Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

Colour coding the co-conformations of a [2]rotaxane flip-switch

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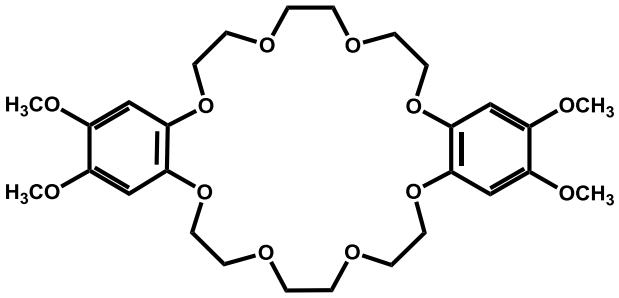
General Comments:

All reagents and starting materials were purchased from Aldrich Chemicals and used without further purification. Dimethoxyquinone,[1] the corresponding diol,[2] tetraiodo-dibenzo-24-crown-8[3] and 3,5-dimethoxybenzoic anhydride[4] were prepared according to literature procedures. Solvents were dried using an Innovative Technologies Solvent Purification System. Microwave synthesis was carried out in a 10 mL vessel on a CEM Discover microwave at 200W. Thin layer chromatography (TLC) was performed using Teledyne Silica gel 60 F_{254} plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230 – 400 mesh). Flash column chromatography was performed using Teledyne Ultra Pure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash R_f. All flash chromatography was performed under pressure (80 - 160 mL/min.) for normal phase silica, with increasing pressure corresponding to larger columns. Unless otherwise stated, all flash chromatography applied gradient elution from 0 - 100 % with increasing polar solvent with respect to less polar solvent. Length of column (column volume) was determined by separation on TLC. Deuterated solvent (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. NMR spectra were recorded on a Bruker Avance 500 spectrometer, with working frequency of 500.13 MHz for ^{1}H nuclei and 125.7 MHz for ^{13}C nuclei. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. Electrospray ionization (ESI) mass spectra were measured on a Micromass LCT time-of-flight mass spectrometer. Solutions of 50-100 ng/μL were prepared in CH_3CN and injected for analysis at a rate of 5 μL/min using a syringe pump.

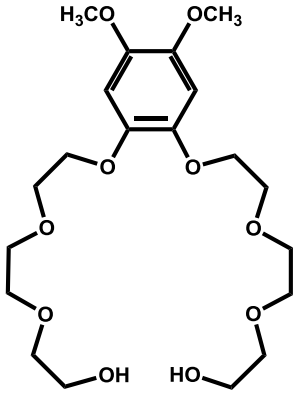
1. B. Batanero, F. Barba, *Org. Lett.*, 2005, **7**, 2567.
2. T. Czekanski, M. Hanack, J. Y. Becker, J. Bernstein, S. Bittner, L. Kaufman-Orenstein, D.Peleg, *J. Org. Chem.*, 1991, **56**, 1569.
3. J. J. Pak, J. L. Mayo, E. Shurdha, *Tet. Lett.*, 2006, **47**, 233.
4. F. Kazemi, H. Sharghi, M. A. Naseri, *Synthesis*, 2004, **2**, 205.

Synthesis of 4,5,4',5'-tetramethoxydibenzo-24-crown-8:



4,5,4',5'-tetraiododibenzo-24-crown-8 (3.00 g, 0.00313 mol), $CsCO_3$ (15.3 g, 0.0471 mol), and 1,10-phenanthroline (4.52 g, 0.0252 mol) were dissolved in anhydrous MeOH (50 mL) in an 80 mL microwave reaction vessel with a stir bar. CuI (4.78 g, 0.0252 mol) was then added to the vessel in the dark and the mixture was microwaved for 5 hr at 110 ˚C. Resulting mixture was filtered, washed with MeOH and the filtrate was concentrated. This was then dissolved in $CHCl_3$ (100 mL), washed with H_2O (3 x 20 mL), dried ($MgSO_4$) and concentrated. The product was then purified and isolated by flash column chromatography on RP-C_{18} silica gel using H_2O:MeOH gradient elution (20 % - 100 % MeOH), yielding a white solid. Yield: 0.765 g, 43 %. ^{1}H-NMR ($CDCl_3$): δ = 6.60 (s, 4H), 4.14 (t, ^3J = 4.5 Hz, 8H), 3.87 (t, ^3J = 4.5 Hz, 8H), 3.82 (s, 8H), 3.78 ppm (s, 12H); HRMS (ESI): *m/z* 591.2417 (calc.) for $C_{28}H_{40}O_{12}Na$ $[M\text{-}Na]^+$, found 591.2431.

