtained from tetranitro-derivative **S16**.[1] Colorless solid; ^{1}H NMR (300 MHz, DMSO): δ = 0.88 (t, $^3J_{H,\ H}$ = 6.6 Hz, 3 H, CH_3), 1.20 (m, 10 H, CH_2), 1.28 (m, 2H, CH_2), 3.66 (m, 2 H, CH_2), 6.07 (s, 4 H, NH_2 aromatic), 6.59 (d, $^3J_{H,\ H}$ = 9.0 Hz, 4 H, ArH), 7.23 (d, $^3J_{H,\ H}$ = 9.0 Hz, 4 H, ArH), 7.49 (d, $^3J_{H,\ H}$ = 9.0 Hz, 4 H, ArH), 7.65 (d, $^3J_{H,\ H}$ = 8.7 Hz, 4 H, ArH), 10.49 (s, 2 H, NH aromatic) ppm; MS (HiRes MALDI-FT, 3-HPA): *m/z* = 772.1577 [*M*+Na]$^+$, calcd monoisotopic peak ($^{12}C_{32}{}^1H_{39}{}^{14}N_5{}^{16}O_8{}^{32}S_4Na$) 772.1579.



S18 **7**

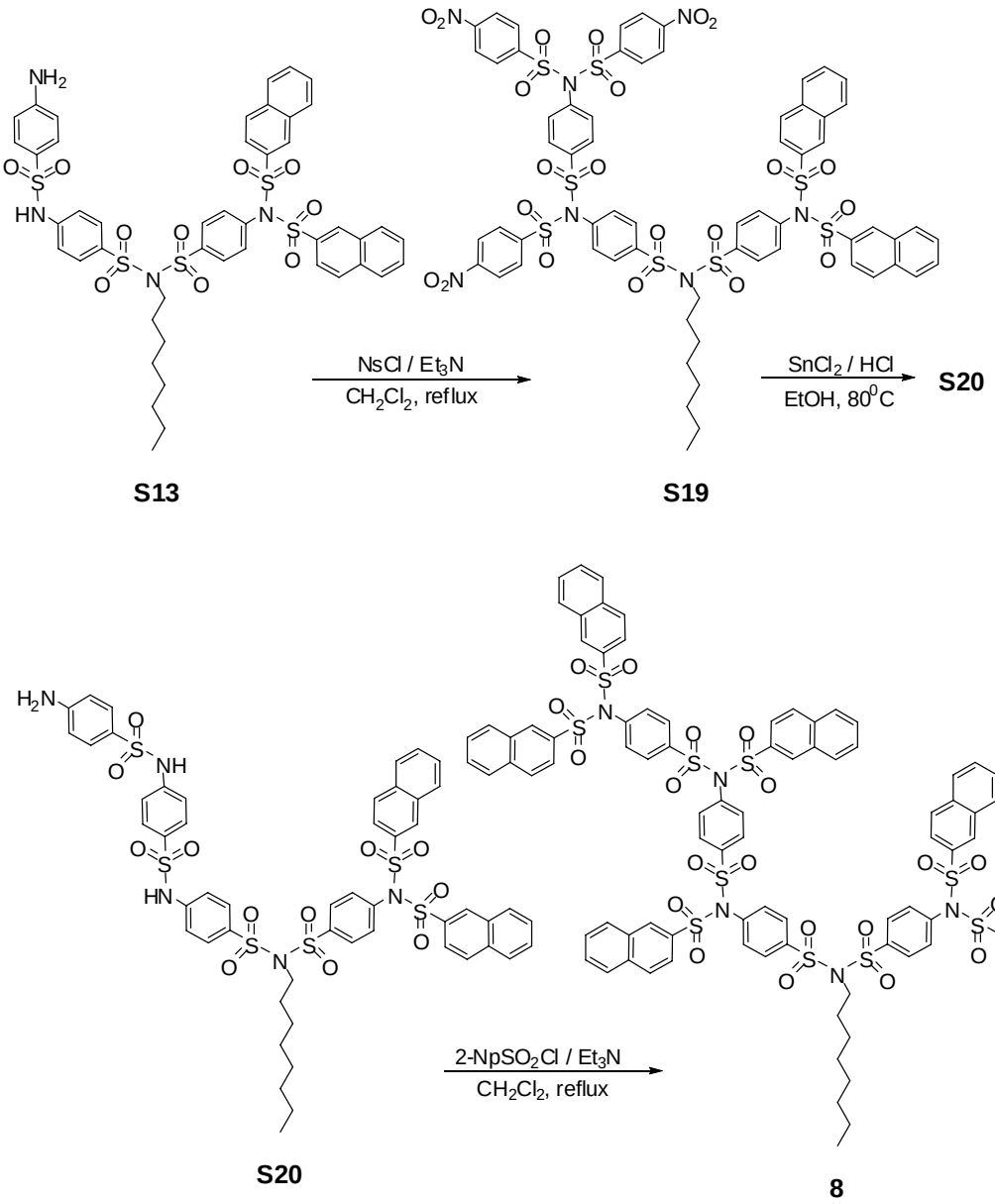
Scheme S 6. Synthesis of compound **7**.

Compound 7. The synthesis is shown in Scheme S6. The triamine **S18** was prepared by the published procedure. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.60); colorless solid; m.p. 131 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H,\ H}$ = 6.3 Hz, 3 H, CH_3), 1.26 (m, 10 H, CH_2), 1.74 (m. 2 H, CH_2), 3.72 (m, 2 H, CH_2), 7.16 (d, $^3J_{H,\ H}$ = 8.4 Hz, 2 H, ArH), 7.23 – 7.36 (m, 4 H, ArH), 7.59 – 7.83 (m, 16 H, ArH), 7.87 – 8.10 (m, 30 H, ArH), 8.49 (s, 6 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.09, 22.60, 26.59, 28.94, 29.14, 30.09, 31.70, 50.11, 122.74, 122.83, 127.97, 128.02, 128.05, 129.15, 129.49, 129.66, 129.75, 129.77, 129.89, 129.91, 130.78, 130.82, 131.85, 131.87, 132.29, 132.59, 132.71, 135.52, 135.61, 138.41, 139.38, 139.69, 140.04, 141.01, 141.75 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1912.21 [*M*+Na]$^+$, elemental analysis calcd (%) for $C_{92}H_{75}N_5O_{20}S_{10}$ (1891.25): C 58.43, H 4.00, N 3.70, S 16.95; found C 58.22, H 4.17, N 3.41, S 17.01.

