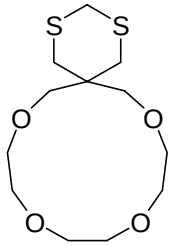
General Procedures

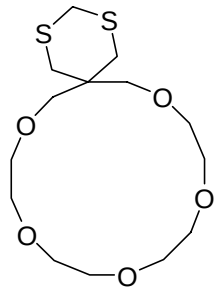
GC-MS spectra were recorded on a Hewlett-Packard HP 6890 Series GC system and mass selective detector. ^{1}H NMR spectra were recorded on a Varian Mercury (400 MHz). Proton NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet(sex), septet (sept), multiplet (m), and broad (br). All moisture-sensitive reactions were performed in oven dried glassware under a positive pressure of nitrogen unless otherwise noted. "Concentrated" refers to the removal of volatile solvents via distillation using a Buchi rotary evaporator at water aspirator pressure, followed by residual solvent removal at high vacuum when necessary. "Dried" refers to pouring onto, or passing through, anhydrous sodium sulfate or magnesium sulfate followed by filtration. Analytical thin layer chromatography (TLC) was carried out on Merck TLC plates precoated with silia gel 60 (0.25 mm layer thickness). Visualization was accomplished using UV light and/or an iodine chamber. Flash column chromatography (FCC) was performed on silica gel 60 (230-400 mesh). Solvent mixtures for TLC and FCC are reported in v1:v2 ratios. Immediately prior to use, diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl, and hexanes were distilled from calcium hydride. All other reagents were used as supplied, assuming reagent purity designated by supplier.

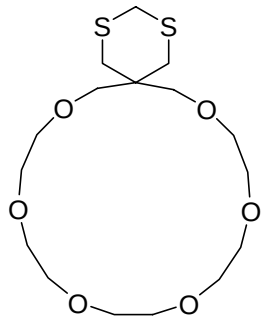
Synthetic Procedures

8,11,14,17-Tetraoxa-2,4-dithia-spiro[5.12]octadecane (5). A solution of 5,5-di(hydroxymethyl)-1,3-dithiane 4 (0.40 g, 2.2 mmol) in 40 ml DMF was stirred under a nitrogen atmosphere. This solution was treated with hexane-washed NaH (0.21 g, 8.8 mmol). After 15 minutes of stirring, tri(ethylene glycol) di-p-tosylate (0.96 g, 2.1 mmol) was added and allowed to stir at room temperature (r.t.) overnight. The resulting mixture was carefully treated with NH_4Cl and then extracted into ether. The ethereal layer was washed 4x with NH_4Cl and 2x with water to remove all DMF, dried, and then concentrated. FCC (1:1 ethyl acetate: hexanes) gave 0.54 g yellow oil (88%). ^{1}H NMR ($CDCl_3$, 400 Hz) 3.64-3.72 (m, 18H), 2.72 (s, 4H); MS (EI) *m*/*z* (relative intensity) 294 (M^+, 30), 144 (60), 98 (100), 85 (60).



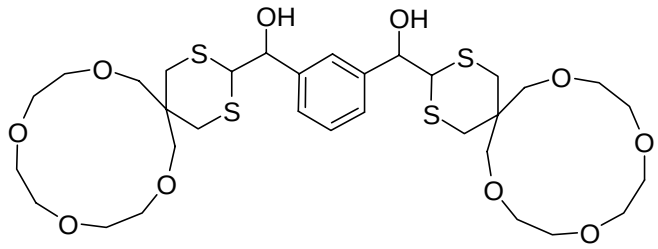
8,11,14,17,20-Pentaoxa-2,4-dithia-spiro[5.15]heneicosane (6). A solution of 5,5-di(hydroxymethyl)-1,3-dithiane 4 (0.41 g, 2.3 mmol) in 40 ml DMF was stirred under a nitrogen atmosphere. This solution was treated with hexane-washed NaH (0.22 g, 9.2 mmol). After 15 minutes of stirring, tetra(ethylene glycol) di-p-tosylate (1.09 g, 2.2 mmol) was added and allowed to stir at r.t. overnight. The resulting mixture was carefully treated with NH_4Cl and then extracted into ether. The ethereal layer was washed 4x with NH_4Cl and 2x with water to remove all DMF, dried, and then concentrated. FCC (1:1 ethyl acetate: hexanes) gave 0.70 g yellow oil (95%). ^{1}H NMR ($CDCl_3$, 400 Hz) 3.64-3.69 (m, 22H), 2.76 (s, 4H); MS (EI) *m*/*z* (relative intensity) 338 (M^+, 40), 195 (30), 144 (80), 98 (95), 85 (100).