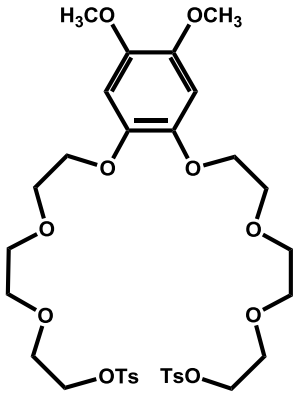
Synthesis of 4,5-dimethoxy-1,2-ethoxyethoxyethoxydiol:



4,5-Dimethoxycatechol (6.00 g, 0.0353 mol), $CsCO_3$ (57.4 g, 0.1763 mol), and 2-[2-(2-chloroethoxy)ethoxy]ethanol (15.4 mL, 0.1059 mol) were dissolved in anhydrous MeCN (500

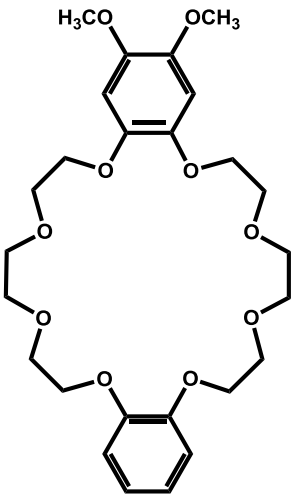
mL) and refluxed for one week under a nitrogen atmosphere. The solution was cooled, filtered and concentrated under reduced pressure. This was then dissolved in CH_2Cl_2 (200 mL), washed with H_2O (3 x 30 mL), dried ($MgSO_4$) and concentrated. The product was then purified and isolated by flash column chromatography on silica gel using $CHCl_3$:MeOH elution (99:1), yielding a light brown oil. Yield: 3.83 g, 25 %. ^{1}H-NMR ($CDCl_3$): δ = 6.63 (s, 2H), 3.92 (s, 6H), 3.83-3.58 (m, 24H), 3.14 ppm (s, 2H).

Synthesis of 4,5-dimethoxy-1,2-ethoxyethoxyethoxyditosylate:



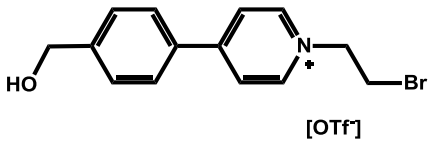
4,5-dimethoxy-1,2-ethoxyethoxyethoxydiol (2.65 g, 0.0061 mol), triethylamine (6.17 g, 0.0610 mol), p-dimethylaminopryidine (74.5 mg, 0.610 mmol) and p-toluenesulfonyl chloride (3.49 g, 0.0183 mol) were added to DCM (250 mL) at 0 ^{o}C under a nitrogen atmosphere with stirring continued overnight. The mixture was filtered and a solution of Et_2O:H_2O (3:100 mL) was added to the solution. The organic layer was extracted, washed with 2M HCl (3 x 50 mL), then washed with 1M $NaHCO_3$ (3 x 50 mL), then washed with H_2O (2 x 50 mL), dried ($MgSO_4$) and solvent removed under pressure. Excess p-toluenesulfonyl chloride was extracted using (petroleum ether:toluene) 1:1 mixture, yielding an off-white solid. Yield: 3.13 g, 25 %. ^{1}H-NMR ($CDCl_3$): δ = 7.78 (d, ^{3}J = 8.1 Hz, 4H), 7.32 (d, ^{3}J = 8.1 Hz, 4H), 6.63 (s, 2H), 3.92 (s, 6H), 4.16-3.56 (m, 24H), 2.42 ppm (s, 6H).

