Supporting Information for *ChemPhysChem* Z401

Two-Dimensional Molecular Electronics Circuits

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Introduction. In this supplement, we provide additional information related to the various control molecules and experiments utilized to establish the molecular structure / device property relationships that led to the mechanistic arguments in the paper. We also provide a more detailed description of the various measurement procedures, as well as the fabrication techniques for both the micrometer-scale and nanometer-scale devices utilized here. Finally, we provide synthetic details for some of the mechanically interlocked compounds and their precursors that were utilized here and whose synthesis has not been described previously in the literature.

Control Devices for the [2]Rotaxane Molecular Switch Tunnel Junction Device. Several control compounds, in addition to the principal [2]rotaxanes (**I** and **II**) discussed in the text, were used[1,2] in this work They are illustrated in Figure A1. The [2]catenane and the [2]pseudorotaxane, which are also discussed in the text have had the characteristics of the solid-state devices fabricated from them discussed elsewhere.[2] In this Supplementary Material, we will refer to the [2]rotaxane and its controls, using the descriptors **[2]Ra**, **[2]Rb,** and **[2]Rc, and Dba** as defined in Figure A1. The **[2]R** label refers to a [2]rotaxane, meaning that the molecule consists of two mechanically interlocked molecular components — a dumbbell encircled by a ring. **DBa**, which refers to the dumbbell of **[2]Ra**, was also utilized as a control. The large stoppers – one hydrophobic and the other hydrophilic – at either end of the molecules, not only make them amphiphilic, but also lend a relatively large area/molecule in a Langmuir-Blodgett (LB) molecular monolayer film. In this discussion, we will first present a summary of what the measured solution-phase switching mechanisms of these molecules. We will then discuss their performance within a solid-state device.

For **[2]Ra and [2]Rc**, the tetracationic cyclophane ring can encircle and bind to either the modified tetrathiafulvalene (TTF) site or the dioxynaphthalene (DNP) site. The major difference between these two compounds is the thiomethyl group, that protrudes from the TTF site in **[2]Rb** and points toward the DNP site, and constitutes a "speed bump", slowing the translation of the cyclophane ring down considerably by providing a ~ 24 kcal mol^{-1} energy barrier. In **[2]Ra**, the energy barrier for the translation of the cylcophane ring between the two sites, as measured by temperature dependent NMR spectroscopy, is approximately 15 kcal mol^{-1}, i. e., considerably lower. In **[2]Rb**, both co-conformations of **[2]Rb** can be isolated.[2] In the case of **[2]Ra**, in the solution phase, both the TTF and the DNP sites compete effectively for the cyclophane ring. The DNP site is preferred below 250K, and the TTF site is preferred above 330K, with nearly equal occupancy at room temperature. The first oxidation state for both molecules corresponds to the removal of an electron from the TTF site. In the case of **[2]Ra**, oxidation of the TTF site is accompanied by movement of the threaded cyclophane ring to the DNP site – a motion that is driven by Coulombic repulsion. In **[2]Rb**, oxidation is also accompanied by Coulombic repulsion-driven movement of the tetracationic cyclophane away from the TTF site. In this molecule, however, translation of the ring to the DNP site is much slower. So much so that it probably behaves effectively as a single-station [2]rotaxane in a solid state device setting. Details of the synthesis and characterization of **[2]Ra** and **[2]Rb** are included below. The corresponding information on **[2]Rc** has been reported elsewhere.[1] This solution phase picture of molecular mechanical switching is likely to be modified somewhat in a solid-state device setting, but it provides a reasonable starting point for thinking about these devices.

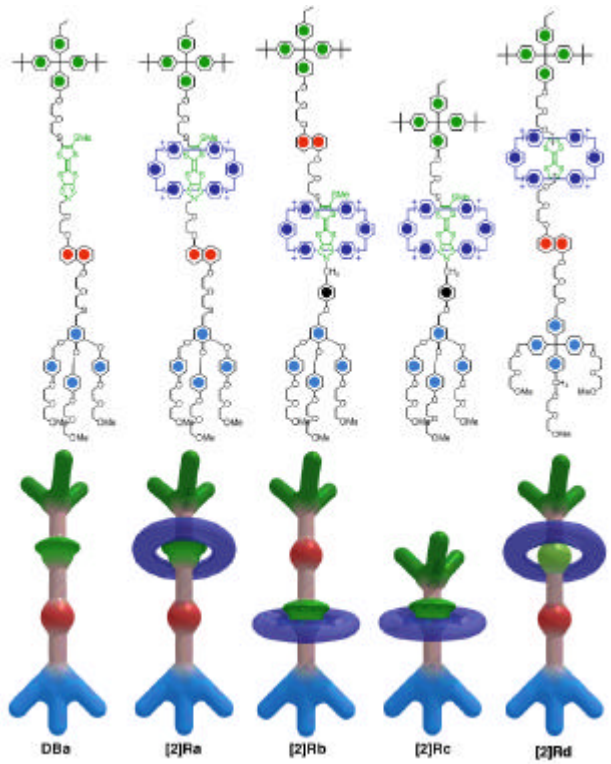

Figure A1. The principal [2]Rotaxane molecule used in this work (**[2]Ra**) plus three other molecules utilized as controls, including the dumbbell component **DBa** of **[2]Ra**. Note that, although **[2]Rb** and **[2]Ra** appear similar, there is a thioether group extending between the two recognition sites in **[2]Rb**, and this raises the activation barrier to ring translation (in solution phase) from 15 to 25 kcalmol^{-1}, effectively making this a single-station rotaxane. **[2]Rc** is a single station rotaxane.

Device Fabrication and Testing Procedure. The molecular switching components were prepared as Langmuir monolayers and transferred to substrates that were pre-patterned with n-type polycrystalline silicon (polySi) electrodes. The poly-Si electrodes were fabricated as follows: Low-pressure, SiH_4 CVD was used to deposit 1500 Å of amorphous Si onto 1100 Å of SiO_2 on a <100> silicon wafer at 525 °C. The film was exposed to air at room temperature for several minutes to form a passivating SiO_2 layer, and then crystallized under N_2 at 650 °C. Poly-Si films were implanted with 55 keV P^+ ions and 1 mm film of SiO_2 was grown by CVD to prevent out-gassing of the phosphorus. The dopant P atoms were activated at 1000 °C, and then a 6:1 mixture of NH_4F(aq):HF(aq) was used to etch away the SiO_2. Electrodes were patterned using standard photolithography techniques.

Langmuir monolayers were formed by spreading a chloroform solution of the compounds. All of the compounds used here are unstable toward acids, and both the aqueous subphase of the Langmuir trough, as well as chloroform solvent, will become acidic upon exposure to air. Thus, a dilute buffer (5 x 10^{-4} M Na_2CO_3 / $NaHCO_3$, pH = 10) was used as the aqueous subphase, and the chloroform solvent was stored over basic alumina and distilled immediately prior to use. The molecular materials were

stored as dry powders until they were ready for use. These precautions were absolutely critical for obtaining reliable and reproducible data. All monolayers were transferred at surface pressure between 27 – 30 milliNewtons/meter, at the following molecular areas: **[2]Ra** = 134 $Å^2$/molecule; **[2]Rb**=122 $Å^2$/molecule; **[2]Rc**=119 $Å^2$/molecule. Most devices were fabricated using optical lithography or metal evaporation through shadow masks, to produce a junction area of approximately 50 micrometers squared.

All Langmuir compression sequences were monitored using Brewster Angle Microscopy (BAM), in addition to the surface pressure/area measurements that constitute a normal isotherm. In addition, transferred films were also interrogated by BAM, as well as scanning probe microscopy (SPM). We have demonstrated[3] previously that BAM is sensitive to the presence of molecular domains that are formed in monolayers of [2]pseudorotaxanes and [2]catenanes, when those domains are larger than a few micrometers in diameter. Various types of SPM, including friction force microscopy, tapping mode topographic measurements, and surface potential microscopy, are all sensitive to the formation of domains that are 0.1 micrometers in diameter and larger. None of the films reported in this supplement exhibited any structure when probed by either BAM or SPM techniques.

Much smaller devices (0.05 - 0.005 micrometers squared) were prepared using electron beam lithography to define the electrode patterns in the polySi film. The molecular monolayer was deposited as described above. It is generally not possible to carry out lithographic patterning directly on top of a molecular monolayer film, because the film is unstable toward such simple processes as resist spinning, etc. Therefore, we developed the following procedure to enable lithographic processing on a molecular monolayer at nanometer-scale dimensions. After the molecular monolayer was deposited, a 15 nm thick titanium film was evaporated on top of the molecular monolayer (thereby coating the entire top surface of the wafer) using electron-beam evaporation of titanium. The wafer was then mounted on the rotating chuck of a spin coater. A PMMA film, which serves as an electron-beam lithographic resist material, was then deposited on top of the titanium film by spin coating. The patterns for the top electrode were then written into the PMMA film using electron beam lithography (30 kV and 400 nanoCoulombs/cm^2 electron flux). The pattern was developed for 60 seconds

in a 3:1 methyl isobutyl ketone: isopropanol solution. A 100 nanometer thick film of aluminum was deposited through the patterns in the PMMA film onto the titanium film, and the PMMA film was then removed using an acetone wash, leaving the lithographically defined aluminum wire behind as the top or second electrode. For the specific case of a 16-bit memory, four parallel aluminum electrodes, each with a width of 70 nm, and with an interelectrode separation of 0.5 micrometers were deposited on top of and perpendicular to the bottom polycrystalline silicon electrodes. At this point, the titanium film protective layer still covers the surface of the entire wafer, excepting the top surface of the deposited aluminum wires. This titanium protective layer is a metallic film, and it will electrically short all of the devices in the memory circuit together if it is not removed. It was therefore selectively removed from the regions that were not covered with the aluminum electrodes using reactive ion etching. This step very likely removed the molecular monolayer that was also not sandwiched between the electrode pairs, leaving the crossbar device circuit on top of the SiO_2 coated silicon wafer. The crossbar circuit was then ready for electrical analysis.

In order to address isolated devices, the polySi electrode was connected to a voltage source, and the titanium/aluminum electrode was connected to ground through a current preamplifier. Isolated device measurements were carried out as previously described.[4] There were several critical measurements, and they were performed as follows:

Remnant Molecular Signature. This is a measurement of the hysteresis loop of a molecular switch tunnel junction, and yields information relevant to the relative and absolute switching amplitudes, and the voltages required to switch the devices. It is a measurement that is typically immune to parasitic capacitances. For this measurement, a series of voltage 'write' pulses, τ seconds in duration, separated by a voltage increment V_{step}, and tracing out a sequence starting at $-V_{max}$ to $+V_{max}$ and then back to $-V_{max}$ again, are applied. After each voltage pulse, the status of the device is read by monitoring the current level through the device at some small bias V_{read}. A mechanical relay was utilized to isolate the ammeter from the device except when the device was being read. This was done to prevent saturation of the ammeter while the device was

being written. Typical values in volts (V) were $-V_{max}$ = –3.0 V; $+V_{max}$ = +3.0 V, V_{step} = 0.02 V; V_{read} = –0.2 V to 0.2 V; τ = 0.1 to 1 seconds.

Device Cycling and Volatility Measurements. Device cycling measurements consist of alternatively opening and closing the switches at the appropriate voltages determined by the remnant molecular signature response function. All of our molecular switch tunnel junctions are in the switch-open state (low current level) when initially prepared. A voltage pulse of magnitude V_{close} is applied to the device for a time τ, and the current through the device is read at a low, non perturbative voltage V_{read} for a period of a few seconds. A voltage pulse of magnitude V_{open} is then applied for a time τ, and the current through the device is again read at V_{read} for a period of a few seconds. The final plot is V_{read} versus time, and devices were cycled up to 500 times in a single experiment. Volatility measurements are carried out similarly, except that V_{read} was applied for up to 2000 seconds, or, for the least volatile of the devices, intermittently over a period of several hours or days. A mechanical relay was utilized to isolate the ammeter from the device except when the device was being read. This was done to prevent saturation of the ammeter while the device was being written. Typical values were τ = 0.1 to 1 seconds, and V_{read} = –0.2 V to 0.2 V.