Compound 8. The synthesis is shown in Scheme S7. Recrystallized from hot benzene; colorless solid; yield 53%; m.p. 251 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^3J_{H,\ H}$ = 6.3 Hz, 3 H, CH_3), 1.26 (br. s, 10 H, CH_2), 1.72 (br. s, 2 H, CH_2), 3.70 (m, 2 H, CH_2), 7.18-7.28 (m, 6 H, ArH), 7.35 (d, $^3J_{H,\ H}$ = 8.7 Hz, 2 H, ArH), 7.60 – 7.80 (m, 12 H, ArH), 7.82 – 8.14 (m, 34 H, ArH), 8.42 (s, 1 H, ArH), 8.47 (s, 2 H, ArH), 8.49 (s, 1 H, ArH), 8.54 (s, 2 H, ArH) ppm; MS (HiRes ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1912.2140 [*M*+Na]$^+$, calcd monoisotopic peak ($^{12}C_{92}{}^1H_{75}{}^{14}N_5{}^{16}O_{20}{}^{32}S_{10}Na$) 1912.2110 elemental analysis calcd (%) for $C_{92}H_{75}N_5O_{20}S_{10}$ (1891.25): C 58.43, H 4.00, N 3.70, S 16.95; found C 58.67, H 4.02, N 3.87, S 16.93.

Compound S19. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.76); yellowish solid; yield 83%; m.p. 149 – 153 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,\ H}$ = 6.3 Hz, 3 H, CH_3), 1.29 (m, 10 H, CH_2), 1.75 (m, 2H, CH_2), 3.73 (m, 2 H, CH_2), 7.23 – 7.38 (m, 6 H, ArH), 7.63 – 7.81 (m, 4 H, ArH), 7.89 – 8.09 (m, 14 H, ArH), 8.14 (d, $^3J_{H,\ H}$ = 8.7 Hz, 2 H, ArH), 8.20 (d, $^3J_{H,\ H}$ = 8.7 Hz, 4 H, ArH), 8.40 – 8.57 (m, 8 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.09, 22.60, 26.59, 28.96, 29.15, 30.13, 31.71, 50.15, 122.80, 124.60, 124.72, 127.99, 128.05, 129.20, 129.64, 129.68, 129.79, 129.91, 130.07, 130.16,

130.79, 131.89, 132.10, 132.28, 132.64, 135.53, 135.61, 137.95, 138.76, 139.53, 140.62, 140.66, 142.21, 143.63, 143.71, 151.11, 151.24 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1552.11 $[M + Na]^+$; elemental analysis calcd (%) for $C_{64}H_{55}N_7O_{22}S_8$ (1530.68): C 50.22, H 3.62, N 6.41, S 16.76; found C 49.98, H 3.78, N 6.34, S 16.69

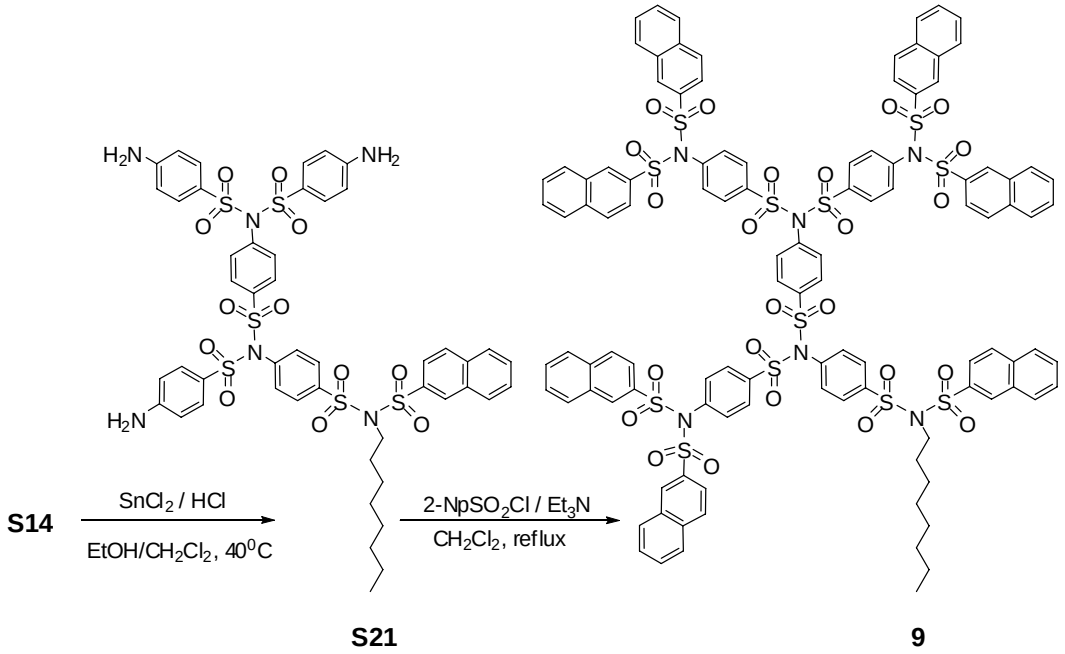


Scheme S 7. Synthesis of compound **8**.

Compound S20. Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.68 (m, 2H, CH_2), 3.65 (m, 2 H, CH_2), 6.58 (m, 2 H, ArH), 7.14 (m, 4 H, ArH), 7.25 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, ArH), 7.49 (m, 2 H, ArH), 7.58 – 7.84 (m, 8 H, ArH), 7.85 – 8.12 (m, 10 H, ArH), 8.48 (s, 2 H, ArH) ppm; MS (HiRes MALDI-FT, 3-HPA): *m/z* = 1152.1761 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{52}{}^1H_{51}{}^{14}N_5{}^{16}O_{12}{}^{32}S_6Na$) 1152.1756.

Compound 9. The synthesis is depicted in Scheme S8. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.40); colorless solid; yield 46%; m.p. 141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.18 (m, 10 H, CH_2), 1.69 (m. 2 H, CH_2), 3.73 (m, 2 H, CH_2), 7.20 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.22 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.25 –

7.38 (m, 6 H, ArH), 7.58 – 8.16 (m, 52 H, ArH), 8.49 (s, 4 H, ArH), 8.51 (s, 2 H, ArH), 8.58 (s, 1 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.09, 22.57, 26.53, 28.90, 29.04, 29.94, 31.66, 49.98, 122.57, 122.73, 122.79, 127.84, 128.01, 128.06, 129.46, 129.64, 129.66, 129.70, 129.76, 129.90, 129.95, 130.29, 130.29, 130.83, 131.83, 131.87, 131.88, 132.17, 132.48, 132.72, 132.78, 135.37, 135.51, 135.55, 136.26, 138.06, 139.08, 139.54, 139.62, 140.07, 140.12, 140.64, 142.49 ppm; MS (MALDI-TOF, DCTB mix): *m/z* = 2256.94 $[M+Na]^+$; elemental analysis calcd (%) for $C_{108}H_{86}N_6O_{24}S_{12}$ (2236.64): C 58.00, H 3.88, N 3.76, S 17.20; found C 58.15, H 4.02, N 3.75, S 17.31.



