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Synthesis of linear oligo-TTFs and their [2]rotaxanes with cyclobis(paraquat-*p*-phenylene)

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Two linear oligo-TTFs were synthesised employing a stepwise strategy involving two different thiolate protecting groups. These linear TTFs were incorporated into donor–acceptor rotaxanes with the cyclic acceptor, cyclobis(paraquat-*p*-phenylene).‡ Moreover, a prototype rotaxane based on a bis(pyrrolo)-TTF was prepared and studied.

Introduction

Rotaxanes are a class of interlocked molecules containing a dumbbell-shaped component (a rod and two bulky stoppers), around which a cyclic entity is encircled. The bulky stoppers prevent the cyclic entity from dethreading. The translational isomerism of rotaxanes[1] offers the possibility for employing such interlocked molecules as molecular machines (Fig. 1).[2] The reversible redox properties of tetrathiafulvalene (TTF) make it a good candidate as an electron donor unit in donor–acceptor based rotaxanes with the cyclic acceptor, cyclobis(-paraquat-*p*-phenylene) **4** (Fig. 2).[3] Thus a rotaxane, containing two different TTFs, whose redox potentials can be finely tuned by varying their substitution, could possibly be a molecular switch.

The first TTF-based rotaxane was reported by Stoddart and coworkers[1g] and contained one central bis(2-oxypropylene-dithio)-substituted TTF and two hydroquinone donor sites in the dumbbell component. We have reported another rotaxane based on a tetramercapto-substituted TTF (Fig. 3).[1h]

As an extension to this work, a rotaxane containing three derivatised units of **2** has been prepared in order to study the shuttling motions upon electrochemical oxidation. Moreover, a rotaxane containing derivatives of the two different TTFs **2** and **3** is reported (Fig. 4). However, both these rotaxanes suffer from the problem of *cis–trans* isomerism. As a solution to this problem we describe the synthesis of the first prototype rotaxane based on the bispyrrolo-TTF **1**, which is a strong π-donor (Fig. 4). An association constant of 7900 M^{-1} was obtained for the pseudorotaxane complex between **1** and **4** in acetone,[4] while the association constant for the TTF·**4** complex is 2600 M^{-1} in acetone.[5]

Results and discussion

Preparation of linear oligo-tetrathiafulvalenes

In order to prepare linear molecules containing multiple TTFs, the stepwise strategy outlined in Scheme 1 was employed. This strategy relies on the availability of at least two orthogonal thiolate protecting groups (PG_1 and PG_2). The cyanoethyl group has been commonly employed as a protecting group for TTF-thiolates.[6] Recently, the *p*-nitrophenylethyl group was used successfully in combination with the cyanoethyl group for a stepwise deprotection–alkylation (Scheme 2).[7]

Thus, it should be possible to stepwise deprotect a TTF containing one cyanoethyl group and one *p*-nitrophenylethyl group (Scheme 3). The key compounds **14** and **15** were prepared by unsymmetrical phosphite-mediated cross couplings.[8] Different combinations of 1,3-dithiole-2-thiones and 1,3-dithiol-2-ones were tried in these couplings and the highest yield of the TTF **14** is obtained when reacting the ketone **6** with the thione **10**.

The *p*-nitrophenylethyl monoprotected thione **10** can be prepared in two ways (Scheme 4): (a) treatment of **16**[7] with 1 equiv. of caesium hydroxide monohydrate followed by excess methyl iodide in DMF; (b) treatment of **7**[6] with 1 equiv. of caesium hydroxide monohydrate followed by 2-(4-nitrophenyl)-ethyl bromide in CH_3CN.

Selective monoalkylation is now possible, thus treatment of **14** with 1 equiv. of caesium hydroxide monohydrate and subsequently 1,2-bis(2-iodoethoxy)ethane in DMF (Scheme 5) generated the iodide **17** in 77% yield. This compound was then reacted with the bisthiolate generated by treating **18**[6] with 2 equiv. caesium hydroxide monohydrate to afford the tris(tetrathiafulvalene) **19** in 83% yield. The two *p*-nitrophenylethyl protecting groups were then removed upon treatment with 2 equiv. of caesium hydroxide, and the resulting bisthiolate was then reacted with 1-{2-[2-(2-iodoethoxy)ethoxy]-ethoxy}-4-(triphenylmethyl)benzene[1g] **23a** (Scheme 5) in DMF, affording the dumbbell-shaped compound **20** in 82% yield.