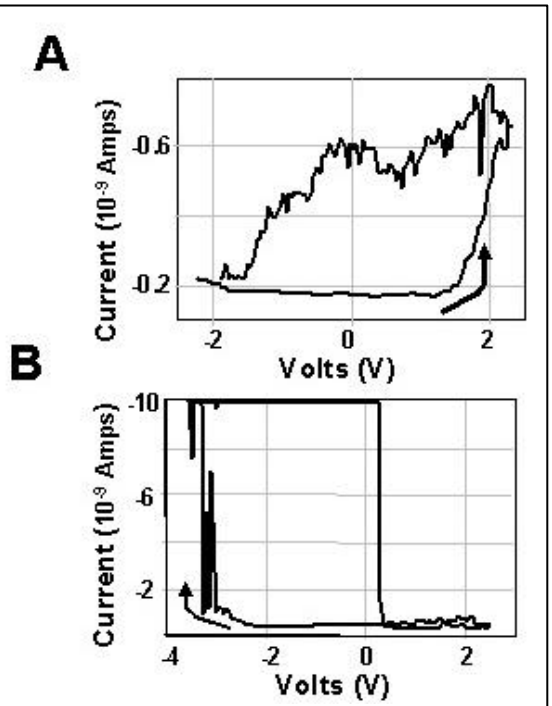

Figure A2. Remnant molecular signature curves for the two switching mechanisms of **[2]Ra**. While Curve B exhibits a much larger amplitude switching response than Curve A, the voltage at which the closed switch is opened (about +0.5 V here) fluctuates from cycle to cycle. Such fluctuations make this switching mechanism inoperable within a crossbar circuit environment.

Crossbar Memory Measurements. For the testing of crosspoint circuits as memories, each wire in the circuit (8 wires for a 4×4 16-bit circuit, or 12 wires for a 6×6 36-bit circuit) was independently controlled using a relay-based switching matrix. Electrical

connections to the memory were established using a pressure-contact probe card. In order to change the state of a device, the address voltage was split evenly between the top and bottom electrodes that defined the junction, and all other electrodes were grounded. After some configuration of open and closed switches was written into the circuit, the status of the entire circuit was probed, one device at a time, by applying a small V_{read} bias to the polySi electrode that intersected that device, and connecting the top intersecting electrode to ground through the current preamplifier. The conditions for addressing individual devices were similar to those used for the device cycling and volatility measurements.

Solid-State Device Performance Characteristics. A summary of the performance characteristics for MSDs fabricated from the compounds shown in Figure A1, plus a simpler control molecule, eicosanoic acid ($C_{19}H_{39}CO_2H$), are listed in Table A1.

Table A1

Molecule	Volatility	Vclose	Vopen	1/0 ratio	cycles/device
[2]Ra (high bias mode)	Hrs-Days	–3.0±0.1V #	+1.5±1.0V#	500	Order (1000); stable
[2]Ra (low bias mode)	15-20 min	+2.0±0.1V	-1.7±0.2V	3-10	Order (50) in micron scale device (stable); Order (1000) in nano-scale device (stable)
[2]Rb	5-10 min	+1.8±0.15V	–1.8±0.15V	1.5-2.5	Order (100) (stable);
[2]Rc	3-5 min	+1.8±0.15V	–1.8±0.15V	1.5-2.5	Order (5) in micron-scale device (unstable); Order (50) in a nano-scale device (stable)
[2]Rd	15-20 min	+2.0±0.1V	–1.7±0.2V	5-10	Order (100) in micron-scale device.
DBA	0 -1 min	–4.0V±1.5V#	>0V#	unstable	Not cyclable
Eicosanoic Acid	No switch	No switch	No switch	No switch	No switch

These numbers varied across device preparations and were very sensitive to the surface pressure and area/molecule values of the Langmuir monolayer at the point that the film was transferred to the wafer. Devices from a single preparation operated similarly to one another.

Two distinct switching mechanisms were apparent in devices fabricated from **[2]Ra** (Figure A2). One mechanism was characterized by a remnant molecular signature hysteresis loop at relatively low bias (V_{close} = +2.0 V; V_{close} = –1.7 V) and a second mechanism that was activated at a higher bias (V_{close} = –3.0 V; V_{open} ~ +1.5 V). Based on the various control molecules employed here, as well as our experience with other molecular switch tunnel junctions fabricated from [2]catenanes and [2]pseudorotaxanes and other controls, we have developed a qualitative mechanistic model. We believe that these two hysteresis loops are both related to oxidation of the TTF site, and that both involve movement of the cyclophane ring. The higher bias process is effectively a field-driven ionization of the molecular monolayer, and is accompanied by ring motion. As discussed in the main body of the text, such electrical

breakdown is expected in any molecular monolayer-based device, and is observed in all of our devices. However, for devices that were based on the control molecules, such as **DBa**, **[2]Rb**, **[2]Rc**, or eicosanoic acid, this electrical breakdown does not form the basis for a stable switch. For the case of **[2]Ra** and **[2]Rd** operated using the higher bias switching mechanism, certain of the device switching characteristics can be very stable. For example, the devices can be repeatedly cycled, they exhibit excellent volatility characteristics, and they can exhibit very large amplitude current changes upon switching (Figure A3). However, because it is a field-driven process, rather than a current-driven process, at least one of the switching voltages that characterizes the remnant molecular signature hysteresis loop is unstable. Furthermore, since this mechanism is field-activated, a sufficiently large magnitude bias, either positive or negative-valued, will cause the devices to switch. For these reasons, the high-bias switching mechanism is not useful for forming a crossbar memory, because the voltages required to switch the MSTJs are not well defined.

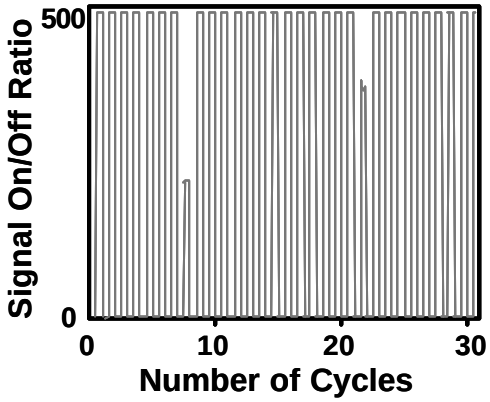

Figure A3. Device cycling of **[2]Ra** operated in the high-bias mode.

The address voltages for the low-bias switching mechanism were highly reproducible from device to device, and from circuit to circuit, exhibiting variations of ±0.15 volts (V). The control molecules **DBa** and eicosanoic acid, as well as a host of other controls that were based on the [2]catenane device previously reported, do not exhibit this low-bias, stable switching response. Control devices fabricated from **[2]Rb** and **[2]Rc** exhibited a slight low-bias switching response, although nothing that was as large in magnitude as either **[2]Ra** or **[2]Rb**. For the **[2]Rb** and **[2]Rc** controls, some ring motion is expected upon oxidation of the TTF site, but translation of the ring to a second site is prohibited by an energy barrier for the case of **[2]Rb**, and by the absence of a second site in the case of **[2]Rc**.

Synthesis and Characterization. Here, we describe the synthesis and characterization, in solution, of two amphiphilic [2]rotaxanes designed specifically for

integration into a device setting. Both of the [2]rotaxanes contain a hydrophobic tetraarylmethane stopper and a hydrophilic dendritic stopper – the syntheses of which have been described previously.[5] The [2]rotaxanes also consist of two π-electron rich stations, a tetrathiafulvalene (TTF) unit and a dioxynaphthalene (DNP) ring system, which can act as stations for the tetracationic cyclophane ($CBPQT^{4+}$) to reside around. The two [2]rotaxanes differ in the arrangement of the π-electron rich units – one (**1**•$4PF_6$) in which the SMe group of the TTF group points toward the DNP group, and the other (**2**•$4PF_6$) where the SMe group points away from the DNP ring system. This seemingly small change in the orientation of the TTF unit causes large changes in the physical properties of these rotaxanes – both in solution and in the device setting. The dumbbell **18**—the precursor to **1**•$4PF_6$—was synthesized according to Scheme 1. Alkylation of the tetraarylmethane stopper **6** with the monotosylate **5** in MeCN with a LiBr catalyst gave **7** in 80% yield. Consequent bromination of the free alcohol with Ph_3P in CBr_4 gave the bromide **8** in good yield (94%), which could be coupled with 2-[4-(2-cyanoethylthio)-5-methylthio-1,3-dithiol-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole[6] (**11**) following its *in situ* deprotection with CsOH to give **13** in 74% yield. The tosyl protecting group on the TTF unit was removed using NaOMe in a THF-MeOH mixture in excellent yield (95%). The resultant pyrrole nitrogen in **14** was alkylated with the chloride **17** of the hydrophilic stopper and, following purification by column chromatography, the dumbbell **18** was isolated in 83% yield. In order to synthesize the [2]rotaxane **1**•$4PF_6$, the tetracationic cyclophane $CBPQT^{4+}$ was introduced using a clipping procedure as shown in Scheme 2. The dumbbell, **20**•$2PF_6$, and dibromo-*p*-xylene **21**, were dissolved in anhydrous DMF and stirred at room temperature for 10 days. The resulting precipitate was subjected directly to column chromatography and the pure [2]rotaxane was isolated as a brown solid in 23% yield. However, the brown solid was subsequently found to consist of a mixture of two translational isomers in a approximately 1:1 ratio. The separation of these isomers, and their characterization, has been described previously.[7] The two translational isomers could be isolated at room temperature on the laboratory timescale, and the barrier to their interconversion was found to be 24 kcal mol^{-1} in acetone solution at room temperature.

In order to test our hypothesis that it was indeed the SMe group that was the barrier to the shuttling of $CBPQT^{4+}$, the [2]rotaxane **3**•$4PF_6$ was synthesized according to Schemes 1 and 2, in which the SMe group was replaced by the more bulky SEt group. As in the previous case, the [2]rotaxane was isolated as a mixture of translational isomers – **3**•$4PF_6$•GREEN – where $CBPQT^{4+}$ resides around the TTF unit – and **3**•$4PF_6$•RED – where $CBPQT^{4+}$ resides around the DNP ring system. Perhaps surprisingly, the main isomer was **3**•$4PF_6$•RED. This isomer was isolated by preparative thin layer chromatography (PTLC). After isolation of **3**•$4PF_6$•RED, various attempts to observe the shuttling of $CBPQT^{4+}$ from the DNP station to the TTF station were carried out by ^1H NMR spectroscopy. However, no interconversion was observed, even at elevated temperatures (425 K). This observation is consistent with our hypothesis that it is the SMe group of the [2]rotaxane **1**•$4PF_6$ that is the steric barrier to the shuttling of $CBPQT^{4+}$.