Synthesis of 4,5-dimethoxydibenzo-24-crown-8:



$CsCO_3$ (91.3 g, 0.280 mol) was suspended in dry MeCN (1 L), catechol (5.14 g, 0.0467 mol) was dissolved in dry MeCN (500 mL) and added to the suspension (via syringe) which was then brought to reflux under a nitrogen atmosphere. 4,5-dimethoxy-1,2-ethoxyethoxyethoxyditosylate (34.7 g, 0.0467 mol) was dissolved in MeCN (500 mL) which was filled in a glass syringe (50 mL) and added dropwise via a syringe pump over a period of one week. Refluxing was continued for an additional week. The mixture was cooled and solid filtered off and solution concentrated. The residue was then dissolved in $CHCl_3$ (400 mL), washed with H_2O (3 x 100 mL), dried ($MgSO_4$) and solvent removed under pressure. The product was then purified and isolated by flash column chromatography on RP-C_{18} silica gel using H_2O:MeOH gradient elution (20 % - 100 % MeOH), yielding a white solid. Yield: 9.26 g, 39 %. ^{1}H-NMR ($CDCl_3$): δ = 6.88 (m, 4H), 6.57 (s, 2H), 4.16-3.56 (m, 24H), 3.92 ppm (s, 6H).

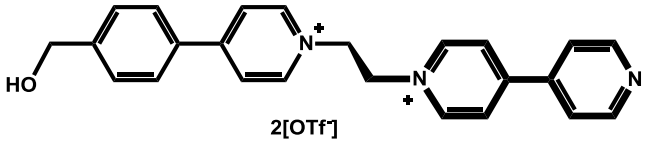
Synthesis of [4-(4-(hydroxymethyl)phenylpyridinium)ethylbromide][OTf]:



4-pyridinephenylmethanol (1.250 g, 0.0067 mol) and 1,2-dibromoethane (11.69 mL, 0.1351 mol) were dissolved in butanol (30mL) in a thick-walled 80 mL vessel and microwaved for 3 h at

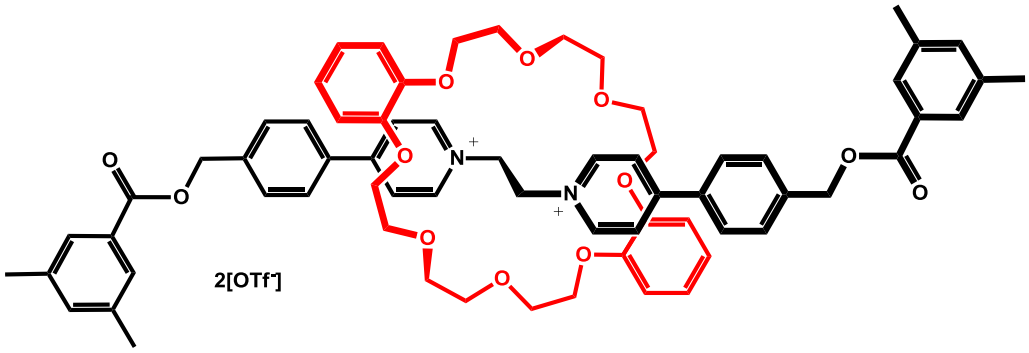
80 ˚C. The reaction mixture was cooled in the fridge and resulting precipitate was filtered and washed with cold $MeNO_2$. The white solid was then anion exchanged to the triflate salt by two layer NaOTf(aq)/$MeNO_2$. The $MeNO_2$ layer was washed with H_2O (4 x 10 mL) and concentrated to yield white powder. Yield: 2.51 g, 84 %.

Synthesis of 4-(4-(hydroxymethyl)phenylpyridinium)ethyl[4,4'-bipyridinium][OTf]$_2$:



[4-(4-(hydroxymethyl)phenylpyridinium)ethylbromide][OTf] (0.765 g, 0.0201 mol) and 4,4'-bipyridine (1.258 g, 0.0081 mol) were dissolved in $MeNO_2$ (25 mL) and added to a thick-walled 80 mL vessel with stir bar and microwaved for 1 h at 70 ˚C. The solution was filtered hot and the resulting precipitate washed with methanol. The precipitate was collected and recrystallized from H_2O. The resulting white crystals were anion exchanged to the triflate salt by way of a two layer NaOTf (aq)/$MeNO_2$ extraction. The $MeNO_2$ layer was washed with H_2O (4 x 10 mL) and concentrated to yield white powder. Yield: 630.0 mg, 47 %.