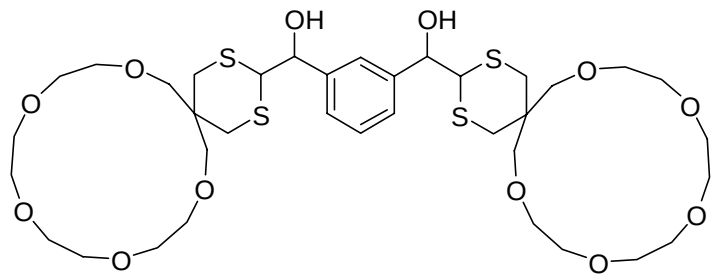


8,11,14,17,20,23-Hexaoxa-2,4-dithia-spiro[5.18]tetracosane (7). A solution of 5,5-di(hydroxymethyl)-1,3-dithiane 4 (0.41 g, 2.3 mmol) in 40 ml DMF was stirred under a nitrogen atmosphere. This solution was treated with hexane-washed NaH (0.22 g, 9.2 mmol). After 15 minutes of stirring, penta(ethylene glycol) di-p-tosylate (1.18 g, 2.2 mmol) was added and allowed to stir at r.t. overnight. The resulting mixture was carefully treated with NH_4Cl and then extracted into ether. The ethereal layer was washed 4x with NH_4Cl and 2x with water to remove all DMF, dried, and then concentrated. FCC (1:1 ethyl acetate: hexanes) gave 0.72 g clear oil (87%). ^{1}H NMR ($CDCl_3$, 400 Hz) 3.61-3.69 (m, 26H), 2.76 (s, 4H); MS (EI) *m*/*z* (relative intensity) 382 (M^+, 10), 239 (20), 144 (50), 99 (80), 85 (100).

{3-[Hydroxy-(8,11,14,17-tetraoxa-2,4-dithia-spiro[5.12]octadec-3-yl)-methyl]-phenyl}-(8,11,14,17-tetraoxa-2,4-dithia-spiro[5.12]octadec-3-yl)-methanol (**8**). A solution of **5** (0.130 g, 0.44 mmol) in 10 ml freshly distilled THF was cooled to -20°C and 1.6 M *n*-butyllithium (0.41 ml, 0.66 mmol) was added while stirring under a N_2 atmosphere. The reaction mixture was stirred at this temperature for 2 hours, after which the reaction was further cooled to -78°C, and isophthalaldehyde (0.030 g, 0.22 mmol) in 2 ml THF was added via syringe. The resulting mixture was allowed to slowly warm to r.t. over a period of 2 hours, then stirred overnight. The resulting yellow solution was washed 2x with 10 ml sat. NH_4Cl, extracted into ether, dried and concentrated. FCC (1:50 MeOH:$CHCl_3$) gave 0.150 g clear oil (94%). ^{1}H NMR (CD_3CN, 400 Hz) 7.41 (b, 1H), 7.30 (d, J = 1.2 Hz, 3H), 4.82 (m, 2H), 4.16 (dd, J_1 = 1.6 Hz, J_2 = 6.8 Hz, 2H), 3.53-3.62 (m, 32H), 3.44 (s, 2H), 2.70-2.78 (m, 4H), 2.52-2.58 (m, 4H).