Next, a linear molecule containing two differently substituted tetrathiafulvalenes was prepared, the first TTF unit containing methylthio substituents in the 5(4),5′-positions and the other methoxycarbonyl groups in the 5(4),5′-positions (Scheme 6), from the diester **15**, which was treated with one equiv. of caesium hydroxide to afford the monothiolate that was then reacted with the iodide **17**, generating the bis(tetrathiafulvalene) **21** in 85% yield. Deprotection of **21** by treatment of the bisthiolate with 2 equiv. caesium hydroxide monohydrate and addition of 2 equiv. of **23a**[1g] gave the dumbbell **22** in 65% yield. Both compounds **20** and **22** are mixtures of *cis–trans* isomers.

Finally, a dumbbell based on the bis(pyrrolo)-TTF **1** was

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‡The IUPAC name for cyclobis(paraquat-*p*-phenylene) is 1(1,4),2(4,1),6(1,4),7(4,1)-tetrapyridina-4,9(1,4)-dibenzenacyclodecaphane-1^1,2^1,6^1,7^1-tetraium.

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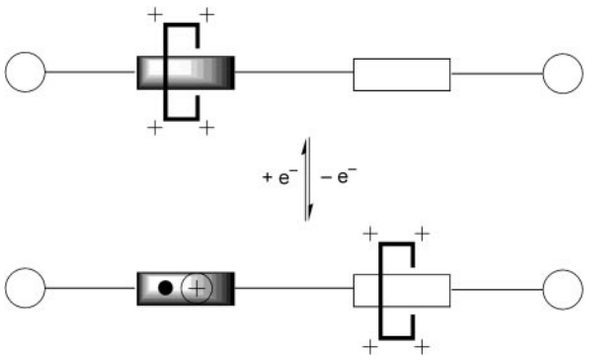


Fig. 1 Redox-controlled switch.

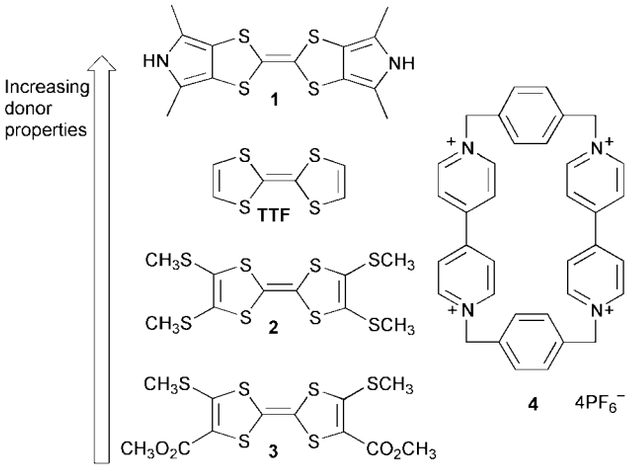


Fig. 2 Donor properties of compounds **1**–**4**

obtained in a yield of 81% by reacting bispyrrolo-TTF **1** with sodium hydride and the bromide **23b** (Scheme 7).

Preparation of rotaxanes

The rotaxane **27** was prepared in 20% yield by reacting the dumbbell **20** with 1,1″-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluorophosphate) **26** and 1,4-bis(bromomethyl)benzene **25** in DMF and subjecting the mixture to 10 kbar for 4 d (Scheme 8). In a similar way the rotaxanes **28** and **29** were obtained, in yields of 35% and 26%, respectively (Fig. 4). The UV-Vis of **27** and **28** revealed charge transfer absorption bands at λ_{max} 788 nm (ε 496 M^{-1} cm^{-1}) and λ_{max} 748 nm (ε 1150 M^{-1} cm^{-1}), whereas **29** exhibited a charge transfer band at λ_{max} 807 nm (ε 310 M^{-1} cm^{-1}).