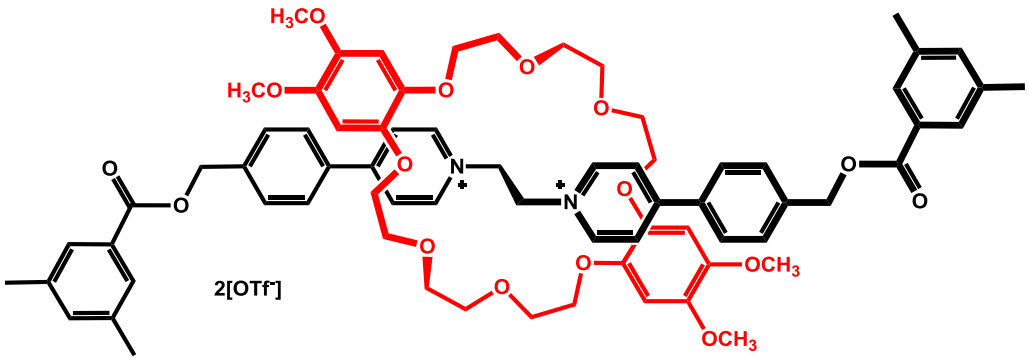
Synthesis of 1:



[1,2-bis(4-pyridinium-4-benzylalcohol)ethane][OTf]$_2$ (0.100 g, 0.175), dibenzo-24-crown-8 (0.392 g, 0.874 mmol) and 3,5-dimethylbenzoic anhydride (0.148 g, 0.524 mmol) were dissolved in dry 7:3 ($CHCl_3$: MeCN) (30 mL) under nitrogen atmosphere. A catalytic amount of

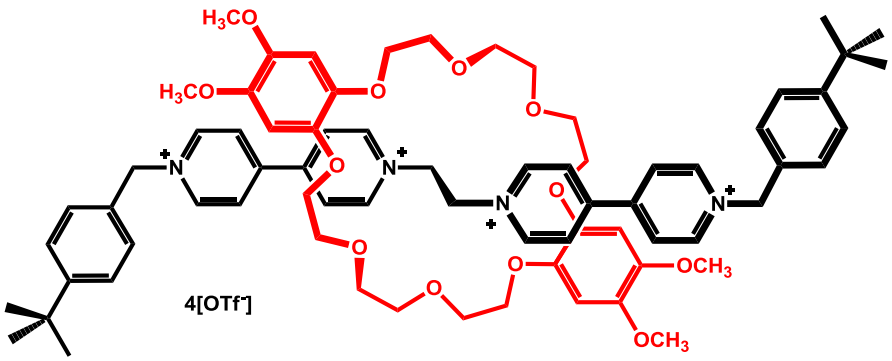
tributylphosphine (10 µL) was added via glass syringe and stirring continued for 3 h. The solvent was removed under reduced pressure, and the product stirred in toluene. The precipitate formed was filtered, washed with toluene several times and dried under reduced pressure. The off-white precipitate was collected. Yield: 0.047 g, 24 %. ^{1}H-NMR (CD_3CN): δ = 9.02 (d, ^{3}J = 6.4 Hz, 4H), 7.95 (d, ^{3}J = 6.4 Hz, 4H), 7.71 (s, 4H), 7.67 (m, 8H), 7.30 (s, 2H), 6.64 (dd, $^{3}J_{meta}$ = 3.5 Hz, 4H), 6.45 (dd, $^{3}J_{ortho}$ = 6.0 Hz, 4H), 5.48 (s, 4H), 5.44 (s, 4H), 4.02 (m, 24H), 2.38 ppm (s, 12H); HRMS (ESI): m/z 1197.5265 (calc.) for $C_{68}H_{74}N_2O_{12}BF_4$ $[M\text{-}BF_4]^+$, found 1197.5337.