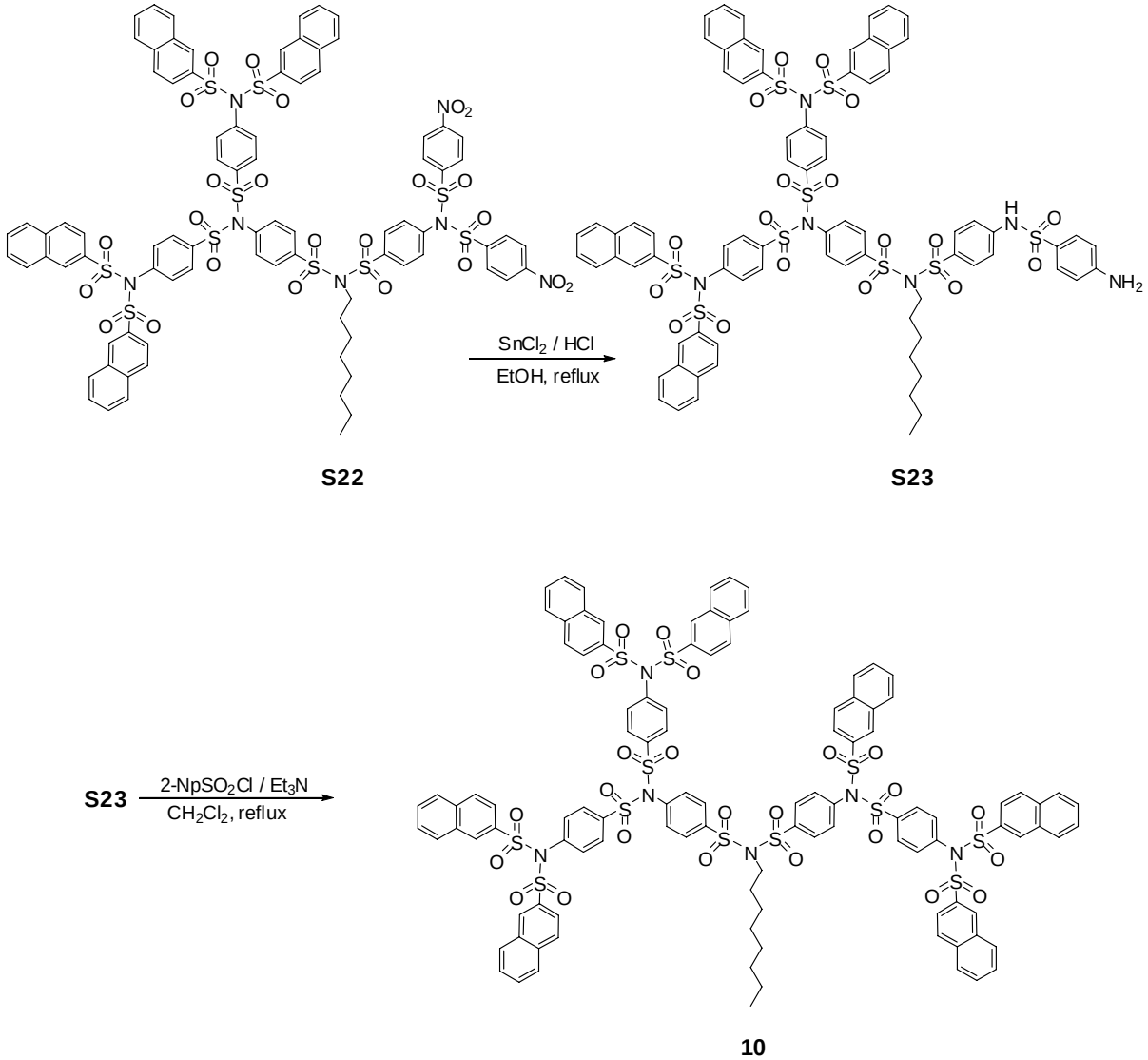
Scheme S 8. Synthesis of **9**.

Compound S21. Yellowish solid; ^{1}H NMR (300 MHz, DMSO): δ = 0.82 (t, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.55 (m, 2H, CH_2), 3.77 (m, 2 H, CH_2), 6.63 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 6.65 (d, $^3J_{H,H}$ = 9.0 Hz, 4 H, ArH), 7.16 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 7.26 – 7.50 (m, 8 H, ArH), 7.71 – 8.24 (m, 10 H, ArH), 8.49 (s, 1 H, ArH) ppm; MS (HiRes ESI, $CHCl_3$/MeOH): *m/z* = 1117.1705 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{48}{}^1H_6{}^{14}N_6{}^{16}O_{12}{}^{32}S_6Na$) 1117.1709.

Compound 10. The synthesis is shown in Scheme S9. Chromatographic separation (silica gel, $CHCl_3$, R_f = 0.40); colorless solid; yield 74%; m.p. 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.76 (m. 2 H, CH_2), 3.75 (m, 2 H, CH_2), 7.18 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.23 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.25 – 7.35 (m, 6 H, ArH), 7.58 – 8.10 (m, 52 H, ArH), 8.45 (s, 1 H, ArH) 8.47 (s, 4 H, ArH) 8.51 (s, 2 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.58, 26.58, 28.94, 29.11, 30.25, 31.68, 50.21, 122.68, 122.74, 122.85, 127.99, 128.03, 129.26, 129.43, 129.63, 129.67, 129.71, 129.75, 129.77, 129.89, 130.03, 130.79, 130.81, 130.98, 131.81, 131.84, 131.88, 132.34, 132.42, 132.71, 135.17, 135.49, 135.53, 135.57, 135.58, 135.64, 138.49, 139.02, 139.66, 139.76, 140.07, 140.39, 141.21, 141.58 ppm; MS (MALDI-FT, DCTB mix): *m/z* = 2257.23 $[M+Na]^+$; elemental analysis calcd (%) for $C_{108}H_{86}N_6O_{24}S_{12}$ (2236.64): C 58.00, H 3.88, N 3.76, S 17.20; found C 58.11, H 3.89, N 3.75, S 17.08.

Compound S23. The compound was obtained from the previously described dinitro-derivative **S22**.[1] Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.23 (m, 10 H, CH_2), 1.71 (m, 2H, CH_2), 3.64 (m, 2 H, CH_2), 4.29 (s, 2H, NH_2), 6.59 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.11 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.19 (d, $^3J_{H,H}$ = 8.7

Hz, 2 H, ArH), 7.31 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 7.59 – 7.85 (m, 16 H, ArH), 7.88 – 8.08 (m, 18 H, ArH), 8.49 (s, 4 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.11, 22.60, 26.57, 28.91, 29.11, 30.14, 31.69, 49.87, 114.06, 118.18, 122.71, 125.98, 128.04, 128.06, 128.36, 129.37, 129.62, 129.68, 129.77, 129.94, 130.84, 131.84, 132.12, 132.72, 133.52, 135.45, 135.53, 138.16, 139.73, 140.02, 141.96, 142.75, 151.51 ppm; MS (HiRes MALDI-FT, 3-HPA): *m/z* = 1687.1937 [*M*+Na]$^{+}$, calcd monoisotopic peak ($^{12}C_{78}{}^{1}H_{68}{}^{14}N_{6}{}^{16}O_{18}{}^{32}S_{9}Na$) 1687.1974.