Table 1 Peaks (*m*/*z*) assigned in the ESMS and MALDI MS spectra

	27		**28**	
	ESMS	MALDI MS	ESMS	MALDI MS
$[M-4PF_6]^{4+}$	682	682	570	
$[M-4PF_6]^{3+}$		909	760	760
$[M-4PF_6]^{2+}$		1364		1139
$[M-4PF_6]^{+}$	2728	2728		2278
$[M-3PF_6]^{4+}$	718			
$[M-3PF_6]^{3+}$	958	958	808	
$[M-3PF_6]^{2+}$			1212	
$[M-3PF_6]^{+}$	2873	2873		2423
$[M-2PF_6]^{4+}$	754.5			
$[M-2PF_6]^{2+}$	1510		1284	
$[M-2PF_6]^{+}$	3018			2568
$[M-1PF_6]^{+}$	3163			
$[dumbbell]^{3+}$	737			
$[dumbbell]^{2+}$	1105			
$[dumbbell]^{+}$		2208		1758

Table 2 ESMS/MS data rotaxanes (*m*/*z*)

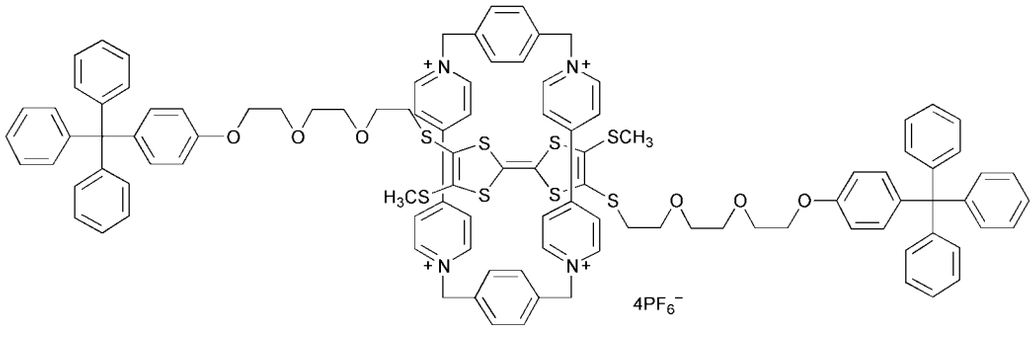
Parent ion $[M-4PF_6]^{4+}$	Daughter ions $[C_8H_8]^{+}$	$[C_{28}H_{24}N_4]^{2+}$	$[C_{18}H_{16}N_2]^{\cdot+}$	$[dumbbell]^{2+}$
27 682	104	208	260	1105
28 570		208	260	879

Electrospray mass spectrometry (ESMS) and matrix assisted laser desorption ionization (MALDI)

The rotaxanes were characterized using ES and MALDI mass spectrometry. The data concerning **27** and **28** are listed in Table 1. It can be seen that the compounds give peaks arising from loss of PF_6^-. Peaks resulting from fragmentation of the rotaxane structures are also observed in the spectra. The daughter ion spectra (ESMS/MS) of selected parent ions are recollected in Table 2. Collisional activation of $[M-4PF_6]^{4+}$ by argon results in fragmentation of the supramolecular structure. The breakdown of the tetracationic cyclophane is accompanied by one or two electron transfers from the dumbbell to the cyclophane (Scheme 9). A similar fragmentation pattern was previously observed in related catenanes.[9]

^{1}H NMR spectroscopy

According to ^{1}H NMR spectroscopy the multiple-TTF rotaxanes **27** and **28** only contain one encircled unit of **4**. However, as a result of the *cis–trans* isomerism, their ^{1}H NMR spectra are complicated. Actually, 6 isomers of **27** and 4 isomers of **28** are possible. The spectrum of **27** is shown in Fig. 5. The cyclophane bipyridinium α-protons resonate as one



5
cis/trans

Fig. 3 Mono-TTF based rotaxane.