It was anticipated that the relatively high barrier (24 kcal mol^{-1}) to the shuttling of $CBPQT^{4+}$ in **1**•$4PF_6$ in the solution phase would be mirrored in the device setting and therefore this [2]rotaxane would not be a good candidate as an effective switch. Thus, the task of removing this barrier to shuttling was the next challenge. In order to remove this barrier, it was decided that a molecule should be synthesized in which the SMe group of the TTF unit points away from the DNP ring system. However, repeated attempts to carry out the synthesis of such a dumbbell component—in which the TTF unit was effectively rotated by 180°—resulted in a mixture of unidentifiable products. Therefore, it became necessary to change the relative positions of the TTF unit and DNP ring system units in order to attain our goal. The synthesis of **2**•$4PF_6$ is shown in Scheme 3. The synthesis of compound **24** has been described[3] previously, as it constituted the linear portion of a [2]pseudorotaxane which has been previously integrated into a device setting. In order to construct the dumbbell **27**, the free alcohol of compound **22** was initially converted to a mesyl group (**22**→**23**) in 95% yield, to an iodide (**23**→**24**) in 93% yield and finally to an thiocyanate group (**24**→**25**) in 81%. The

thiocyanate **25** could also be obtained directly from the mesyl derivative **23** in 97% yield. The isothiocyanate group was reduced *in situ* with $NaBH_4$, and the resulting thiolate was consequently coupled with the hydrophilic chloride[6] **26** in THF to give the dumbbell **27** in 90% yield. The synthesis of the [2]rotaxane **2**•$4PF_6$ was completed by the introduction of $CBPQT^{4+}$ using a clipping procedure. The dumbbell **27**, the dicationic salt **20**•$2PF_6$ and dibromo-*p*-xylene (**21**), were dissolved in anhydrous DMF and stirred at room temperature for 10 days. The resulting precipitate was subjected directly to column chromatography and the pure [2]rotaxane **2**•$2PF_6$ was isolated as a brown solid in 15% yield. In addition, it was possible to carry out this clipping procedure at elevated pressure. The dumbbell **27**, the dicationic salt **20**•$2PF_6$ and dibromo-*p*-xylene (**21**), were dissolved in anhydrous DMF in a teflon tube and subjected to 10 kbar pressure at room temperature for 3 days. The resultant green solution was subjected to column chromatography and the pure [2]rotaxane **2**•$2PF_6$ was isolated as a brown solid in 47% yield, an outcome which indicates the advantage of carrying out this type of reaction at ultrahigh pressures. It became clear from chromatography — both thin layer and column chromatography — that **2**•$4PF_6$ also consisted of a mixture of translational isomers — **2**•$2PF_6$•GREEN and **2**•$2PF_6$•RED. However, it was not possible to isolate these isomers on the laboratory timescale. This failure indicates that the barrier to the shuttling of $CBPQT^{4+}$ in **2**•$2PF_6$ is much lower than in the case of **1**•$4PF_6$. An ^1H NMR spectrum of the mixture in MeCN at room temperature revealed that the ratio of isomers was approximately 1:1. It was possible to interconvert the translational isomers using temperature as a control. At higher temperatures (~345 K), the ratio shifts to >90 % in favor of **2**•$4PF_6$•GREEN. However, at lower temperatures (~240 K), the ratio shifts almost completely in favor of of **2**•$4PF_6$•RED. This observation was supported by a temperature controlled UV-Vis experiment. At room temperature in MeCN, a charge-transfer (CT) band for both the TTF-$CBPQT^{4+}$ interaction — centered around ~795 nm — and the NP-$CBPQT^{4+}$ interaction — centered around ~540 nm — were clearly evident. Upon an increase in temperature, the CT band centered around ~795 nm increased in intensity and the band centered around ~540 nm decreased in intensity.

The reverse was true upon a decrease in temperature. Additionally, upon dissolving **2**•4PF_6 in DMSO, the equilibrium shifts almost entirely in favour of **2**•4PF_6•GREEN, a situation which is coupled with a deep green coloration of the solvent. From these observations, it is clear that, in theory at least, **2**•4PF_6 has properties much more becoming of a good candidate for a molecular switch, i.e., the barrier to the shuttling of $CBPQT^{4+}$ between the two π-electron rich stations is much smaller than that of **1**•4PF_6.

The synthesis of hydrophilic stopper precursor **31** is shown in Scheme 4. It is used subsequently, as outlined in Scheme 5, to synthesize the [2]rotaxane **40**•4PF_6. The tetraarylmethane derivative **29** was obtained in 41% by carrying out a Friedel-Crafts reaction between phenol and the chloride obtained from **28**. Palladium-catalyzed alkoxycarbonylation of the triflate ester of **29** gave the ester **30** in 77% yield. Subsequent radical bromination of the three aryl methyl groups present in **30** with NBS in CCl_4 yielded the tribromide which was then used as a tris-alkylating agent on diethyleneglycol monomethyl ether. Finally, reduction of the product with $LiAlH_4$ gave the hydrophilic stopper precursor **31** in an overall yield of 18% for these last three steps. Now, refer to Scheme 5. Alkylation of the hydrophobic stopper precursor **6** with the monotosylate **33** in MeCN afforded the alcohol **34** in 80% yield. Subsequent tosylation of this alcohol gave, in a yield of 94%, the monotosylate, which was used to alkylate the free phenolic hydroxyl function in **36**. After deprotection, the half-dumbbell compound **37** was isolated in 96%. The primary alcohol function in **37** was alkylated with the benzylic chloride **38** obtained from **31**. Following purification by column chromatography, the dumbbell-shaped compound **39** was isolated in 37% yield. The procedure, whereby **39** acts as the template for clipping the tetracationic cyclophane around it, went in a good 45% yield, following counterion exchange.

EXPERIMENTAL SECTION: Molecular Synthesis and Characterization Details

General. Chemicals were purchased from Aldrich and were used as received, unless indicated otherwise. The compounds 4-[bis-(4-tert-butyl-phenyl)-(4-ethyl-phenyl)-methyl]-phenol[1] (**6**), 2-(2-{5-[2-(2-hydroxyethoxy)ethoxy]naphthalen-1-yloxy}ethoxy) ethyl tosylate (**5**), 2-[4-(2-cyanoethylthio)-5-methylthio-1,3-dithiole-2-ylidene]-*N*-tosyl-

(1,3)-dithiolo[4,5-*c*]pyrrole (**11**) 2-[4,5-bis(cyanoethylthio)-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole[5] (**12**), 4-{3,4,5-tris-[(2-(2-methoxy)-ethoxy)ethoxybenzyloxy]-benzyloxy}benzyl chloride[1] (**17**), compound **22**, 3,4,5-tris-[(2-(2-methoxy)ethoxy) ethoxybenzyloxy]benzyl chloride[1] (**26**) and 1,1′′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluorophosphate)[6] (**20**•2PF_6) were all prepared according to literature procedures. Solvents were dried according to literature procedures.[7] All reactions were carried out under an anhydrous argon atmosphere. Thin layer chromatography (tlc) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in I_2 vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were determined on an Electrothermal 9100 apparatus or a Büchi melting point apparatus and are uncorrected. ^1H and ^{13}C spectra were recorded (at room temperature except where stated otherwise) on either a Bruker AC200 (200 and 50 MHz, respectively), Bruker ARX400 (400 and 100 MHz, respectively), Bruker ARX500 or Bruker AMX500 (500 and 125 MHz, respectively) spectrometer, using residual solvent as the internal standard. All chemical shifts are quoted on a δ scale, and all coupling constants are expressed in Hertz (Hz). Electron Impact Ionization Mass Spectrometry (EIMS) was performed on a AUTO-SPEC instrument. Fast Atom Bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with krypton primary atom beam, utilizing a *m*-nitrobenzyl alcohol matrix. InfraRed (IR) spectra were recorded on a Perkin-Elmer 580 spectrophotometer. UV-Vis spectra were recorded on a Cary 100 Bio spectrophetometer. Microanalyses were performed by Quantitative Technologies, Inc.

Compound 7. A solution of **6** (2.38 g, 4.99 mmol) and the monotosylate **4** (2.45 g, 4.99 mmol) in anhydrous MeCN (50 mL) containing K_2CO_3 (6.9 g, 50 mmol), LiBr (0.2 g, cat) and 18-crown-6 (~50 mg), was heated under reflux for 20 h. After cooling down to room temperature the reaction mixture was filtered and the residue washed with MeCN (50 mL). The combined organic phase filtrate was concentrated *in vacuo* and the brown oily residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by

column chromatography (SiO_2:CH_2Cl_2/MeOH 49:1). The colorless band (R_f = 0.2) was collected and the solvent evaporated to give a colorless oil, which was redissolved in CH_2Cl_2 (20 mL) and concentrated providing 3.20 g (80%) of the title compound **7** as a white foam. Data for **7**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.26 (t, J = 7.6 Hz, 3H), 1.33 (s, 18H), 2.19 (s, 1H), 2.65 (q, J = 7.6 Hz, 2H), 3.71–3.82 (m, 4H), 3.97–4.10 (m, 6H), 4.14–4.19 (m, 2H), 4.27–4.35 (m, 4H), 6.80–6.88 (m, 4H), 7.06–7.15 (m, 10H), 7.24–7.42 (m, 6H), 7.90 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.4, 28.3, 31.5, 34.4, 61.9, 63.2, 67.4, 68.0, 68.1, 69.8, 70.0, 70.1, 72.7, 105.9 (2), 113.3, 114.6, 114.9, 124.2, 125.2, 125.3, 126.7, 126.8, 126.9, 130.8, 131.1, 132.3, 139.9, 141.4, 144.3, 144.7, 148.4, 154.3, 154.4, 156.6; MS(FAB) *m/z* (%) 794 (63) $[M]^+$; $C_{53}H_{63}O_6$: calcd C 80.07, H 7.86; found C 79.85, H 7.88.

Compound 8. Ph_3P (0.70 g, 2.67 mmol) was added portionwise to a solution of the alcohol **7** (1.75 g, 2.20 mmol) and CBr_4 (0.88 g, 2.65 mmol) in anhydrous CH_2Cl_2 (15 mL) at room temperature. The reaction mixture was stirred for 16 h, whereupon additional CBr_4 (0.88 g, 2.65 mmol), followed by Ph_3P (0.70 g, 2.67 mmol) was added and the reaction mixture was stirred for another 24 h. After concentration, the residue was purified by column chromatography (SiO_2:CH_2Cl_2/hexane 2:1). The colorless band (R_f = 0.3) was collected and the solvent evaporated, affording a colorless oil, which was repeatedly dissolved in CH_2Cl_2 (3 × 50 mL) and concentrated to provide 1.77 g (94%) of the title compound **8** as a white foam. Data for **8**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.26 (t, J = 7.6 Hz, 3H), 1.33 (s, 18H), 2.65 (q, J = 7.6 Hz, 2H), 3.54 (t, J = 6.2 Hz, 2H), 3.94–4.10 (m, 8H), 4.14–4.19 (m, 2H), 4.28–4.36 (m, 4H), 6.80–6.89 (m, 4H), 7.06–7.15 (m, 10H), 7.24–7.42 (m, 6H), 7.90 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.4, 28.3, 30.5, 31.5, 34.4, 63.2 (CAr_4), 67.4, 68.0, 69.8, 70.0, 70.2, 71.6 (1), 105.8 (2), 113.3, 114.7, 114.9, 124.2, 125.2, 125.3, 126.7, 126.8 (2), 130.8, 131.1, 132.3, 139.9, 141.4, 144.3, 144.7, 148.3, 154.3, 154.4, 156.6; MS(FAB) *m/z* (%) 858 (30) $[M+2]^+$; $C_{53}H_{61}BrO_5$: calcd C 74.20, H 7.17; found C 74.36, H 7.20.

Compound 13. A solution of 2-[4-(2-cyanoethylthio)-5-methylthio-1,3-dithiole-2-ylidene]-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole **(11)** (0.27 g, 0.51 mmol) in anhydrous THF (35 mL) was degassed (Ar, 10 min) before a solution of $CsOH•H_2O$ (0.090 g, 0.54 mmol) in anhydrous MeOH (3.5 mL) was added dropwise via a syringe over a period of 1 h at room temperature. The mixture was stirred for 15 min, whereupon a solution of the bromide **8** (0.46 g, 0.54 mmol) in anhydrous THF (5 mL) was added in one portion and the reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated and the resulting yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with brine (100 mL), H_2O (2 × 100 mL) and dried ($MgSO_4$). Removal of the solvent gave a orange/yellow foam, which was purified by column chromatography (SiO_2:CH_2Cl_2/hexane 4:1). The broad yellow band (R_f = 0.3) was collected and concentrated affording a yellow foam, which was repeatedly dissolved in CH_2Cl_2 (2 × 20 mL) and concentrated to give 0.47 g (74%) of the title compound **13** as a yellow foam. Data for **13**: ^{1}H NMR (200 MHz, CD_3COCD_3) δ = 1.19 (t, J = 7.6 Hz, 3H), 1.28 (s, 18H), 2.37 (s, 3H), 2.39 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 3.07 (t, J = 6.3 Hz, 2H), 3.83 (t, J = 6.3 Hz, 2H), 3.94–4.06 (m, 6H), 4.14–4.19 (m, 2H), 4.26–4.34 (m, 4H), 6.84 (d, J = 8.9 Hz, 2H), 6.88–6.96 (m, 2H), 7.05–7.13 (m, 10H), 7.22–7.43 (m, 10H), 7.79–7.85 (m, 4H); MS(FAB) *m/z* (%) 1252 (100) $[M]^+$; $C_{69}H_{73}NO_7S_7$: calcd C 66.15, H 5.87, N 1.12; found C 66.34, H 6.02, N 1.05.