Synthesis of 3:



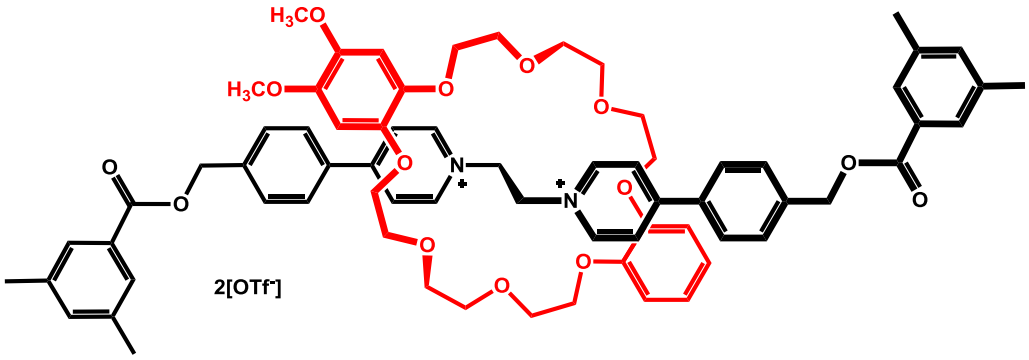
[1,2-bis(4-pyridinium-4-benzylalcohol)ethane][OTf]$_2$ (117.0 mg, 0.1680 mmol), 4,5,4',5'-tetramethoxybenzo-24-crown-8 (764.0 mg, 1.3436 mmol) and 3,5-dimethylbenzoic anhydride (166.0 mg, 0.5880 mmol) were dissolved in dry 7:3 ($CHCl_3$: MeCN) (30 mL) under nitrogen atmosphere. A catalytic amount of tributylphosphine (10 µL) was added via glass syringe and stirring continued for 3 h. The solvent was removed under reduced pressure, and the product stirred in toluene. The precipitate formed was filtered, washed with toluene several times and dried under reduced pressure. The red precipitate was collected. Yield: 59.1 mg, 23 %. ^{1}H-NMR (CD_3CN): δ = 9.02 (d, ^{3}J = 6.2 Hz, 4H), 7.99 (d, ^{3}J = 6.2 Hz, 4H), 7.71 (s, 4H), 7.66 (m, 8H), 7.32 (s, 2H), 6.31 (s, 4H), 5.47 (s, 4H), 5.44 (s, 4H), 4.00 (m, 16H), 3.96 (s, 8H), 3.45 (s, 12H), 2.38 ppm (s, 12H); HRMS (ESI): *m/z* 1379.5179 (calc.) for $C_{73}H_{82}F_3N_2O_{19}S$ $[M\text{-}OTF]^+$, found 1379.5179, *m/z* 615.2827 (calc.) for $C_{72}H_{82}N_2O_{16}$ $[M]^{2+}$, found 615.2823.

Synthesis of 4:



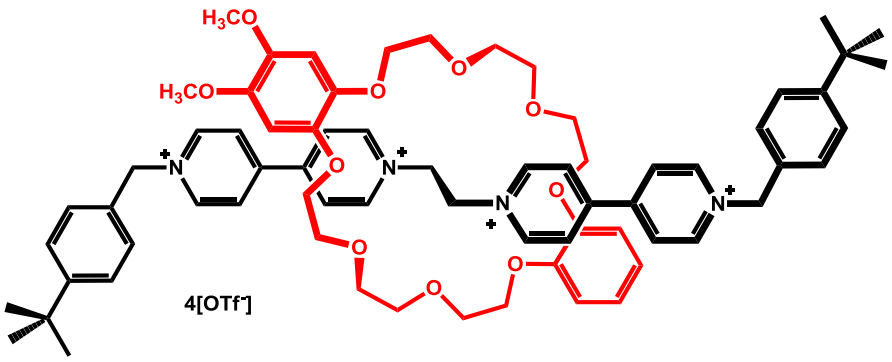
[1,2-bis(pyridinium)ethane][OTf]$_2$ (85.0 mg, 0.133 mmol), 4,5,4',5'-tetramethoxybenzo-24-crown-8 (605.0 mg, 1.064 mmol) and 4-(tert-Butyl)benzylbromide (0.098 mL, 0.532 mmol) were dissolved in a minimum amount of $MeNO_2$ (6 mL) and microwaved for 5 min at 50 ˚C. To this was added 4 drops of sat'd NaOTf(aq) and microwaved for an additional 15 min at 50 ˚C. The two layers were separated and the $MeNO_2$ layer washed with H_2O (3 x 1.5 mL), dried over $MgSO_4$ and the solvent removed. The residue was stirred in toluene and remaining solid filtered. The resulting solid was stirred in $CHCl_3$ and remaining purple solid filtered and dried. Yield: 40.7 mg, 17 %. ^{1}H-NMR (CD_3CN): δ = 9.25 (d, ^{3}J = 6.8 Hz, 4H), 8.98 (d, ^{3}J = 6.8 Hz, 4H), 8.33 (d, ^{3}J = 6.8 Hz, 4H), 8.21 (d, ^{3}J = 6.8 Hz, 4H), 6.8 Hz, 4H), 6.29 (s, 4H), 5.81 (s, 4H), 5.61 (s, 4H), 4.10 (s, 8H), 4.01 (m, 16H), 3.44 ppm (s, 12H), 1.34 (s, 18H); HRMS (ESI): *m/z 750.2792* (calc.) for $C_{74}H_{90}F_6N_4O_{18}S_2$ [M -2OTF]$^{2+}$, found 750.2757, *m/z 1649.5111* (calc.) for $C_{75}H_{90}F_9N_4O_{21}S_3$ [M-3OTF]$^+$, found 1649.5108.