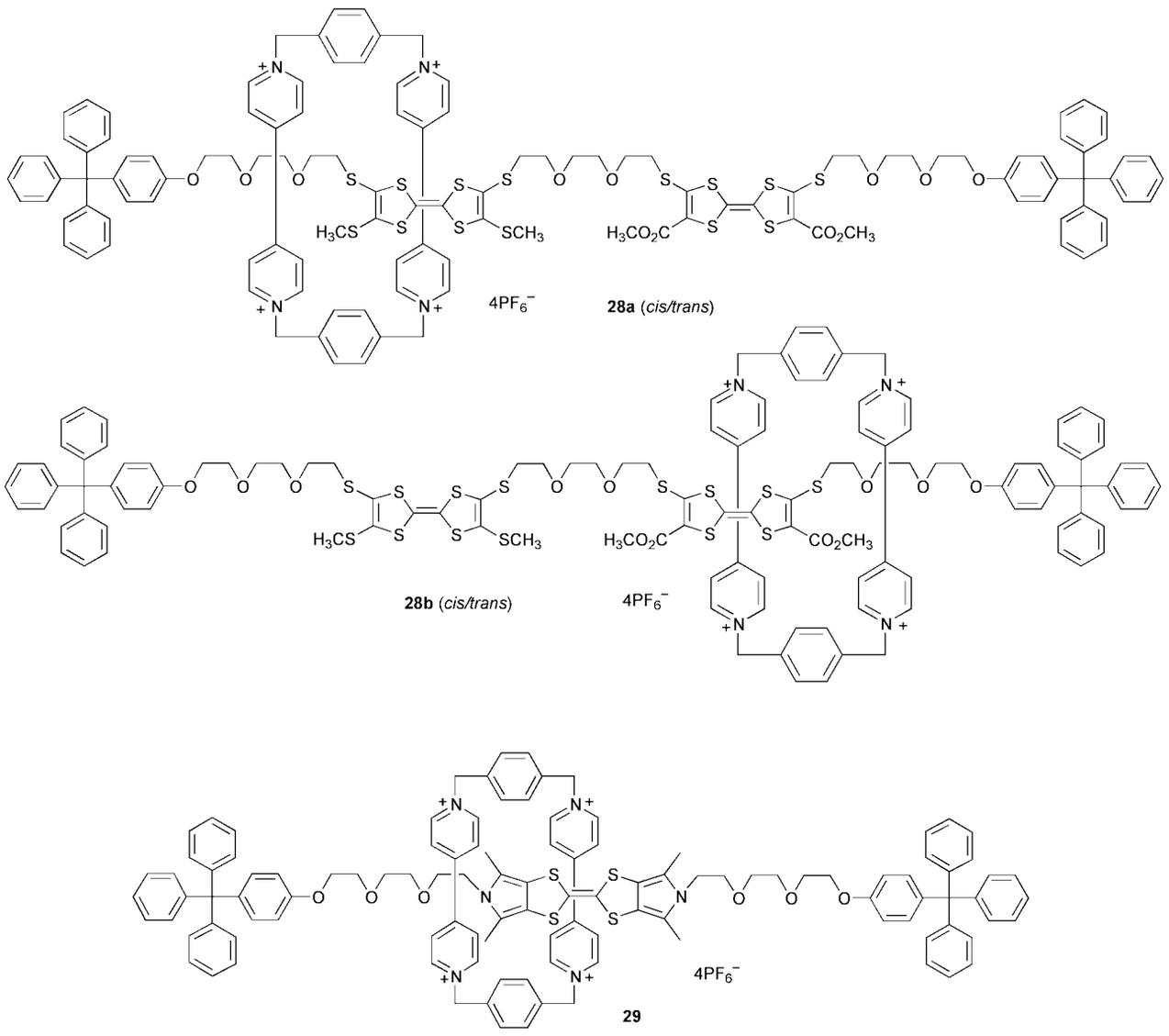
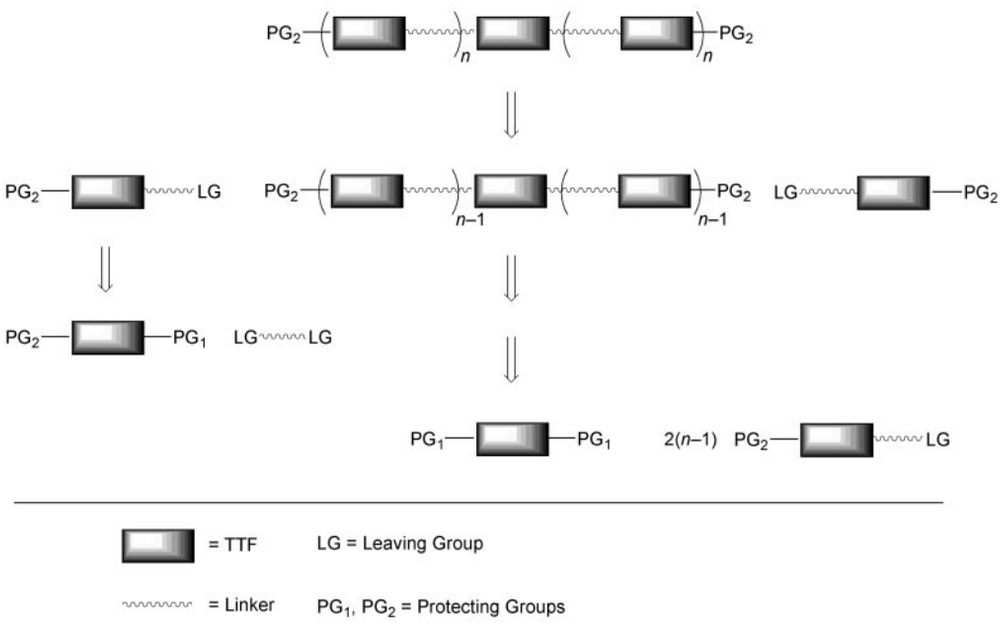
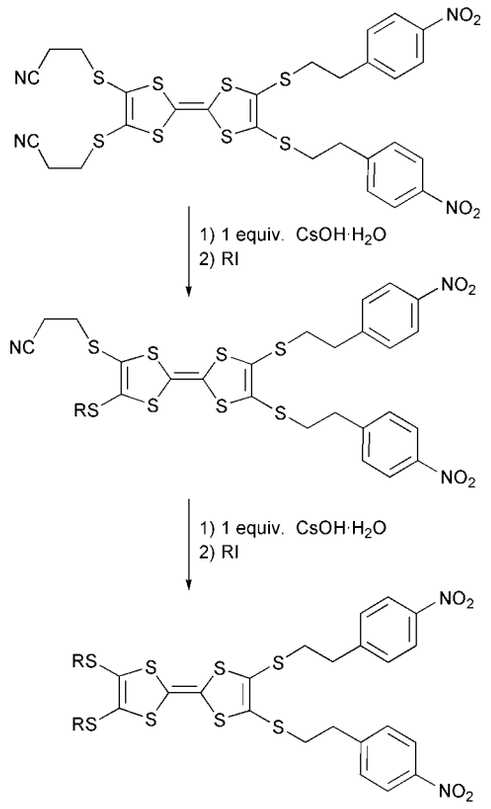