Compound 14. Compound **13** (0.42 g, 0.34 mmol) was dissolved in anhydrous THF-MeOH (1:1 v/v, 50 mL) and degassed (Ar, 10 min) before NaOMe (25% in MeOH, 1.1 mL, 0.27 g, 5.0 mmol) was added in one portion. The yellow solution was heated under reflux for 20 min before being cooled to room temperature, whereupon the solvent was evaporated. The yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 100 mL) and dried ($MgSO_4$). Concentration gave a yellow foam, which was subjected to column chromatography (SiO_2:CH_2Cl_2). The yellow band (R_f = 0.5) was collected and concentrated to provide 0.35 g (95%) of the title compound **14** as a yellow foam. Data for **14**: ^{1}H NMR (200 MHz, CD_3COCD_2) δ = 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 2.42 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 3.09 (t, J = 6.4 Hz, 2H), 3.85 (t, J = 6.4

Hz, 2H), 3.93–4.05 (m, 6H), 4.14–4.19 (m, 2H), 4.28–4.32 (m, 4H), 6.79 (s, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 7.05–7.13 (m, 10H), 7.24–7.39 (m, 6H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 10.35 (br s, 1H); MS(FAB) *m/z* (%) 1098 (100) $[M]^+$; $C_{62}H_{67}NO_5S_6$: calcd C 67.78, H 6.15, N 1.27; found C 67.81, H 6.15, N 1.24.

Dumbbell 18. Compound **14** (0.23 g, 0.21 mmol) and the chloride **17** (0.21 g, 0.23 mmol) were dissolved in anhydrous DMF (10 mL) and degassed (Ar, 10 min) before NaH (0.021 g of a 60% suspension in mineral oil, 0.53 mmol) was added. The reaction mixture was stirred for 45 min at room temperature, causing the initially yellow solution to become more orange. H_2O (40 mL) was added (dropwise until no more gas evolution was observed), followed by addition of brine (40 mL). The yellow precipitate was filtered and dried. The crude product was purified by column chromatography (SiO_2:CH_2Cl_2/EtOAc 2:1). The yellow band (R_f = 0.4) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (3 × 20 mL) and concentrated providing 0.34 g (83%) of the title compound **18** as a yellow foam. Data for **18**: ^{1}H NMR (400 MHz, CD_3COCD_3) *d* = 1.17 (t, *J* = 7.6 Hz, 3H), 1.26 (s, 18H), 2.38 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 6.4 Hz, 2H), 3.26 (s, 9H), 3.45–3.48 (m, 6H), 3.60–3.63 (m, 6H), 3.74–3.79 (m, 6H), 3.81 (t, *J* = 6.4 Hz, 2H), 3.90–4.00 (m, 6H), 4.05–4.13 (m, 8H), 4.24–4.27 (m, 4H), 4.88 (s, 2H), 4.96 (s, 2H), 5.00 (s, 6H), 6.72 and 6.75 (AB q, *J* = 2.1 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 9.1 Hz, 2H), 6.83 (s, 2H), 6.88–6.93 (m, 8H), 7.03–7.12 (m, 10H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.22–7.33 (m, 8H), 7.36 (d, *J* = 8.8 Hz, 4H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H); MS(FAB) *m/z* (%) 1966 (100) $[M]^+$; $C_{112}H_{127}NO_{18}S_6$: calcd C 68.37, H 6.51, N 0.71; found C 68.17, H 6.49, N 0.66.

Slow [2]Rotaxane 1•4PF$_6$. A solution of **18** (0.28 g, 0.14 mmol), **20**•2PF$_6$ (0.30 g, 0.42 mmol) and 1,4-bis(bromomethyl)benzene **21** (0.11 g, 0.42 mmol) in anhydrous DMF (10 mL) was stirred for 10 d at room temperature (after approx. 1 d the color changed from white to dark green and a white precipitate was formed). The green suspension was directly subjected to column chromatography (SiO_2) and unreacted **18** was eluted with

Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the brown band containing **1**•$4PF_6$ was collected. Most of the solvent was removed under vacuum (T < 30 °C) followed by addition of H_2O (50 mL). The resulting precipitate was collected by filtration, washed with Et_2O (20 mL) and dried affording 0.10 g (23%) of the title compound **1**•$4PF_6$ as a brown solid. Data for **1**•$4PF_6$: m.p. 150 °C (dec). The data given below are for the 1:1 mixture of the two translational isomers; MS(FAB) *m/z* (%) 2921 (4) $[M - PF_6]^+$, 2776 (9) $[M - 2PF_6]^+$, 2631 (6) $[M - 3PF_6]^+$, 1966 (3) (dumbbell), 1388 (10) $[M - 2PF_6]^{2+}$, 1315.5 (13) $[M - 3PF_6]^{2+}$, 1243 (6) $[M - 4PF_6]^{2+}$; UV-vis (Me_2CO, 298 K) l_{max} 540 nm (e = 670 L mol^{-1} cm^{-1}), 805 nm (e = 810 L mol^{-1} cm^{-1}); $C_{148}H_{159}F_{24}N_5O_{18}P_4S_6$•$2H_2O$: calcd C 57.26, H 5.29, N 2.26; found C 56.86, H 5.19, N 2.11.

Separation of the Translational Isomers of 1•4PF$_6$. The two translational isomers were separated using preparative thin layer chromatography (PTLC), which was performed at room temperature with Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) as the eluent. Immediately after elution, the red band (R_f = 0.45) containing **1**•$4PF_6$•RED was extracted into Me_2CO. The solvent was removed *in vacuo* (T < 10 °C) and the red residue was dissolved in CD_3COCD_3, giving a red solution, which was cooled to –78 °C in a Me_2CO/dry ice bath for storage. Data for **1**•$4PF_6$•RED: ^1H NMR (500 MHz, CD_3COCD_3, 225 K) d = 1.10 (t, J = 7.6 Hz, 3H), 1.18 (s, 18H), 2.49 (s, 3H), 2.50–2.60 (m, 4H), 3.20 (s, 3H), 3.23 (s, 6H), 3.72–3.76 (m, 8H), 4.00–4.05 (m, 8H), 4.12–4.16 (m, 2H), 4.26–4.31 (m, 2H), 4.34–4.45 (m, 10H), 4.78 (s, 2H), 4.87 (s, 2H), 4.95 (s, 4H), 5.00 (s, 2H), 5.91–6.05 (m, 9H), 6.14 (t, J = 8.2 Hz, 1H), 6.29 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 8.2 Hz, 1H), 6.76–6.80 (m, 6H), 6.86–6.94 (m, 8H), 7.01–7.06 (m, 10H), 7.22–7.28 (m, 8H), 7.38 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 5.8 Hz, 2H), 7.59 (d, J = 5.8 Hz, 2H), 7.70 (d, J = 6.3 Hz, 2H), 7.72 (d, J = 6.6 Hz, 2H), 8.06 (s, 2H), 8.16 (s, 2H), 8.29 (s, 2H,), 8.36 (s, 2H), 9.07 (d, J = 6.6 Hz, 2H), 9.09 (d, J = 6.9 Hz, 2H), 9.19 (d, J = 6.4 Hz, 2H), 9.34 (d, J = 6.5 Hz, 2H), the signals from 5 x CH_2O (10 H) lie underneath

the H_2O signal, which appears at 3.26–3.69 ppm; UV–vis (CD_3COCD_3, 298 K) l_{max} 540 nm. Although **1**•4PF_6•GREEN appears to be less polar than **1**•4PF_6•RED, it was only possible to extract an extremely small amount of **1**•4PF_6•GREEN (R_f = 0.45) from the silica on the PTLC plate. The UV–vis spectrum recorded in CD_3COCD_3 at 298 K of this fraction showed, as expected, only a broad CT absorption band centered on 801 nm. As a consequence of the extremely limited amount of **1**•4PF_6•GREEN isolated from the PTLC experiment, it was not possible to record a ^{1}H NMR spectrum. Alternatively, it was possible to shift the equilibrium of the two translational isomers from 1:1 to 9:1 in favor of **1**•4PF_6•GREEN by heating a CD_3SOCD_3 solution of the brown 1:1 mixture to 425 K. The data given below are for the major isomer in CD_3SOCD_3 at 410 K. Data for **1**•4PF_6•GREEN: ^{1}H NMR (500 MHz, CD_3SOCD_3, 410 K) d = 1.23 (t, J = 7.6 Hz, 3H), 1.31 (s, 18H), 2.62 (q, J = 7.6 Hz, 2H), 2.68 (s, 3H), 3.30 (s, 9H), 3.33 (t, J = 6.2 Hz, 2H), 3.49–3.54 (m, 6H), 3.62–3.66 (m, 6H), 3.77–3.83 (m, 6H), 3.89–3.92 (m, 2H), 3.90–4.00 (m, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.11–4.23 (m, 10H), 4.32–4.36 (m, 2H), 4.45–4.47 (m, 2H), 4.90 (s, 2H), 5.05 (s, 6H), 5.11 (s, 2H), 5.86 and 5.90 (AB q, J = 13.1 Hz, 8H), 6.16 and 6.17 (AB q, J = 2.0 Hz, 2H), 6.83–6.89 (m, 6H), 6.95–6.99 (m, 6H), 7.03–7.11 (m, 12H), 7.20–7.41 (m, 14H), 7.83 (d, J = 8.0 Hz, 2H), 7.87 (s, 8H), 8.08 (d, J = 6.3 Hz, 8H), 9.29 (d, J = 6.3 Hz, 8H).

Compound 23. MsCl (0.05 mL, 0.078 g, 0.68 mmol) was added dropwise to an ice-cooled solution of compound **22** (0.50 g, 0.42 mol) and Et_3N (0.21 mL, 0.15 g, 1.48 mmol) in anhydrous CH_2Cl_2 (40 mL). The yellow reaction mixture was stirred for 1 h at 0 °C, whereupon the ice bath was removed. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with H_2O (3 x 50 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow oil, which was subjected to column chromatography (SiO_2:CH_2Cl_2/MeOH 99:1). The yellow band (R_f = 0.4) was collected and concentrated to give 0.50 g (95%) of the title compound **23** as a yellow foam. Data for **23**: ^{1}H NMR (500 MHz, CD_3COCD_3) d = 1.22 (t, J = 7.6 Hz, 3H), 1.31 (s, 18H), 2.45 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H), 3.10 (s, 3H), 3.78 (t, J = 6.4 Hz, 2H), 3.82–3.84

(m, 2H), 3.87–3.89 (m, 2H), 3.93–3.95 (m, 4H), 4.04–4.06 (m, 2H), 4.11–4.13 (m, 4H), 4.29–4.31 (m, 2H), 4.35–4.37 (m, 2H), 4.43–4.45 (m, 2H), 6.77 and 6.78 (AB q, *J* = 2.0 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.07–7.15 (m, 10H), 7.32 (d, *J* = 8.6 Hz, 4H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H); MS(FAB) *m/z* (%) 1263 (100) $[M]^+$; $C_{67}H_{77}NO_9S_7$: calcd C 63.62, H 6.14, N 1.11; found C 63.55, H 5.85, N 1.24.

Compound 24. Compound **23** (0.50 g, 0.40 mmol) was dissolved in anhydrous Me_2CO (50 mL) and NaI (0.59 g, 3.94 mmol) was added in one portion. The reaction mixture was heated under reflux for 14 h, before being cooled to room temperature and the solvent removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 x 70 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow foam, which was purified by column chromatography (SiO_2:CH_2Cl_2). The yellow band (R_f = 0.6) was collected and concentrated to provide 0.48 g (93%) of the title compound **24** as a yellow foam. Data for **24**: ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.21 (t, *J* = 7.6 Hz, 3H), 1.31 (s, 18H), 2.43 (s, 3H), 2.60 (q, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 6.2 Hz, 2H), 3.75 (t, *J* = 6.4 Hz, 2H), 3.79–3.81 (m, 2H), 3.83–3.85 (m, 2H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.90–3.93 (m, 2H), 4.00–4.02 (m, 2H), 4.08–4.10 (m, 4H), 4.26–4.28 (m, 2H), 4.32–4.33 (m, 2H), 6.75 and 6.77 (AB q, *J* = 2.1 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.09–7.16 (m, 10H), 7.32 (d, *J* = 8.5 Hz, 4H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H); MS(FAB) *m/z* (%) 1295 (100) $[M]^+$; $C_{66}H_{74}INO_6S_6$: calcd C 61.14, H 5.75, N 1.08; found C 61.28, H 5.46, N 0.99.