Synthesis of 5:



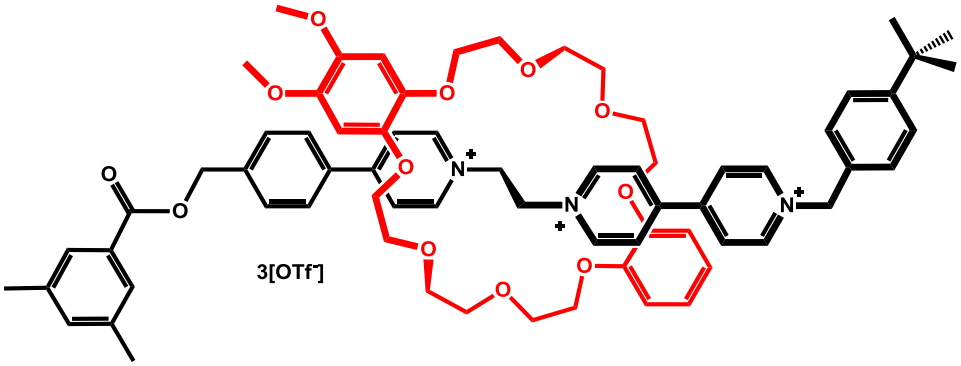
[1,2-bis(4-pyridinium-4-benzylalcohol)ethane][OTf]$_2$ (100.00 mg, 0.1435 mmol), 4,5-dimethoxydibenzo-24-crown-8 (584.03 mg, 1.1484 mmol) and 4-(tert-butyl)benzyoic anhydride (141.85 mg, 0.5024 mmol) were dissolved in dry 7:3 ($CHCl_3$: MeCN) (30 mL) under nitrogen atmosphere. A catalytic amount of tributylphosphine (10 µL) was added via glass syringe and stirring continued for 3 h. This gives product give quantitative rotaxane formation with no visible production of the capped thread side product. The solvent was removed under reduced pressure, and the product stirred in toluene. The precipitate formed was filtered, washed with toluene several times and dried under reduced pressure. The resulting solid was dissolved in minimum hot MeCN (10 mL) and then cold EtOAc (10 mL) was added and cooled in fridge overnight. The pale orange precipitate was collected. Yield: 173.0 mg, 91 %. ^{1}H-NMR (CD_3CN): δ = 9.04 (d, ^3J = 7.0 Hz, 4H), 7.97 (d, ^3J = 7.0 Hz, 4H), 7.71 (s, 4H), 7.65 (m, 8H), 7.32 (s, 2H), 6.65 (dd, ^3J_o = 6.6 Hz, ^3J_m = 3.7 Hz, 4H), 6.53 (dd, ^3J_o = 6.6 Hz, ^3J_m = 3.7 Hz, 4H), 6.30 (s, 2H), 5.47 (s, 4H), 5.44 (s, 4H), 4.04 (m, 4H), 3.98 (m, 18H), 3.95 (m, 4H), 3.44 (s, 6H), 2.38 ppm (s, 12H); HRMS (ESI): *m/z* 1319.4968 (calc.) for $C_{71}H_{78}F_3N_2O_{17}S$ $[M\text{-}OTF]^+$, found 1319.4960, *m/z 585*.2721 (calc.) for $C_{70}H_{78}N_2O_{14}$ $[M]^{2+}$, found 585.2717.