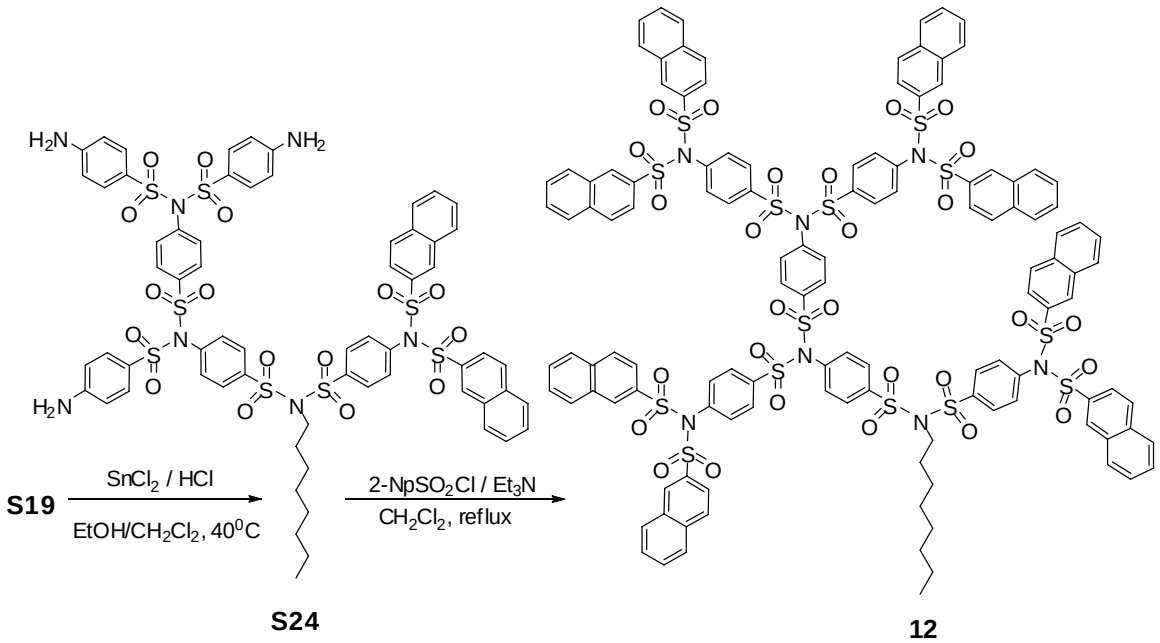
Scheme S 9. Synthesis of compound **10**.

Compound 11. The compound was obtained from the corresponding symmetrical tetraamine[1] via the standard persulfonylation procedure. Purified by column chromatography (R_f = 0.40, silica gel, $CHCl_3$); colorless solid; yield 54%; m.p. 185 – 188 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^{3}J_{H,\,H}$ = 6.3 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.78 (m. 2H, CH_2), 3.76 (m, 2 H, CH_2), 7.18 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 7.28 (m, 4 H, ArH), 7.59 – 7.75 (m, 16 H, ArH), 7.79 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 8 H, ArH), 7.85 – 8.09 (m, 40 H, ArH), 8.46 (m, 8 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.58, 26.58, 28.94, 29.11, 30.37, 31.66, 50.29, 122.72, 127.99, 128.02, 129.41, 129.69, 129.74, 129.89, 130.78, 131.82, 132.32, 132.70, 135.48, 135.50, 138.54, 139.65, 140.05, 141.43 ppm; MS (MALDI-TOF, DCTB Mix 1:10): *m/z* = 2601.89 [*M* + Na]$^{+}$, 2618.84 [*M* + K]$^{+}$, $C_{124}H_{97}N_7O_{28}S_{14}Na$ requires

2602.24, $C_{124}H_{97}N_7O_{28}S_{14}K$ requires 2618.21; elemental analysis calcd (%) for $C_{124}H_{97}N_7O_{28}S_{14}$ (2582.04): C 57.68, H 3.79, N 3.80, S 17.39; found C 57.97, H 3.94, N 3.76, S 17.43.

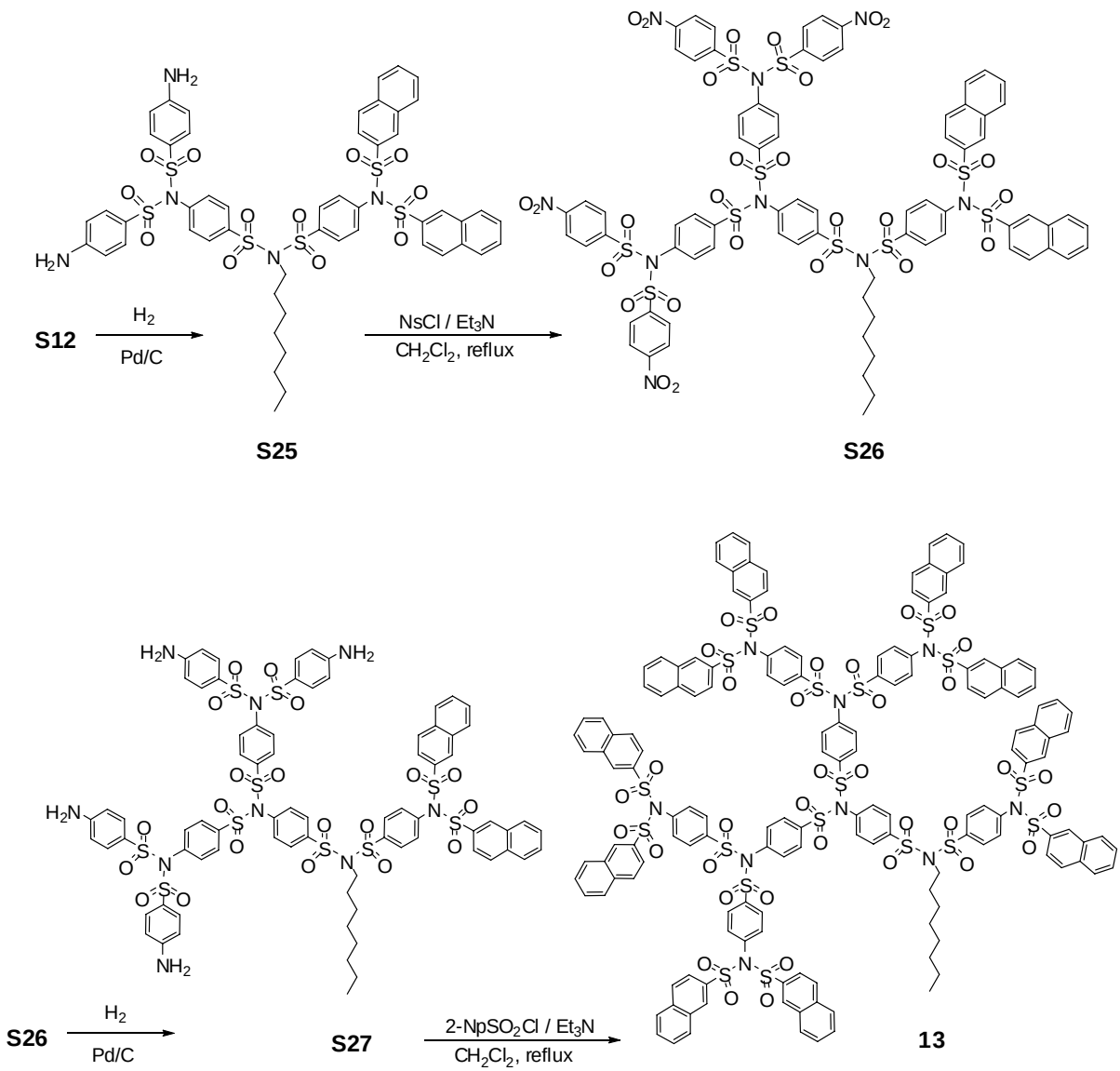
Compound 12. The synthesis is shown in Scheme S10. Chromatographic separation (silica gel, $CHCl_3$, R_f = 0.40); colorless solid; yield 60%; m.p. 175 °C; ^{1}H NMR (300 MHz, DMSO): δ = 0.73 (t, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.08 (m, 10 H, CH_2), 1.54 (m, 2H, CH_2), 3.75 (m, 2 H, CH_2), 7.40 – 7.59 (m, 12 H, ArH), 7.60 – 7.96 (m, 30 H, ArH), 7.98 – 8.30 (m, 30 H, ArH), 8.51 (s, 2 H, ArH), 8.54 (s, 4 H, ArH), 8.56 (s, 2 H, ArH) ppm; ^{13}C NMR (75.5 MHz, DMSO): δ = 14.31, 22.43, 26.25, 28.74, 28.95, 29.81, 31.54, 50.09, 122.79, 128.45, 128.58, 129.65, 129.95, 130.19, 130.40, 130.62, 130.89, 130.99, 131.87, 131.91, 133.09, 133.33, 133.51, 135.17, 135.21, 135.25, 135.55, 135.59, 138.31, 138.83, 139.08, 139.45, 139.55, 139.69, 140.44 ppm; MS (MALDI-FT, DCTB mix): *m/z* = 2602.24 $[M + Na]^+$; elemental analysis calcd (%) for $C_{124}H_{97}N_7O_{28}S_{14}$ (2582.04): C 57.68, H 3.79, N 3.80, S 17.39; found C 57.63, 3.75, N 3.82, S 17.53.