Compound 25. Method A. Compound **24** (0.48 g, 0.37 mmol) was dissolved in anhydrous Me_2CO (40 mL) and KSCN (0.36 g, 3.70 mmol) was added in one portion. The reaction mixture was heated under reflux for 5 h. After being cooled to room temperature, the solvent was removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow foam, which was subjected to column chromatography (SiO_2:CH_2Cl_2/hexane 9:1) The yellow band (R_f = 0.3) was collected and concentrated

to a yellow oil, which was repeatedly redissolved in CH_2Cl_2 (2 x 20 mL) and concentrated to give 0.37 g (81%) of the title compound **25** as a yellow foam.

Method B. Compound **24** (0.54 g, 0.43 mmol) was dissolved in anhydrous Me_2CO (50 mL) and KSCN (1.24 g, 12.8 mmol) was added in one portion. The yellow reaction mixture was heated under reflux for 1 d, whereupon additional KSCN (0.83 g, 8.54 mmol) was added. The reaction mixture was heated under reflux for a further 1 d before being cooled to room temperature. After removal of the solvent the yellow residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (3 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave 0.51 g (97%) of the title compound **25** as a yellow foam. Data for **25**: ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.21 (t, J = 7.6 Hz, 3H), 1.31 (s, 18H), 2.45 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H), 3.38 (t, J = 5.8 Hz, 2H), 3.78 (t, J = 6.4 Hz, 2H), 3.82–3.84 (m, 2H), 3.86–3.88 (m, 2H), 3.93–3.95 (m, 2H), 4.01 (t, J = 5.8 Hz, 2H), 4.05–4.07 (m, 2H), 4.10–4.13 (m, 4H), 4.29–4.31 (m, 2H), 4.36–4.38 (m, 2H), 6.77 and 6.78 (AB q, J = 2.1 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 7.08–7.16 (m, 10H), 7.32 (d, J = 8.5 Hz, 4H), 7.38 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H); MS(FAB) *m/z* (%) 1226 (100) $[M]^+$; IR (KBr) ν 2154 (S-C≡N) cm^{-1}; $C_{67}H_{74}N_2O_6S_7$: calcd C 65.54, H 6.08, N 2.28; found C 65.49, H 6.02, N 2.13.

Dumbbell 27. Compound **25** (0.25 g, 0.20 mmol) and the chloride **26** (0.19 g, 0.24 mmol) were dissolved in anhydrous THF–EtOH (2:1 v/v, 50 mL), after which powdered $NaBH_4$ (0.077 g, 2.04 mmol) was added in one portion. The reaction mixture was stirred for 1 d at room temperature, whereupon it was poured into ice containing saturated aqueous NH_4Cl solution (50 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with H_2O (2 x 50 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow oil, which was purified by column chromatography (SiO_2:CH_2Cl_2/EtOAc 3:2). The yellow band (R_f = 0.4) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (3 x 20 mL) and concentrated to give 0.35 g (90%) of the title compound **27** as a yellow foam.

Data for **27**: ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 2.42 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 2.61 (t, J = 6.5 Hz, 2H), 3.04 (t, J = 6.4 Hz, 2H), 3.29 (s, 9H), 3.48–3.50 (m, 6H), 3.62–3.65 (m, 6H), 3.73–3.81 (m, 14H), 3.82–3.85 (m, 2H), 3.88–3.91 (m, 2H), 3.93–3.95 (m, 2H), 4.07–4.13 (m, 10H), 4.22–4.25 (m, 2H), 4.31–4.33 (m, 2H), 4.87 (s, 2H), 4.96 (s, 4H), 6.73–6.75 (m, 4H), 6.80 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.1 Hz, 1H), 6.93 (d, J = 8.3 Hz, 4H), 6.99 (d, J = 8.1 Hz, 1H), 7.05–7.13 (m, 10H), 7.28–7.32 (m, 7H), 7.35 (d, J = 9.0 Hz, 4H), 7.39 (t, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H); MS(FAB) *m/z* (%) 1965 (100) $[M]^+$; $C_{109}H_{129}NO_{18}S_7$: calcd C 66.60, H 6.61, N 0.71; found C 66.67, H 6.54, N 0.61.

Fast [2]Rotaxane 2•4PF$_6$. Method A. A solution of **27** (0.35 g, 0.18 mmol), **20**•2PF$_6$ (0.38 g, 0.54 mmol) and 1,4-bis(bromomethyl)benzene (**21**) (0.14 g, 0.53 mmol) in anhydrous DMF (10 mL) was stirred for 10 d at room temperature (after approx. 1 d the color changed from white to dark green and a white precipitate was formed). The dark green suspension was subjected directly to column chromatography (SiO_2) and unreacted **27** was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the brown band containing **2**•4PF$_6$ was collected. Most of the solvent was removed under vacuum (T < 30 °C) followed by addition of H_2O (50 mL). The resulting precipitate was collected by filtration, washed with Et_2O (20 mL) and dried affording 0.084 g (15%) of the title [2]rotaxane **2**•4PF$_6$ as a brown solid: m.p. 220 °C (dec).

Method B. A solution of **27** (0.40 g, 0.20 mmol), **20**•2PF$_6$ (0.43 g, 0.61 mmol) and 1,4-bis(bromomethyl)benzene (**21**) (0.16 g, 0.61 mmol) in anhydrous DMF (12 mL) was transferred to a teflon-tube and subjected to 10 kbar pressure at room temperature for 3 d. The dark green solution was subjected directly to column chromatography (SiO_2) and unreacted **27** was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the brown band containing **2**•4PF$_6$ was collected. Most of the solvent was removed *in vacuo* (T < 30 °C) followed by addition of H_2O (200 mL). The resulting precipitate was collected by filtration,

washed with H_2O (30 mL) and Et_2O (40 mL) and dried affording 0.29 g (47%) of the title [2]rotaxane **2**•4PF_6 as a brown solid. Data for **2**•4PF_6: m.p. 215 ºC (dec). The data given below are for the mixture of the two translational isomers; MS(FAB) *m/z* (%) 2919 (3) $[M - PF_6]^+$, 2774 (8) $[M - 2PF_6]^+$, 2629 (9) $[M - 3PF_6]^+$, 1964 (6) (dumbbell), 1387 (11) $[M - 2PF_6]^{2+}$, 1314.5 (24) $[M - 3PF_6]^{2+}$, 1242 (12) $[M - 4PF_6]^{2+}$; UV–vis (MeCN, 298 K) l_{max} 795 nm (e = 1300 L mol^{-1} cm^{-1}), 540 nm (e = 980 L mol^{-1} cm^{-1}); UV–vis (Me_2CO, 298 K) l_{max} 785 nm (e = 740 L mol^{-1} cm^{-1}), 540 nm (e = 760 L mol^{-1} cm^{-1}); UV–vis (Me_2SO, 298 K) l_{max} 765 nm (e = 1310 L mol^{-1} cm^{-1});), 540 nm (e = 640 L mol^{-1} cm^{-1}); $C_{145}H_{161}F_{24}N_5O_{18}P_4S_7$: calcd C 56.80, H 5.29, N 2.28; found C 56.43, H 5.20, N 2.21.

All attempts to separate the two translational isomers by employing PTLC failed on account of the fast shuttling of $CBPQT^{4+}$ between the two recognition sites in **2**•4PF_6. Instead **2**•4PF_6•RED and **2**•4PF_6•GREEN were characterized as a consequence of the fact that in CD_3COCD_3 solution at 245 K, **2**•4PF_6 exists almost exclusively as **2**•4PF_6•RED, whereas in CD_3SOCD_3 solution at 400 K, it exists almost exclusively as **2**•4PF_6•GREEN. Data for **2**•4PF_6•RED: ^{1}H NMR (500 MHz, CD_3COCD_3, 245 K) d = 1.19 (t, J = 7.5 Hz, 3H), 1.28 (s, 18H), 2.27 (s, 3H), 2.44 (d, J = 8.0 Hz, 1H), 2.51 (d, J = 8.0 Hz, 1H), 2.59 (q, J = 7.5 Hz, 2H), 2.87 (t, J = 6.1 Hz, 2H), 3.15 (unresolved t, 2H), 3.24 (s, 6H), 3.28 (s, 3H), 3.49–3.53 (m, 6H), 3.60 (t, J = 6.1 Hz, 2H), 3.63–3.68 (m, 6H), 3.73–3.77 (m, 2H), 3.79–3.83 (m, 8H), 4.03–4.08 (m, 10H), 4.18–4.22 (m, 2H), 4.23–4.27 (m, 4H), 4.30–4.34 (m, 2H), 4.38–4.42 (m, 2H), 4.48–4.52 (m, 2H), 4.67 (s, 2H), 4.88 (s, 4H), 5.88–6.15 (m, 10H), 6.22 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 8.0 Hz, 1H), 6.75 (s, 2H), 6.78–6.86 (m, 8H), 7.07–7.18 (m, 12H), 7.21–7.26 (m, 8H), 7.33 (d, J = 8.4 Hz, 4H), 7.57 (d, J = 6.0 Hz, 2H), 7.61 (d, J = 6.0 Hz, 2H), 7.85 (d, J = 6.0 Hz, 2H), 8.14 (s, 2H), 8.22 (s, 2H), 8.26 (s, 2H), 8.27 (s, 2H), 8.65 (d, J = 6.0 Hz, 2H), 8.97 (d, J = 6.0 Hz, 2H), 9.09 (d, J = 6.0 Hz, 2H), 9.27 (d, J = 6.0 Hz, 2H). Data for **2**•4PF_6•GREEN: ^{1}H NMR (500 MHz, CD_3SOCD_3, 400 K) d = 1.23 (t, J = 7.7 Hz, 3H), 1.31 (s, 18H), 2.63 (q, J = 7.7 Hz, 2H), 2.67 (s, 3H), 2.71 (t, J = 6.5 Hz, 2H), 3.28 (t, J = 7.1 Hz, 2H), 3.30 (s,

9H), 3.49–3.51 (m, 6H), 3.62–3.64 (m, 6H), 3.73–3.78 (m, 10H), 3.92–3.98 (m, 6H), 4.07–4.31 (m, 16H), 4.42–4.44 (m, 2H), 4.88 (s, 2H), 5.01 (s, 4H), 5.83 and 5.89 (AB q, *J* = 12.1 Hz, 8H), 6.34 (br s, 2H), 6.76 (s, 2H), 6.83–6.99 (m, 10H), 7.06–7.12 (m, 10H), 7.18–7.34 (m, 14H), 7.89 (br s, 8H), 8.09 (br s, 8H), 9.27 (br s, 8H).

Compound 28. A solution of 4,4´-dimethylbenzophenone (25.5 g, 121 mmol) in anhydrous THF (80 mL) was added slowly to freshly prepared THF solution of 4-methylphenylmagnesium bromide (4.2 g magnesium turnings, 174 mmol; 27 g of 4-methylphenylbromide 158 mmol; 140 mL of anhydrous THF). The reaction mixture was heated under reflux for 12 h and, after cooling, poured into 200 g of ice containing 10 mL of concentrated H_2SO_4. After extraction with CH_2Cl_2 (3 × 100 mL), the combined organic phase was washed with a 5% aqueous solution of $NaHCO_3$ (100 mL) and H_2O (100 mL). After drying ($MgSO_4$) and evaporation of the solvent, the crude product was recrystallized from hexane to yield 25.0 g (68%) of the compound **28** as a white solid. Data for **28**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.34 (s, 9H), 2.83 (s, 1H), 7.10 (d, *J* = 8.5 Hz, 6H), 7.18 (d, *J* = 8.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.0, 81.6, 127.8, 128.5, 136.6, 144.4; MS(FAB) *m/z* (%) 302 (7) $[M]^+$; $C_{22}H_{22}O$: calcd C 87.38, H 7.33; found C 87.44, H 7.29.