Synthesis of 6:



[1,2-bis(pyridinium)ethane][OTf]$_2$ (100.0 mg, 0.156 mmol), 4,5-dimethoxydibenzo-24-crown-8 (637.1 mg, 1.253 mmol) and 4-(tert-butyl)benzylbromide (0.115 mL, 0.624 mmol) were dissolved in a minimum amount of $MeNO_2$ (6 mL) and microwaved for 5 min at 50 ˚C. To this was added 4 drops of sat'd NaOTf(aq) and microwaved for an additional 15 min at 50 ˚C. The two layers were separated and the $MeNO_2$ layer washed with H_2O (3 x 1.5 mL), dried over $MgSO_4$ and the solvent removed. The residue was stirred in toluene and remaining solid filtered. The resulting solid was dissolved in minimum CH_2Cl_2 and brown solid ppt. upon addition of Et_2O at RT. This was filtered and washed with cold Et_2O. Residue was then purified by column chromatography with 40:60 CH_2Cl_2:(4.5:0.5:5.0 MeOH:2M NH_4Cl:$MeNO_2$). This was then anion exchanged back to the triflate salt to yield the product as a light brown solid. Yield: 57.2 mg, 21 %. ^{1}H-NMR (CD_3CN): δ = 9.30 (d, ^{3}J = 7.0 Hz, 4H), 8.98 (d, ^{3}J = 7.0 Hz, 4H), 8.31 (d, ^{3}J = 7.0 Hz, 4H), 8.22 (d, ^{3}J = 7.0 Hz, 4H), 6.64 (dd, $^3J_{meta}$ = 3.6 Hz, 2H), 6.45 (dd, $^3J_{ortho}$ = 5.9 Hz, 2H), 6.29 (s, 2H), 5.81 (s, 4H), 5.61 (s, 4H), 4.40 (m, 24H), 3.44 (s, 6H), 1.34 ppm (s, 18H); HRMS (ESI): *m/z* 1589.4899 (calc.) for $C_{73}H_{86}F_9N_4O_{19}S$ $[M\text{-}3OTF]^+$, found 1589.4883, *m/z* 720.2687 (calc.) for $C_{72}H_{86}N_4O_{16}S_2$ $[M\text{-}2OTf]^{2+}$, found 720.2695.

Synthesis of 7:



[1-(2-(4-(4-(((3,5-dimethylbenzoyl)oxy)methyl)phenyl)pyridinium)ethyl)-[4,4'-bipyridine]][OTf]$_2$ (150.0 mg, 0.188 mmol), 4,5-dimethoxydibenzo-24-crown-8 (763.1 mg, 1.500 mmol) and 4-(tert-butyl)benzylbromide (0.138 mL, 0.750 mmol) were dissolved in a minimum amount of $MeNO_2$ (6 mL) and microwaved for 5 min at 50 ˚C. To this was added 4 drops of sat'd NaOTf(aq) and microwaved for an additional 15 min at 50 ˚C. The two layers were separated and the $MeNO_2$ layer washed with H_2O (3 x 1.5 mL), dried over $MgSO_4$ and the solvent removed. The residue was stirred in toluene and remaining solid filtered. The resulting solid was dissolved in minimum CH_2Cl_2 and dark brown solid ppt. upon addition of Et_2O at rt. This was filtered and washed with cold Et_2O. Residue was then purified by column chromatography with 30:70 CH_2Cl_2:(4.5:0.5:5.0 MeOH:2M NH_4Cl:$MeNO_2$). This was then anion exchanged back to the triflate salt to yield the product as a light brown solid. Yield: 99.2 mg, 33 %. ^{1}H-NMR (CD_3CN): δ = 9.31 (d, ^{3}J = 7.0 Hz, 2H), 9.03 (d, ^{3}J = 7.0 Hz, 2H), 8.98 (d, ^{3}J = 7.0 Hz, 2H), 8.25 (d, ^{3}J = 7.0 Hz, 2H), 8.18 (d, ^{3}J = 7.0 Hz, 2H), 8.04 (d, ^{3}J = 7.0 Hz, 2H), 7.72 (s, 2H), 7.68 (m, 4H), 7.59 (d, ^{3}J = 7.0 Hz, 2H), 7.50 (d, ^{3}J = 7.0 Hz, 2H), 7.32 (s, 1H), 6.65 (dd, $^3J_{meta}$ = 3.5 Hz, 2H), 6.45 (dd, $^3J_{ortho}$ = 6.0 Hz, 2H), 6.29 (s, 2H), 5.81 (s, 4H), 5.80 (s, 2H), 5.61 (m, 2H), 5.49 (m, 2H),5.26 (s, 2H), 4.00 (m, 24H), 3.44 (s, 6H), 2.38 (s, 6H), 2.16 ppm (s, 9H); HRMS (ESI): *m/z* 1454.4933 (calc.) for $C_{72}H_{82}F_6N_3O_{18}S_2$ $[M\text{-}2OTF]^+$, found 1454.4927, *m/z* 652.7691 (calc.) for $C_{71}H_{82}F_3N_3O_{15}S$ $[M\text{-}OTf]^{2+}$, found 652.7691.