Compound S24. Yellowish solid; ^{1}H NMR (300 MHz, DMSO): δ = 0.82 (t, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.55 (m, 2H, CH_2), 3.77 (m, 2 H, CH_2), 6.63 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 6.65 (d, $^3J_{H,H}$ = 9.0 Hz, 4 H, ArH), 7.16 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, ArH), 7.26 – 7.50 (m, 10 H, ArH), 7.71 – 8.24 (m, 18 H, ArH), 8.49 (s, 2 H, ArH) ppm; MS (HiRes ESI, $CHCl_3$/MeOH): *m/z* = 1462.1800 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{64}{}^1H_{61}{}^{14}N_7{}^{16}O_{16}{}^{32}S_8Na$) 1462.1838.



Scheme S 10. Synthesis of compound **12**.

Compound 13. The synthesis is shown in Scheme S11. Chromatographic separation (silica gel, CH_2Cl_2, R_f = 0.20); colorless solid; yield 62%; m.p. 123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.28 (m, 10 H, CH_2), 1.70 (br. s, 2H, CH_2), 3.69 (m, 2 H, CH_2), 7.16 – 7.30 (m, 16 H, ArH), 7.58 – 7.66 (m, 20 H, ArH), 7.75 – 7.99 (m, 56 H, ArH), 8.42 (s, 8 H, ArH), 8.46 (s, 2 H, ArH) ppm; MS (MALDI-TOF, DCTB mix): *m/z* = 3292.26 $[M + Na]^+$; elemental analysis calcd (%) for $C_{156}H_{119}N_9O_{36}S_{18}$ (3272.82): C 57.25, H 3.66, N 3.85, S 17.64; found C 56.99, 3.65, N 3.84, S 17.58.



Scheme S 11. Synthesis of compound **13**.

Compound S26. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.20); yellowish solid; yield 68%; m.p. 204°C; ^{1}H NMR (500 MHz, DMSO-D_6): δ = 0.78 (t, $^3J_{H,\,H}$ = 6.3 Hz, 3 H, CH_3), 1.17 (m, 10 H, CH_2), 1.56 (br. s, 2 H, CH_2), 3.77 (m, 2 H, CH_2), 7.38 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 7.45 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 7.49 (d, $^3J_{H,\,H}$ = 9 Hz, 4 H, ArH), 7.71 (m, 2 H, ArH), 7.78-7.82 (m, 4 H, ArH), 7.89 (d, $^3J_{H,\,H}$ = 9 Hz, 4 H, ArH), 7.97 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 8.08 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 8.10 (d, $^3J_{H,\,H}$ = 9 Hz, 4 H, ArH), 8.15 (d, $^3J_{H,\,H}$ = 9 Hz, 8 H, ArH), 8.18 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 8.46 (s, 2 H, ArH), 8.50 (d, $^3J_{H,\,H}$ = 9 Hz, 8 H, ArH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 13.83, 21.95, 25.76, 28.25, 28.47, 29.33, 31.08, 49.56, 122.25, 123.26, 125.11, 126.88, 127.96, 128.09, 129.14, 129.68, 129.87, 129.97, 130.05, 130.15, 130.36, 131.34, 132.56, 132.77, 132.88, 134.69, 135.05, 137.60, 138.09, 138.54, 139.55, 140.39, 141.19, 142.39, 151.09 ppm; elemental analysis calcd (%) for $C_{76}H_{63}N_9O_{28}S_{10}$ (1871.01): C 48.79, H 3.39, N 6.74, S 17.14; found C 48.74, 3.41, N 6.82, S 17.15.

Compound S27. ^{1}H NMR (500 MHz, DMSO-D_6): δ = 0.81 (t, $^3J_{H,\,H}$ = 6.3 Hz, 3 H, CH_3), 1.12 (m, 10 H, CH_2), 1.57 (br. s, 2 H, CH_2), 3.79 (m, 2 H, CH_2), 6.42 (s, 8 H, NH_2), 6.63 (d, $^3J_{H,\,H}$ = 8.7 Hz, 8 H, ArH),7.28-7.38 (m, 12 H, ArH), 7.46 (d, $^3J_{H,\,H}$ = 9 Hz, 2 H, ArH), 7.53

(d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 7.72 (m, 2 H, ArH), 7.81-7.85 (m, 8 H, ArH), 7.98 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 8.08-8.15 (m, 6 H, ArH), 8.20 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 8.49 (s, 2 H, ArH) ppm; MS (MALDI-TOF, DCTB mix): *m/z* = 1772.09 $[M + Na]^+$.