Compound 29. A mixture of compound **28** (20 g, 66 mmol) and acetyl chloride (103 g, 1.32 mol) was heated under reflux for 24 h and, after cooling, excess of acetyl chloride was removed *in vacuo*. The yellow oily residue was dissolved in phenol (80 g 0.85 mol) by warming. The reaction mixture was stirred for 18 h at 100 °C and then allowed to cool to room temperature. Toluene (200 mL) was added to the reddish-black mixture. The organic phase was washed with an aqueous solution of NaOH (20 g/L, 7 × 150 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2:CH_2Cl_2). The colorless band (R_f = 0.5) was collected and the solvent evaporated to give 10.2 g (41%) of the compound **29** as an off-white solid. Data for **29**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.34 (s, 9H), 4.71 (s, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 7.06-7.12 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.0, 63.3., 114.2, 128.1,

131.0, 132.3, 135.2, 139.8, 144.4, 153.3; MS(FAB) *m/z* (%) 378 (83) $[M]^+$; $C_{28}H_{26}O$: calcd C 88.85, H 6.92; found C 88.51, H 6.97.

Compound 30. Trifluoromethanesulfonic anhydride (12.5 g, 44 mmol) was added dropwise to a solution of compound **29** (10 g, 26 mmol) in anhydrous CH_2Cl_2 (100 mL) containing 2,6-lutidine (5.3 mL, 6 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.72 g, 45 mmol) at –30 °C. The yellow reaction mixture was stirred for 30 min at –30 °C, whereupon the cool bath was removed. After stirring for 1 h, then H_2O (10 mL) was slowly added and the organic phase was washed with H_2O (100 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was roughly purified by flash column chromatography (SiO_2: CH_2Cl_2 / hexane 1 / 2). The colorless band (R_f = 0.6) was collected and the solvent was removed and the residue was added to a suspension in anhydrous DMF (100 mL), anhydrous MeOH (40 mL) and triethylamine (6.4 g, 63 mmol) followed by palladium (II) acetate (0.65 g, 3 mmol) and 1,3-bis(diphenylphosphino)-propane (1.2 g, 3 mmol). The mixture was heated to 70 °C (during heating the solid dissolves leaving a brown solution) and CO gas was passed into the solution for 8 h. The reaction mixture was then stirred for 7 h at 70 °C under a CO atmosphere. After cooling to room temperature, brine (200 mL) was added and mixture was extracted with CH_2Cl_2 (5 × 50 mL), The combined organic phases were washed with aqueous HCl solution (1N, 100 mL) and brine (5 ×100 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2:CH_2Cl_2 / hexane 1 / 1). The colorless band (R_f = 0.5) was collected and the solvent evaporated to give 14.2 g (77%) of the compound **30** as a pale yellow solid. Data for **30**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.32 (s, 9H), 3.90 (s, 3H), 7.05-7.11 (m, 12H), 7.34 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.9, 52.0, 64.2., 127.6, 128.4, 128.7, 130.9, 131.1, 135.6, 143.6, 152.8, 167.1; MS(FAB) *m/z* (%) 421 (95) $[M]^+$; $C_{30}H_{28}O_2$: calcd C 85.68, H 6.71; found C 85.50, H 6.68.

Compound 31. A mixture of compound **30** (6.26g, 15 mmol), *N*-bromosuccinimide (NBS) (8.21 g, 46 mmol) and 2,2´-azobisisobutyronitrile (AIBN) (50 mg, cat. amount) in

anhydrous CCl_4 (100 mL) was heated under reflux for 6 h. After cooling down to room temperature, the reaction mixture was filtered and the residue washed with CCl_4 (20 mL). The combined organic phase filtrate was concentrated *in vacuo* and the residue was roughly purified by flash column chromatography (SiO_2: CH_2Cl_2). The colorless band (R_f = 0.7 – 0.9) was collected and the solvent was removed to give an off-white semisolid. The solid was dissolved in anhydrous THF (20 mL) then added dropwise to a suspension of diethyleneglycol monomethylether (18 g, 150 mmol), 15-crown-5 (10 mg, cat. amount), NaI (10 mg, cat. amount), NaH (3.0 g, 120 mmol) and anhydrous THF (200 mL). The reaction mixture was heated under reflux for 20 h. After cooling down to room temperature the reaction mixture was filtered and the residue washed with THF (50 mL). The combined organic phase filtrate was concentrated *in vacuo* and the brown oily residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). The solvent was concentrated *in vacuo* to give a dark brown oil. The oil was dissolved in anhydrous THF (200 mL), then powdered $LiAlH_4$ (0.5 g, 13 mmol) was added in small portions over a period of 15 min. The reaction mixture was stirred for 24 h at room temperature , then H_2O (10 mL) was slowly added and the mixture was filtered and the residue washed with THF (20 mL). The combined filtrate was concentrated *in vacuo* and the yellow oily residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 50 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: EtOAc / MeOH 95 / 5). The colorless band (R_f = 0.1) was collected and the solvent evaporated to give 2.05 g (18%) of the compound **31** as a pale yellow oil. Data for **31**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.35 (s, 9H), 3.52-3.54 (m, 6H), 3.63-3.68 (m, 18H), 4.51 (s, 6H), 4.62 (s, 2H), 7.16-7.23 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 58.9, 64.1, 64.7, 69.6, 70.4, 70.5, 71.8, 72.9, 126.1, 126.9, 130.8, 130.9, 131.0, 135.7, 138.4, 146.0; MS(FAB) *m/z* (%) 747 (100) $[M]^+$; $C_{44}H_{58}O_{10}$: calcd C 70.75, H 7.83; found C 70.58, H 7.72.

Compound 33. A *p*-toluenesulfonyl chloride (634 mg, 3.3 mmol) solution in CH_2Cl_2 (10 mL) was added slowly to another ice-cooled CH_2Cl_2 solution of **32** (1.63 g, 3.7 mmol),

triethylamine (2.6 mL, 18.0 mmol) and 4-dimethylaminopyridine (15 mg, cat. amount). The mixture was stirred for 16 h (0^oC to room temperature), then washed with 2N $HCl_{(aq)}$, H_2O, 2N $NaOH_{(aq)}$, and dried ($MgSO_4$). After removal of solvent the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 100/3). A second yellow band (R_f = 0.2) containing the desired product was collected and concentrated to give **33** (989 mg, 45%). Data for **33.** ^{1}H-NMR (CD_3CN, 500 MHz): δ = 2.42 (s, 2H), 2.74 (t, 1H, *J* = 3.7 Hz), 3.45-3.47 (m, 6H), 3.53-3.60 (m, 8H), 4.09 (t, 2H, *J* = 4.3 Hz), 4.21 (s, 2H), 4.25 (s, 2H), 6.34 (s, 1H), 6.37 (s, 1H), 7.41 (d, 2H, *J* = 8 Hz), 7.76 (d, 2H, *J* = 8 Hz). ^{13}C-NMR (CD_3CN, 125 MHz): δ = 20.6, 60.7, 68.1, 68.9, 69.1, 69.8, 69.8, 69.9, 72.2, 116.7, 116.8, 127.7, 129.9, 132.7, 134.4, 134.5, 134.6, 145.3. MS(FAB): *m/z* (%) = 748 (M^+, 6), 594 (M^+-154, 51), 307 (M^+-441, 100).

Compound 34. A 50 mL anhydrous MeCN solution of **33** (990 mg, 1.67 mmol) and **6** (2.38 g, 5.00 mmol) containing potassium carbonate (1.38 g, 10 mmol), lithium bromide (10 mg, cat. amount) and 18-crown-6 (10 mg, cat. amount), was refluxed for 16 h. After cooling down to room temperature, the mixture was filtered and the solid residue was washed with acetone. The combined organic solution was concentrated and the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 100/3). A second yellow band (R_f = 0.2) containing the desired product was collected and concentrated to give **34** (1.59 g, 95%). Data for **34.** ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.16 (t, 3 H, *J* = 7.5 Hz), 1.25 (s, 18H), 2.27 (2 H, *J* = 7.5 Hz), 2.70 (b, 1H), 3.40-3.47 (m, 2H), 3.52-3.60 (m, 10 H), 3.71-3.74 (m, 2H), 4.03-4.05 (m, 2H), 4.21-4.25 (m, 4H), 6.29-6.33 (three singlet, 2 H), 6.75-6.78 (m, 2H), 7.37-7.40 (m, 10H), 7.25-7.27 (m, 4H). ^{13}C-NMR (CD_3CN, 125 MHz): δ = 14.8, 25.1, 27.7, 30.5, 33.8, 60.9, 63.0, 67.3, 67.4, 69.1, 69.2, 69.8, 70.0, 70.1, 70.2, 72.2, 113.3, 116.5, 116.6, 124.3, 126.7, 130.2, 130.4, 131.6, 134.5, 134.6, 139.5, 141.5, 144.4, 144.7, 148.3, 156.6. MS(FAB): *m/z* (%) = 898 (M^+, 42), 383 (M^+-515, 100).

Compound 35. A solution of triethylamine (1.05 mL, 7.6 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to another solution of **34** (853 mg, 0.95 mmol), *p*-toluenesulfonyl chloride (362 mg, 1.9 mmol) and 4-dimethylaminopyridine (10 mg, cat. amount) in

anhydrous CH_2Cl_2 (50 mL). The mixture was stirred for 16 h at room temperature. The mixture was washed with 2N $HCl_{(aq)}$, H_2O, 2N $NaOH_{(aq)}$, and dried ($MgSO_4$). After removal of solvent the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 100/3). A second yellow band (R_f = 0.3) containing the desired product was collected and concentrated to give **35** (880 mg, 88%). ^{1}H-NMR (CD_3CN, 500 MHz): δ = 1.17 (t, 3H, *J* = 7.6 Hz), 1.27 (s, 18H), 2.40 (s, 3H), 2.26 (2H, *J* = 7.6 Hz), 2.70 (b, 1H), 3.40-3.48 (m, 4H), 3.54-3.62 (m, 6H), 3.72-3.75 (m, 2H), 4.03-4.06 (m, 2H), 4.09-4.12 (m, 2H), 4.17-4.23 (m, 4H), 6.26-6.29 (four singlet, 2H), 6.75-6.78 (m, 2H), 7.05-7.13 (m, 10H), 7.25-7.27 (m, 4H), 7.37-7.40 (m, 2H), 7.75-7.77 (m, 2H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 14.6, 20.6, 27.7, 30.5, 33.8, 63.1, 67.4, 67.5, 68.2, 69.1, 69.3, 69.3, 69.3, 69.7, 70.0, 70.1, 110.0, 110.1, 113.4, 113.4, 116.3, 116.4, 116.5, 124.2, 126.7, 127.6, 129.9, 130.3, 130.5, 131.7, 133.1, 134.5, 134.6, 134.6, 134.7, 139.6, 141.6, 144.4, 144.7, 145.1, 148.4, 146.7. MS(FAB): *m/z* (%) = 1052 (M^+, 50), 383 (M^+-669, 100).

Compound 37. A solution of **35** (0.87 g, 0.82 mmol) and **36** (0.33 g, 1.0 mmol) in anhydrous MeCN (50 mL) containing K_2CO_3 (0.45 g, 3.25 mmol), LiBr (20 mg, cat. amount) and 18-crown-6 (20 mg, cat. amount). The reaction mixture was heated under reflux for 36 h. After cooling down to room temperature, the reaction mixture was filtered and the residue washed with MeCN (20 mL). The combined organic phase filtrate was concentrated *in vacuo* to give a dark brown oil. The oil was dissolved in CH_2Cl_2 (20 mL) and a drop of concentrated HCl was added. The mixture was stirred for 2 h at room temperature, then washed with an aqueous solution of NaOH (1N, 20 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2 / EtOH 100 / 3). The yellow band (R_f = 0.2) was collected and the solvent evaporated to give 0.88 g (96%) of the compound **37** as a orange oil. Data for **37**: ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ = 1.21 (t, *J* = 7.6 Hz, 3H), 1.31 (s, 18H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.70 (s, 1H), 3.54-3.81 (m, 14H), 3.97-3.99 (m, 4H), 4.09-4.12 (m, 2H), 4.30-4.33 (m, 8H), 6.47-6.52 (four singlets, 2H), 6.83-6.85 (m, 2H), 6.96-6.99 (m, 2H), 7.10-7.16 (m, 10H), 7.30-7.32 (m, 4H), 7.34-7.40 (m, 2H), 7.85-

7.88 (m, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ = 14.8, 25.1, 27.7, 30.5, 33.8, 60.9, 63.0, 67.3, 67.4, 69.1, 69.2, 69.8, 70.0, 70.1, 70.2, 71.4, 72.2, 106.8, 113.3, 114.3, 116.5, 116.6, 118.2, 120.0, 120.8, 124.3, 125.8, 126.7, 127.8, 129.0, 130.2, 130.4, 131.6, 134.5, 134.6, 139.5, 141.5,144.4, 144.7, 147.7, 148.3, 155.5, 156.6 ; MS(FAB) *m/z* (%) 1128 (55) $[M]^+$; $C_{65}H_{76}O_9S_4$: calcd C 69.12, H 6.78, S 11.36; found C 69.18, H 6.76, S 11.25.