Single Crystal X-ray Diffraction

Crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer using MoK_α radiation and a CCD detector. Decay was monitored using 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined using a riding model. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library[1] and figures drawn with DIAMOND software.[2]

Crystals of [2]rotaxane **4**, were weakly diffracting at high angle which resulted in a poor R(int). Two molecules of *iso*-propyl ether, two molecules of acetonitrile and a single water molecule (with H-bonded H-atoms) were included in the solution. One of the *iso*-propyl ether molecules was modeled with a 50:50 disorder. DFIX, SADI, SIMU and DELU commands were used to give chemically reasonable models for the *iso*-propyl ether molecules. One of the *t*-butyl groups showed “splitting” of the three methyls (C42, C43, C44) but all attempts to model the disorder failed.

1. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
2. DIAMOND 3.2 - CRYSTAL IMPACT, Postfach 1251, D-53002, Bonn, Germany 2009.

Spectral Simulations

All spectra were recorded in $MeNO_2$ solution at a concentration of 1 x 10^{-3} M. For all the multiple component (chromophore) compounds, the complete visible absorption spectra were de-convoluted into individual absorption bands using a least-squares procedure to minimize the difference between the real and simulated spectra. The individual absorption bands of the model [2]rotaxanes **1 – 4** were first simulated using mixed Gauss-Lorentz or split Log-normal functions. Assuming no significant change in the extinction coefficients for the component chromophores **1 – 4** and knowing the distribution of co-conformers to be equal by design, it was possible to successfully simulate the spectra of the test flip-switches **5** and **6**. The calculated spectra of **5** and **6** were indistinguishable from their experimental traces at all wavelengths, thus verifying the procedure. Again, assuming no significant change in the extinction coefficients for the component chromophores **1 – 4** and setting the contributions from **1** = **4** and **2** = **3** the spectrum of the [2]rotaxane flip-switch **7** could be successfully simulated with a ratio of co-conformers of 60:40 for A:B. The calculated spectrum of **7** was indistinguishable from the experimental trace at all wavelengths. Very similar results were observed for spectra recorded in MeCN. Spectra were also recorded in acetone and MeOH but were not as well resolved and attempts to simulate the data did not give satisfactory results.

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Log-normal functions: Metzler, D. E.; Harris, C. M.; Johnson, R. J.; Siano, D, B.; Thomson, J. A. Spectra of 3-Hydroxypyridines. Band Shape Analysis and Evaluation of Tautomeric Equilibria. *Biochemistry*, 1973 **12**, 5377-5392.

Equation used to calculate populations: Kishimoto, S.; Kitahara, S.; Manaba, O.; Hiyama, H. Tautomerism and Dissociation of 4-Arylazo-1-napthols in various solvents. *J. Org. Chem.,* 1978, **43**, 3882-3886.

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