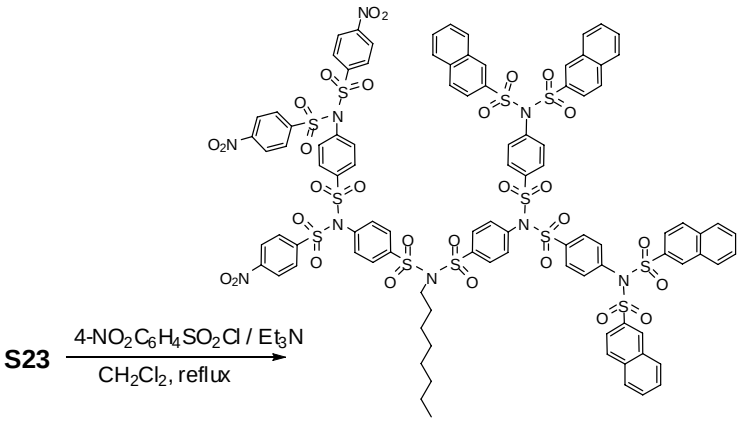
Compound 14. The synthesis is shown in Scheme S12. Chromatographic separation (silica gel, CH_2Cl_2, R_f = 0.20); colorless solid; yield 53%; m.p. 121 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.27 (m, 10 H, CH_2), 1.70 (br. s, 2 H, CH_2), 3.69 (m, 2 H, CH_2), 7.15 – 7.19 (m, 4 H, ArH), 7.22-7.32 (m, 12 H, ArH), 7.61 – 7.71 (m, 20 H, ArH), 7.72-7.78 (m, 10 H, ArH), 7.88 – 8.01 (m, 46 H, ArH), 8.45 (s, 4 H, ArH), 8.47 (s, 6 H, ArH) ppm; MS (MALDI-TOF, DCTB mix): *m/z* = 3292.08 $[M + Na]^+$; elemental analysis calcd (%) for $C_{156}H_{119}N_9O_{36}S_{18}$ (3272.82): C 57.25, H 3.66, N 3.85, S 17.64; found C 57.21, 3.59, N 3.82, S 17.53.

Compound S28. Purified by column chromatography; (silica gel, $CHCl_3$, R_f = 0.20); yellowish solid; yield 32%; m.p. 166 – 176 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.89 (t, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 1.31 (m, 10 H, CH_2), 1.78 (m, 2H, CH_2), 3.79 (m, 2 H, CH_2), 7.25 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.29 – 7.40 (m, 8 H, ArH), 7.63 – 7.94 (m, 16 H, ArH), 7.95 – 8.25 (m, 24 H, ArH), 8.39 – 8.53 (m, 10 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.58, 26.57, 28.95, 29.10, 30.32, 31.68, 50.28, 122.75, 124.57, 124.67, 128.02, 129.43, 129.66, 129.72, 129.75, 129.91, 130.09, 130.20, 130.81, 131.83, 132.11, 132.29, 132.42, 132.75, 135.51, 138.07, 138.63, 138.79, 139.63, 140.09, 140.49, 141.19, 141.92, 143.56, 143.65, 151.11, 151.16 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 2242.13 $[M + Na]^+$; elemental analysis calcd (%) for $C_{96}H_{77}N_9O_{30}S_{12}$ (2221.46): C 51.90, H 3.49, N 5.67, S 17.32; found C 52.13, H 3.56, N 5.59, S 17.17.

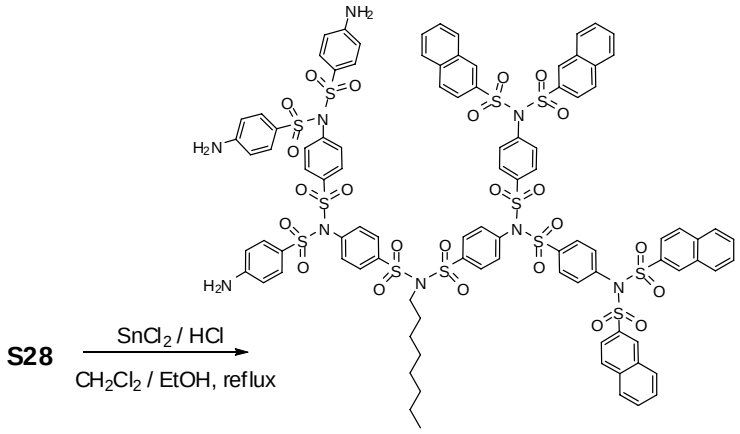
Compound S29. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.28 (m, 10 H, CH_2), 1.74 (br. s, 2 H, CH_2), 3.72 (m, 2 H, CH_2), 4.32 (s, 4 H, NH_2), 4.34 (s, 2 H, NH_2), 6.63-6.69 (m, 6 H, ArH), 8.49 (s, 4 H, ArH) ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 2152.11 $[M + Na]^+$.

Compound 15. The synthesis is shown in Scheme S13. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.42); Colorless solid; yield: 60%; m. p. 150-160°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.77 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.1 (m, 10 H, CH_2), 1.6 (m, 2 H, CH_2), 3.75 (m, 2 H, CH_2), 7.01 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, ArH), 7.25 (d, $^3J_{H,H}$ = 8.5 Hz, 8 H, ArH), 7.48 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, ArH), 7.52 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.64 (d, $^3J_{H,H}$ = 7.4 Hz, 8 H, ArH), 7.72 (s, 2 H, ArH), 7.78 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.90 (m, 32 H, ArH), 8.17 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, ArH), 8.42 (s, 8 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.96, 22.44, 26.40, 28.78, 28.96, 29.87, 31.54, 50.32, 122.54, 127.79, 127.89, 129.59, 129.62, 129.66, 129.79, 130.28, 130.53, 130.72, 131.12, 131.75, 132.66, 134.26, 135.40, 135.46, 136.59, 139.78, 139.85, 141.39 ppm; MS (HiRes MALDI pos.): *m/z* = 2602.2364 $[M+Na]^+$, 2618.2193 $[M+K]^+$; elemental analysis calcd (%) for $C_{124}H_{97}N_7O_{28}S_{14}$ (2582.04): C 57.68, H 3.79, N 3.80, S 17.39; found C 57.41, H 3.80, N 3.68, S 17.24.