Dumbbell 39. $SOCl_2$ (1mL) was added to a solution of compound **31** (0.19 g, 0.26 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 2 h at room temperature, then washed with H_2O (10 mL) and dried ($MgSO_4$). The solvent was concentrated *in vacuo* to give compound **38** a yellow oil. Then compound **38** was dissolved in anhydrous THF (5 mL) and added dropwise to a suspension of compound **39** (0.20g, 0.18 mmol), 15-crown-5 (10 mg, cat. amount), NaI (10 mg, cat. amount), NaH (0.05 g, 2.0 mmol) and anhydrous THF (20 mL). The reaction mixture was heated under reflux for 16 h. After cooling down to room temperature, the reaction mixture was filtered and the residue washed with THF (10 mL). The combined organic phase filtrate was concentrated *in vacuo* and the brown oily residue was purified by column chromatography (SiO_2: ethylacetate). The yellow band (R_f = 0.7) was collected and the solvent evaporated to give 0.125 g (37%) of the dumbbell **39** as a pale yellow oil. Data for **39**: ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ = 1.21 (t, *J* = 7.6 Hz, 3H), 1.31 (s, 18H), 2.62 (q, *J* = 7.6 Hz, 2H), 3.30 (s, 9H), 3.47-3.62 (m, 38H), 3.94-3.96 (m, 4H), 4.05-4.12 (m, 2H), 4.25-4.26 (m, 8H), 4.48-4.49 (m, 8H), 6.26-6.29 (four singlets, 2H), 6.78-6.80 (m, 2H), 6.90-6.93 (m, 2H), 7.05-7.28 (m, 32H), 7.79 (d, *J* = 8.5, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ = 14.8, 25.1, 27.7, 30.5, 33.8, 58.9, 60.9, 63.0, 64.1, 64.7, 67.3, 67.4, 69.1, 69.2, 69.6, 69.8, 70.0, 70.1, 70.2, 70.4, 70.5, 71.4, 71.8, 72.2, 72.9, 106.8, 113.3, 114.3, 116.5, 116.6, 118.2, 120.0, 120.8, 124.3, 125.8, 126.1, 126.7, 126.9, 127.8, 129.0, 130.2, 130.4, 130.8, 130.9, 131.0, 131.6, 134.5, 134.6, 135.7, 138.4, 139.5, 141.5, 144.4, 144.7, 146.0, 147.7, 148.3, 155.5, 156.6; MS(FAB) *m/z* (%) 1858 (100) $[M]^+$; $C_{109}H_{132}O_{18}S_4$: calcd C 70.44, H 7.16, S 6.90; found C 70.42, H 7.12, S 6.86.

[2]Rotaxane 40. A solution of dumbbell **39** (0.125 g, 0.067 mmol), **20**•2PF_6 (0.143 g, 0.205 mmol) and **21** (0.053 g, 0.202 mmol) in anhydrous DMF (10 mL) was stirred for 10 d at room temperature (after approx. 1 d the color changed to dark green and a white precipitate was formed). The green suspension was directly subjected to column chromatography (SiO_2) and unreacted **39** was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the green band containing **40** •4PF_6 was collected. Most of the solvent was removed under vacuum (T < 30 °C) followed by addition of H_2O (50 mL). The resulting precipitate was collected by filtration, washed with Et_2O (20 mL) and dried affording 0.090 g (45%) of the compound [2] rotaxane **40** •4PF_6 as a green solid. Data for **40**•4PF_6: ^{1}H NMR (500 MHz, CD_3CN) δ = 1.13-1.19 (m, 3H), 1.23-1.26 (m, 18H), 2.55- 2.60 (m, 2H), 3.25 (s, 9H), 3.42-4.13 (m, 52H), 4.44 (s, 6H), 4.48 (s, 2H), 5.38-5.71 (m, 8H), 5.91, 5.99, 6.08, 6.19 (four singlets, 2H), 6.47 (d, *J* = 8.5, 1H), 6.56-6.65 (m, 3H), 6.76 (d, *J* = 8.5, 1H), 6.95-6.98 (m, 1H), 7.03-8.02 (m, 48H), 8.38- 8.97 (m, 8H); MS(FAB) *m/z* (%) 2814 (8) $[M-PF_6]^+$, 2668 (13) $[M-2PF_6]^+$, 2523 (8) $[M-3PF_6]^+$; $C_{145}H_{164}F_{24}N_4O_{18}P_4S_4$: calcd C 58.86, H 5.59, N 1.89; found C 58.79, H 5.54, N 1.86.

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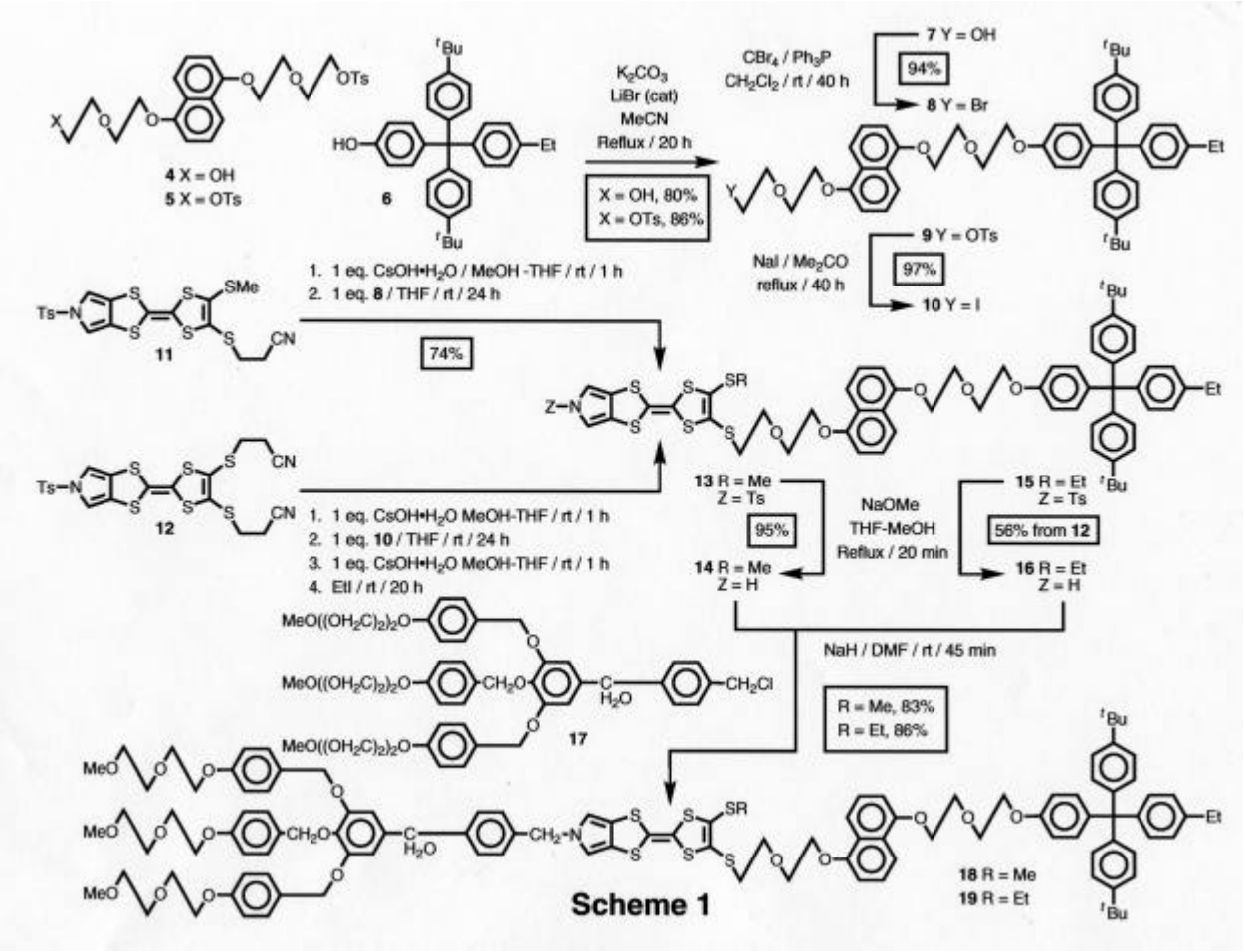
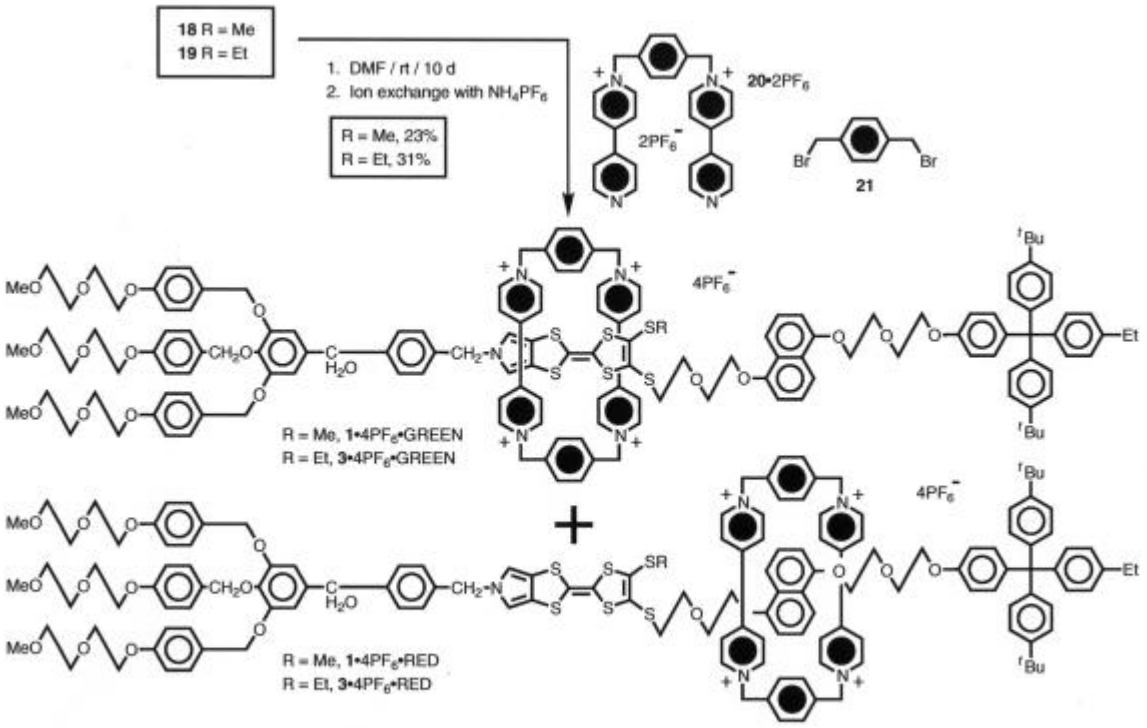
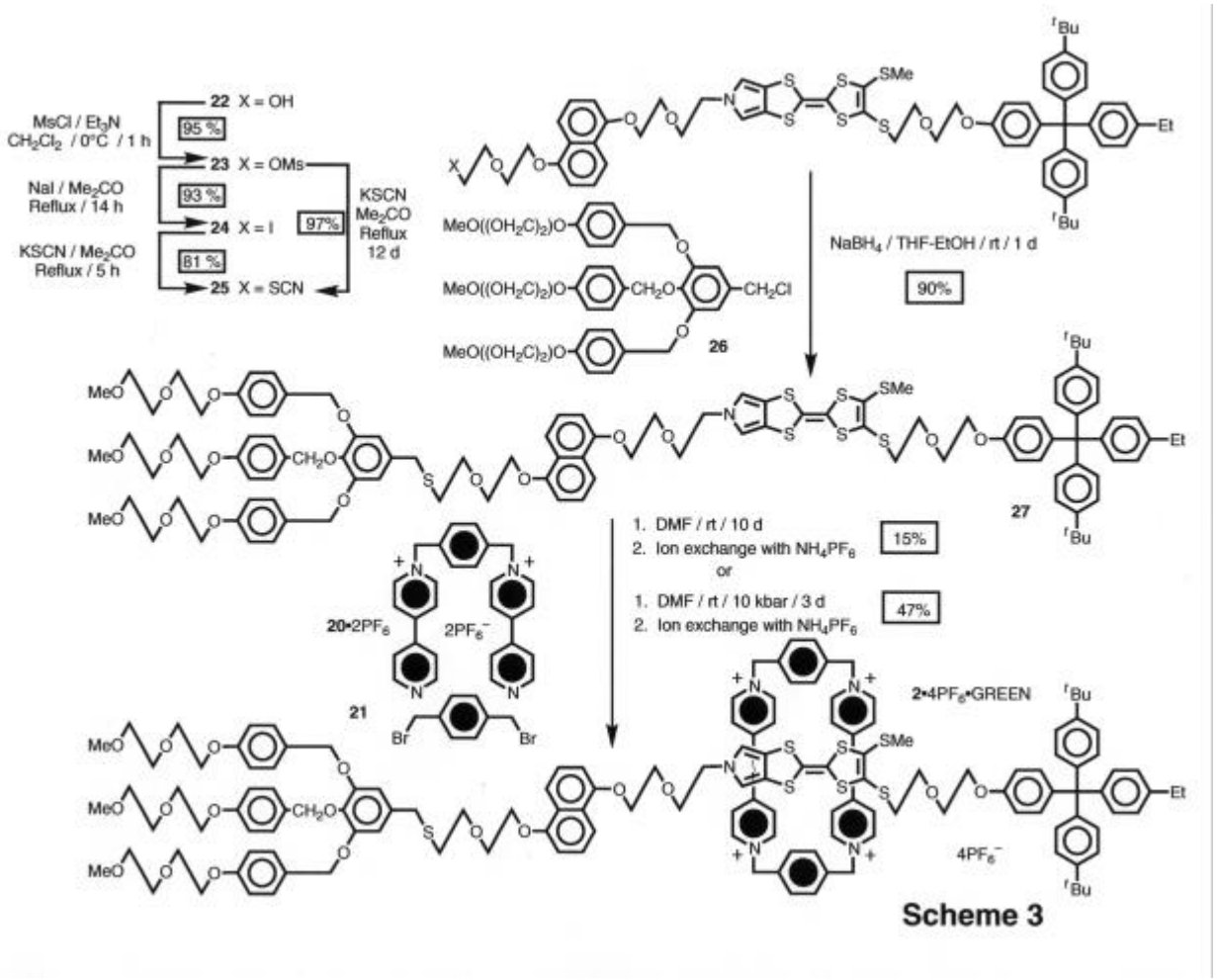
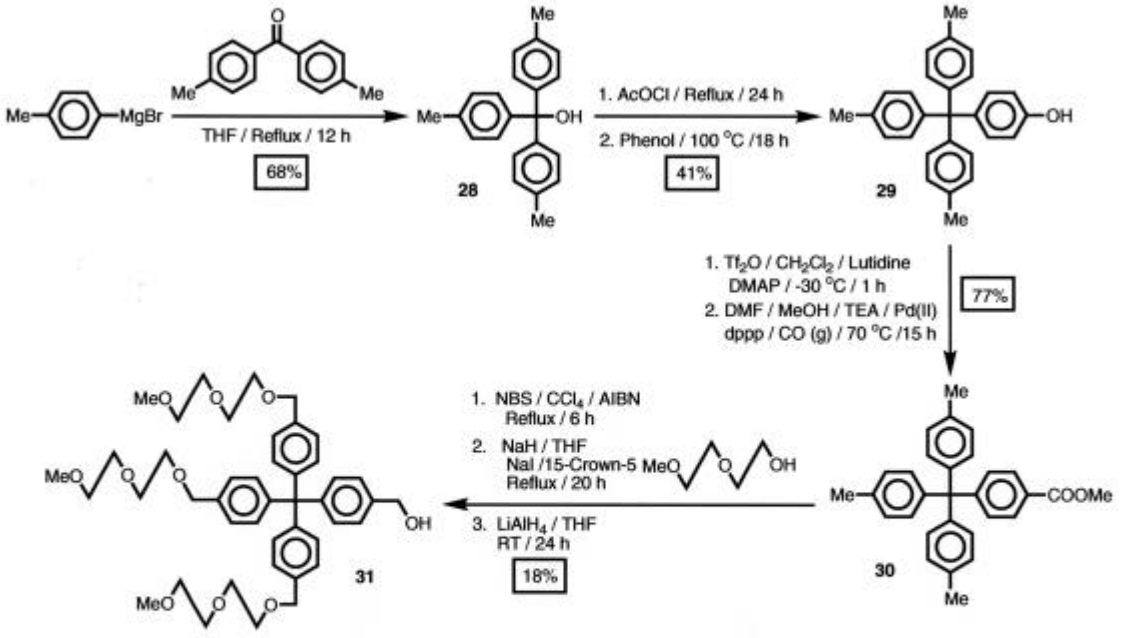