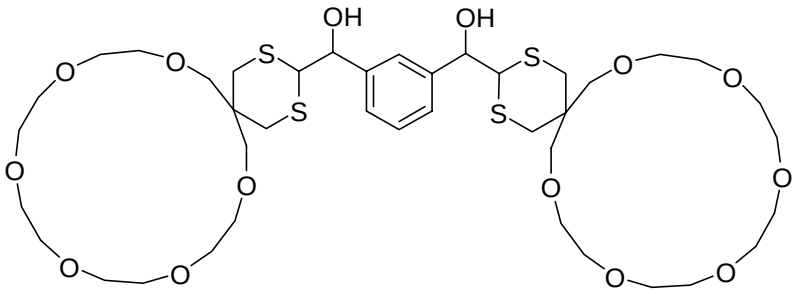


{3-[Hydroxy-(8,11,14,17,20-pentaoxa-2,4-dithia-spiro[5.15]heneicos-3-yl)-methyl]-phenyl}-(8,11,14,17,20-pentaoxa-2,4-dithia-spiro[5.15]heneicos-3-yl)-methanol (**9**). A solution of **6** (0.61 g, 1.8 mmol) in 25 ml freshly distilled THF was cooled to -20°C and 1.6 M *n*-butyllithium (1.7 ml, 2.7 mmol) was added while stirring under a N_2 atmosphere. The reaction mixture was stirred at this temperature for 2 hours, after which the reaction was further cooled to -78°C, and isophthalaldehyde (0.12 g, 0.9 mmol) in 3 ml THF was added via syringe. The resulting mixture was allowed to slowly warm to r.t. over a period of 2 hours, then stirred overnight. The resulting yellow solution was washed 2x with 25 ml sat. NH_4Cl, extracted into ether, dried and concentrated. FCC (1:50 MeOH:$CHCl_3$) gave 0.60 g clear oil (82%). ^{1}H



NMR ($CDCl_3$, 400 Hz) 7.47 (b, 1H), 7.37 (b, 3H), 4.89 (m, 2H), 4.20 (m, 2H), 3.60-3.69 (b, 42H), 2.75-2.87 (m, 4H), 2.59-2.63 (m, 4H).

(8,11,14,17,20,23-Hexaoxa-2,4-dithia-spiro[5.18]tetracos-3-yl)-{3-[(8,11,14,17,20,23-hexaoxa-2,4-dithia-spiro[5.18]tetracos-3-yl)-hydroxy-methyl]-phenyl}-methanol (**10**). A solution of **7** (1.11 g, 2.9 mmol) in 40 ml freshly distilled THF was cooled to -20°C and 1.6 M *n*-butyllithium (3.6 ml, 5.8 mmol) was added while stirring under a N_2 atmosphere. The reaction mixture was stirred at this temperature for 2 hours, after which the reaction was further cooled to -78°C, and isophthalaldehyde (0.18 g, 1.34 mmol) in 5 ml THF was added via syringe. The resulting mixture was allowed to slowly warm to r.t. over a period of 2 hours, then stirred overnight. The resulting yellow solution was washed 2x with 50 ml sat. NH_4Cl, extracted into ether, dried and concentrated. FCC (1:50 MeOH:$CHCl_3$) gave 1.01 g clear oil (84%). ^{1}H NMR ($CDCl_3$, 400 Hz) 7.46 (b, 1H), 7.37 (b, 3H), 4.88 (m, 2H), 3.99 (m, 2H), 3.61-3.68 (b, 48H), 2.47 (b, 2H), 2.75-2.84 (m, 4H), 2.57-2.63 (m, 4H).



Transport Experiments. Performed in a conventional U-tube (i.d. = 15 mm) made of Pyrex glass. The donor solutions were prepared the following way: 1 mmol $K_2HPO_4 \cdot 3H_2O$ was mixed with 0.1 mmol methyl viologen diiodide and brought to a final volume of 100 ml with deionized water. The pH of the solution was 8. The receiving solutions were prepared by adding1 mmol $K_2HPO_4 \cdot 3H_2O$ and diluting to 100 ml with deionized water, yielding a pH=8 solution. The nitrogen bubbled ionophoric solutions (12 ml $CHCl_3$) ranged from 3-18 mM. Both the donor and receiving solutions (4 ml) were carefully overlayered on the denser ionophoric solution and magnetically stirred in a room temperature water bath. The amounts of migrated methyl viologen were determined photometrically at 256 nm in a 1-cm quartz cell with a Beckman DU-640 UV/Vis spectrophotometer.

Computational details. The initial geometry of the complex of **10** and viologen was generated with CambrigeSoft Chem3D and further optimized using Gaussian 98 package at PM3 (semi-empirical) level of theory.

PM3 optimized geometry (XYZ Cartesian coordinates):

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