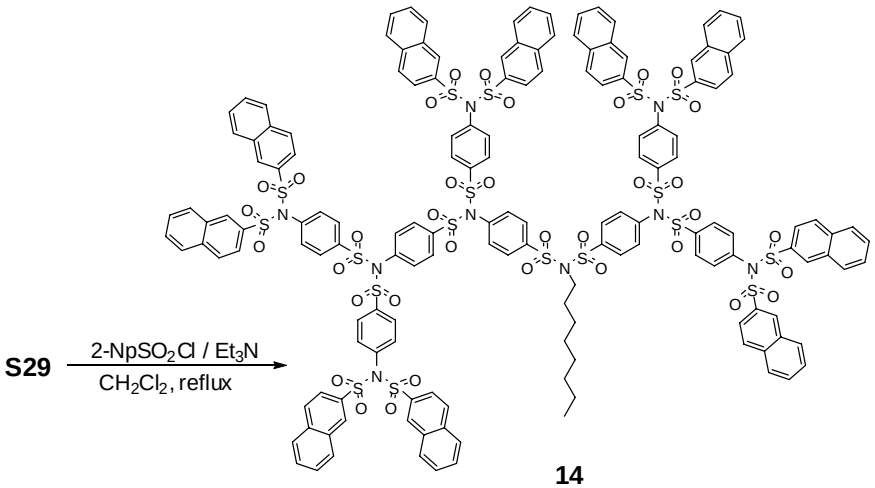
Compound S30. To a solution of *n*-octylamine (0.75 g, 5.80 mmol) and Et_3N (5 ml, 36 mmol) in dichloromethane (10 mL) 3-nitrophenylsulfonyl chloride (4 g, 18 mmol) was added. The solution was refluxed for 3 h. The solvent was removed under reduced pressure; the viscous residue was triturated with methanol. The solid precipitate was filtered through a glass filter and thoroughly washed with cold methanol to give a colorless solid. Yield: 2.75 (95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.28 (m, 10 H, CH_2), 1.75 (m. 2 H, CH_2), 3.82 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, CH_2), 7.86 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, ArH), 8.47 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, ArH), 8.58 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 8.91 (s, 2 H, ArH); ^{13}C NMR (75.5 MHz, CDCl3): δ = 14.05, 22.58, 26.46, 28.89, 29.04, 30.00, 31.67, 50.47, 123.56, 128.54, 130.70, 133.83, 141.65, 148.25, 166.25 ppm; MS (ESI pos.,$CHCl_3/CH_3OH$): *m/z* = 522.00 [*M*+Na]+; elemental analysis calcd (%) for $C_{20}H_{25}N_3O_8S_2$ (499.56): C 48.09, H 5.04, N 8.41, S 12.84; found C 48.09, H 5.14, N 8.28, S 12.89.



S28

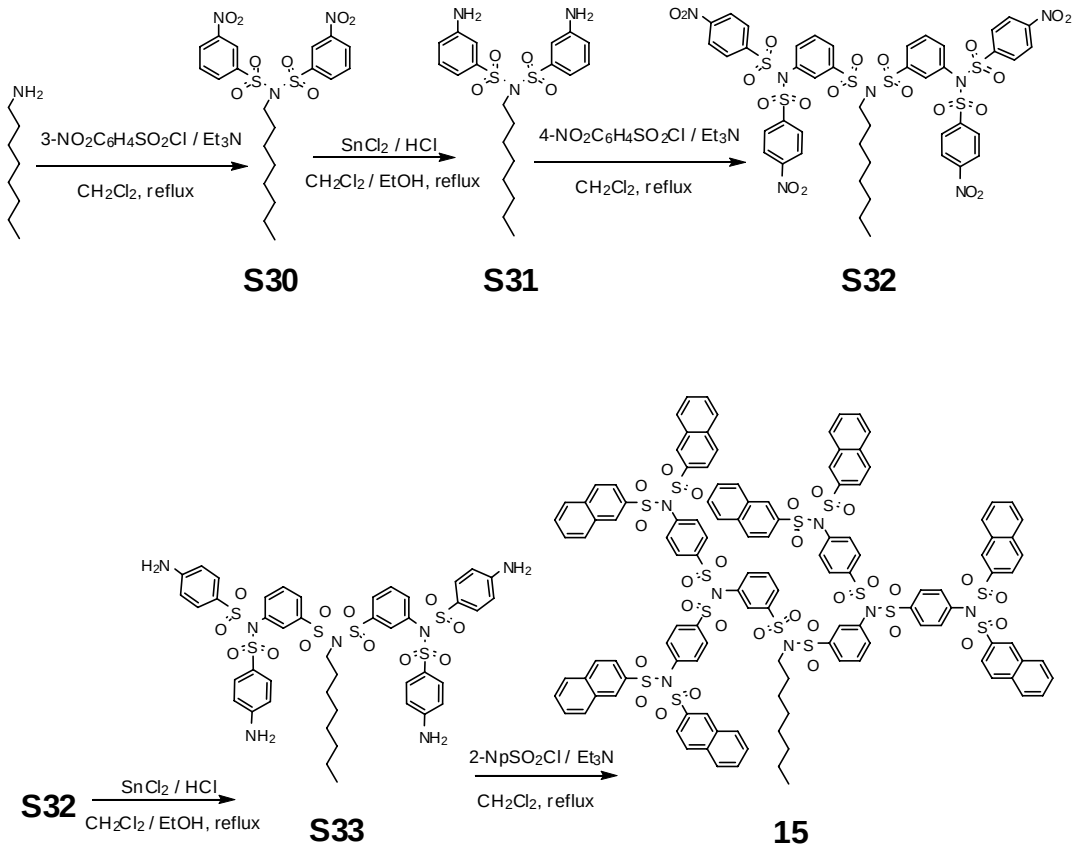


S29



14

Scheme S 12. Synthesis of compound **14**.

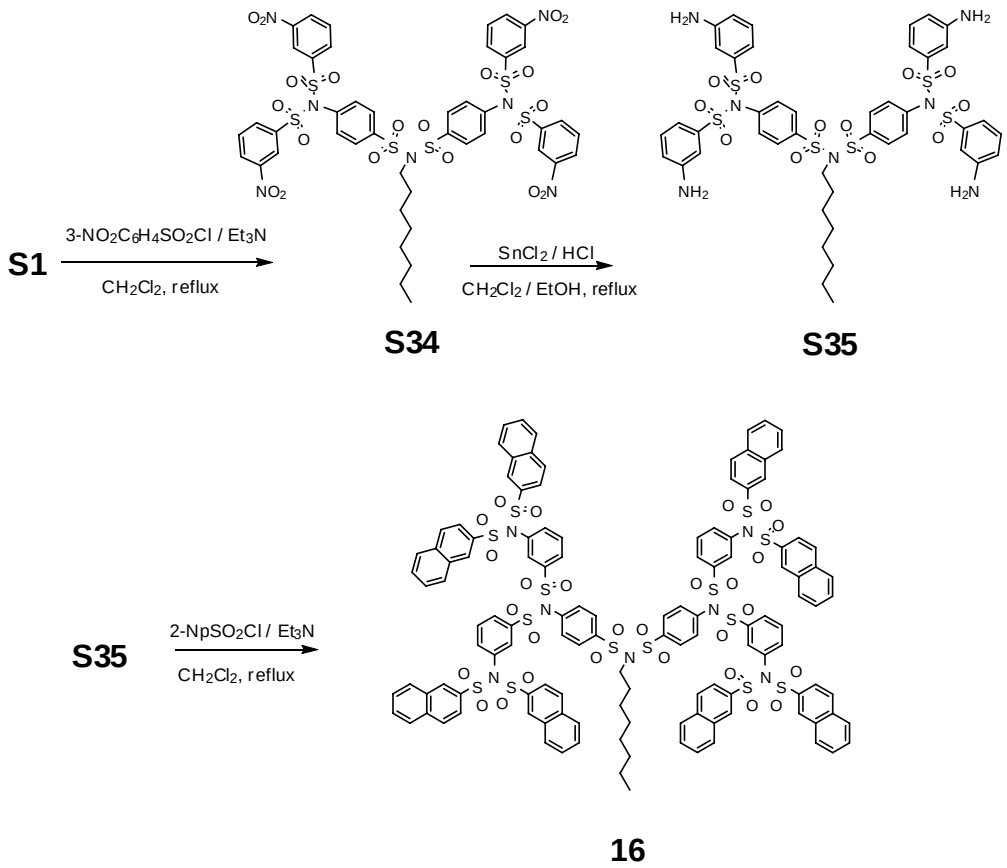


Scheme S 13. Synthesis of compound **15**.