4 X = OH
5 X = OTs
6
K2CO3
LiBr (cat)
MeCN
Reflux / 20 h
X = OH, 80%
X = OTs, 86%
CBr4 / Ph3P
CH2Cl2 / rt / 40 h
7 Y = OH
94%
8 Y = Br
NaI / Me2CO
reflux / 40 h
9 Y = OTs
97%
10 Y = I
11
1. 1 eq. CsOH•H2O / MeOH -THF / rt / 1 h
2. 1 eq. 8 / THF / rt / 24 h
74%
12
1. 1 eq. CsOH•H2O MeOH-THF / rt / 1 h
2. 1 eq. 10 / THF / rt / 24 h
3. 1 eq. CsOH•H2O MeOH-THF / rt / 1 h
4. EtI / rt / 20 h
13 R = Me
Z = Ts
95%
14 R = Me
Z = H
NaOMe
THF-MeOH
Reflux / 20 min
15 R = Et
Z = Ts
56% from 12
16 R = Et
Z = H
NaH / DMF / rt / 45 min
17
R = Me, 83%
R = Et, 86%
18 R = Me
19 R = Et
Scheme 1


18 R = Me
19 R = Et
1. DMF / rt / 10 d
2. Ion exchange with NH4PF6
R = Me, 23%
R = Et, 31%
20•2PF6
2PF6-
21
4PF6-
R = Me, 1•4PF6•GREEN
R = Et, 3•4PF6•GREEN
R = Me, 1•4PF6•RED
R = Et, 3•4PF6•RED

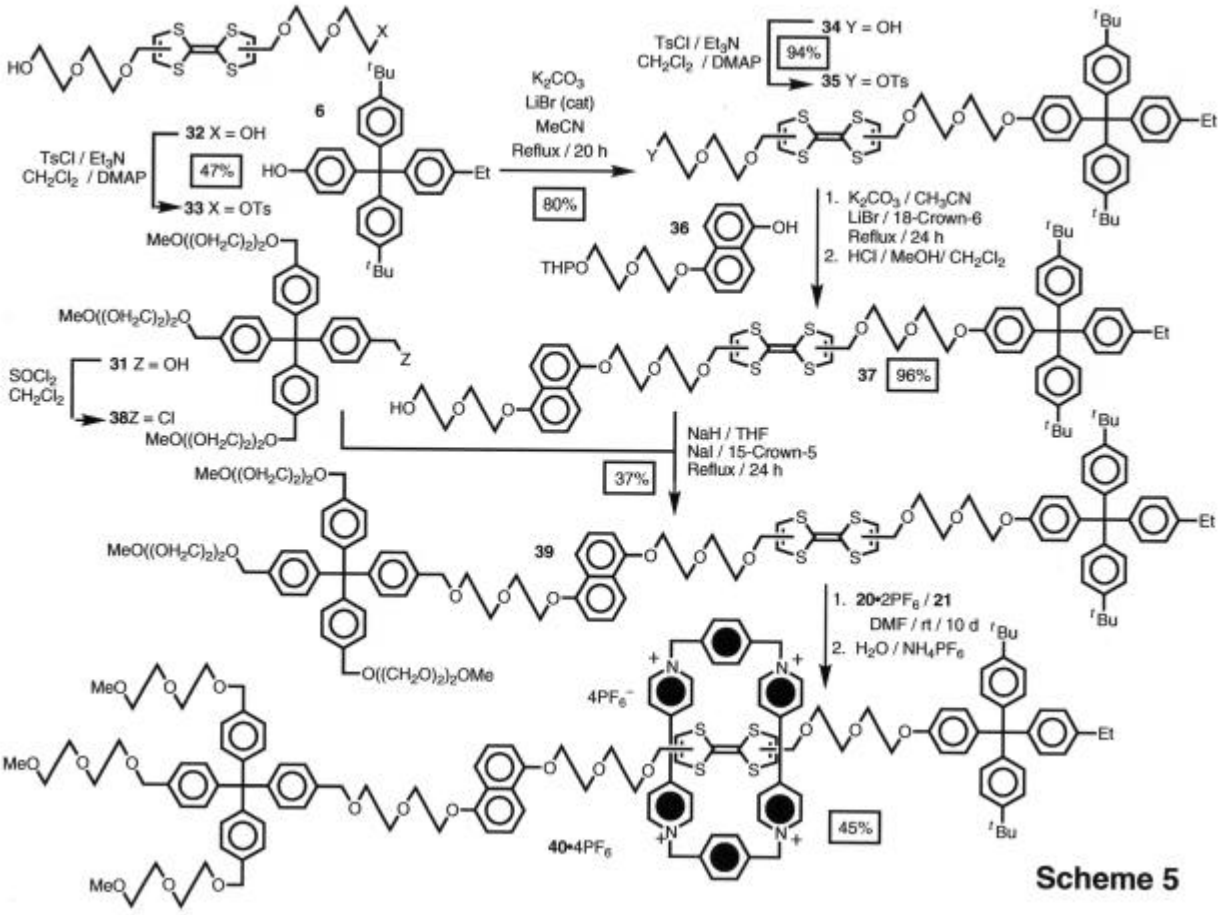
Scheme 2


22 X = OH
MsCl / Et3N
CH2Cl2 / 0°C / 1 h
95 %
23 X = OMs
NaI / Me2CO
Reflux / 14 h
93 %
24 X = I
97%
KSCN / Me2CO
Reflux / 5 h
81 %
25 X = SCN
KSCN
Me2CO
Reflux
12 d
26
NaBH4 / THF-EtOH / rt / 1 d
90%
27
1. DMF / rt / 10 d
2. Ion exchange with NH4PF6
15%
or
1. DMF / rt / 10 kbar / 3 d
2. Ion exchange with NH4PF6
47%
20•2PF6
2PF6−
21
2•4PF6•GREEN
4PF6−

Scheme 3


Me
MgBr
THF / Reflux / 12 h
68%
28
1. AcOCl / Reflux / 24 h
2. Phenol / 100 °C /18 h
41%
29
1. Tf2O / CH2Cl2 / Lutidine
DMAP / -30 °C / 1 h
2. DMF / MeOH / TEA / Pd(II)
dppp / CO (g) / 70 °C /15 h
77%
30
COOMe
1. NBS / CCl4 / AIBN
Reflux / 6 h
2. NaH / THF
NaI /15-Crown-5
Reflux / 20 h
3. LiAlH4 / THF
RT / 24 h
18%
31
MeO
OH

Scheme 4


6
32 X = OH
33 X = OTs
TsCl / Et3N
CH2Cl2 / DMAP
47%
K2CO3
LiBr (cat)
MeCN
Reflux / 20 h
80%
34 Y = OH
35 Y = OTs
TsCl / Et3N
CH2Cl2 / DMAP
94%
36
THPO
1. K2CO3 / CH3CN
LiBr / 18-Crown-6
Reflux / 24 h
2. HCl / MeOH/ CH2Cl2
37
96%
31 Z = OH
38 Z = Cl
SOCl2
CH2Cl2
NaH / THF
NaI / 15-Crown-5
Reflux / 24 h
37%
39
1. 20•2PF6 / 21
DMF / rt / 10 d
2. H2O / NH4PF6
4PF6−
40•4PF6
45%

Scheme 5