Compound S31. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^{3}J_{H,\,H}$ = 6.9 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.69 (m. 2 H, CH_2), 3.65 (t, $^{3}J_{H,\,H}$ = 8.1 Hz, 2 H, CH_2), 3.97 (s, 4 H, NH_2), 6.9 (d, $^{3}J_{H,\,H}$ = 6 Hz, 2 H, ArH), 7.25-7.4 (m, 6 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.62, 25.54, 26.61, 28.96, 29.10, 29.82, 30.33, 31.73, 49.66, 113.67, 117.515, 119.79, 129.79, 140.86, 147.18 ppm; MS (ESI pos.,$CHCl_3$/CH_3OH): *m/z* = 462.14 [*M*+Na]+.

Compound S32. No purification required; colorless solid; yield 88%; m.p. 260°C; ^{1}H NMR (300 MHz, DMSO): δ = 0.83 (t, $^{3}J_{H,\,H}$ = 6.9 Hz, 3 H, CH_3), 1.08 (m, 10 H, CH_2), 1.36 (m. 2 H, CH_2), 3.68 (m, 2 H, CH_2), 7.71 (m, 4 H, ArH), 7.87 (t, $^{3}J_{H,\,H}$ = 8.1 Hz, 2 H, ArH), 8.17 (m, 10 H, ArH), 8.53 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 8 H, ArH); ^{13}C NMR (75.5 MHz, DMSO): δ = 14.38, 22.47, 28.70, 28.87, 31.57, 125.27, 125.70, 127.38, 128.80, 130.43, 130.67, 132.24, 133.83, 137.07, 143.00, 151.59 ppm; elemental analysis calcd (%) for $C_{44}H_{41}N_7O_{20}S_6$ (1180.22): C 44.78, H 3.5, N 8.31, S 16.30; found C 45.02, H 3.43, N 8.41, S 16.54.

Compound S33. ^{1}H NMR (300 MHz, DMSO): δ = 0.83 (t, $^{3}J_{H,\,H}$ = 6.9 Hz, 3 H, CH_3), 1.19 (m, 10 H, CH_2), 1.36 (m, 2 H, CH_2), 3.60 (m, 2 H, CH_2), 6.42 (s, 8 H, NH_2), 6.60 (d, $^{3}J_{H,\,H}$ = 8.7 Hz 8 H, ArH), 7.37 (m, 10 H, ArH), 7.56 (s, 2 H, ArH), 7.72 (t, $^{3}J_{H,\,H}$ = 8.1 Hz, 2 H, ArH), 7.97 (d, $^{3}J_{H,\,H}$ = 8.1 Hz 2 H, ArH); MS (HiRes ESI pos.,$CHCl_3$/CH_3OH): *m/z* = 1082.1656 $[M+Na]^{+}$, 1098.1361 $[M+K]^{+}$.



Scheme S 14. Synthesis of compound **16**.

Compound 16. The synthesis is shown in Scheme S14. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.46). Yield: 79%; m.p. 180-190°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.77 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.1 (m, 10 H, CH_2), 1.6 (m, 2 H, CH_2), 3.57 (m, 2 H, CH_2), 7.15 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.33 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H, ArH), 7.48 (t, $^3J_{H,H}$ = 7.9 Hz, 4 H, ArH), 7.55 (m, 8 H, ArH), 7.62 (m, 8 H, ArH), 7.78 (s, 4 H, ArH), 7.8-8.0 (m, 40 H, ArH), 8.45 (s, 8 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.96, 22.44, 26.40, 28.78, 28.96, 29.87, 31.54, 50.32, 122.70, 127.81, 127.99, 129.54, 129.64, 129.72, 129.74, 129.94, 130.16, 130.74, 131.78, 132.12, 135.45, 135.48, 135.52, 137.66, 138.21, 139.94, 141.34 ppm; MS (HiRes MALDI pos.): *m/z* = 2602.2389 $[M+Na]^+$, 2618.2193 $[M+K]^+$; elemental analysis calcd (%) for $C_{124}H_{97}N_7O_{28}S_{14}$ (2582.04): C 57.68, H 3.79, N 3.8, S 17.39; found C 57.44, H 3.88, N 3.81, S 17.12.

Compound S34. Purified by column chromatography (silica gel, $CHCl_3$, R_f = 0.32). Yellowish solid; yield: 64 %; m.p. 215°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.3 (m, 10 H, CH_2), 1.77 (m. 2 H, CH_2), 3.76 (m, 2 H, CH_2), 7.30 (d, $^3J_{H,H}$ = 9.3 Hz, 4 H, ArH), 7.90 (t, $^3J_{H,H}$ = 16.2 Hz, 4 H, ArH), 8.07 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), 8.29 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, ArH), 8.63 (d, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 8.80 (s, 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.06, 22.58, 26.57, 28.93, 29.11, 30.08, 31.70, 50.73, 123.98, 129.17, 129.78, 130.92, 132.01, 134.01, 138.01, 140.33, 142.01, 148.39 ppm; MS (ESI pos.,$CHCl_3$/CH_3OH): *m/z* = 1202.06 $[M+Na]_+$; elemental analysis calcd (%) for $C_{44}H_{41}N_7O_{20}S_6$ (1180.22): C 44.78, H 3.50, N 8.31, S 16.15; found C 45.06, H 3.75, N 8.13, S 16.15.

Compound S35. ^{1}H NMR (300 MHz, DMSO): δ = 0.84 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.22 (m, 10 H, CH_2), 1.57 (m, 2 H, CH_2), 3.76 (m, 2 H, CH_2), 5.79 (s, 8 H, NH_2), 6.83 (d, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 6.92 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, ArH), 7.05 (s, 4 H, ArH), 7.23 (t, $^3J_{H,H}$ = 7.8

Hz, 4 H, ArH), 7.33 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 4 H, ArH), 7.98 (d, $^{3}J_{H,\,H}$ = 8.7 Hz, 4 H, ArH); MS (HiRes MALDI pos.): *m/z* = 1082.1566 $[M+Na]^{+}$, 1098.1317 $[M+K]^{+}$

References

[1] Lukin, O.; Gramlich, V.; Kandre, R.; Zhun, I.; Felder, T.; Schalley, C. A.; Dolgonos, G. *J. Am. Chem. Soc*. **2006**, *128*, 8964-8974.