Fig. 4 Structures **28a**, **28b** and **29**

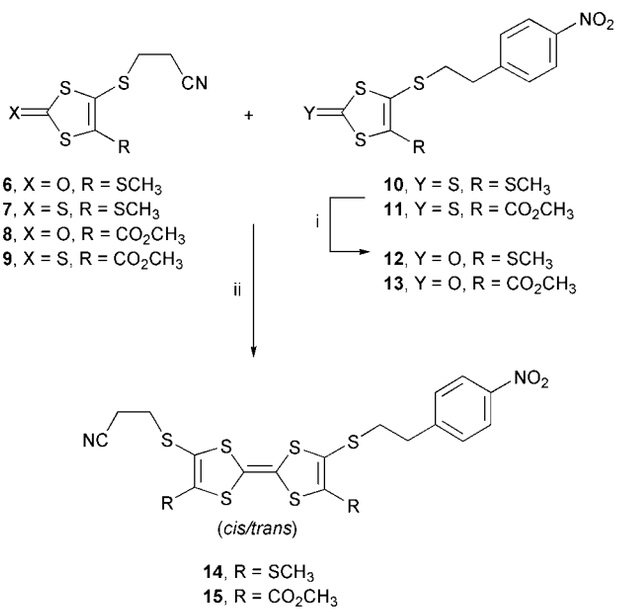


Scheme 1 Retrosynthetic strategy for preparing linearly connected oligo-TTFs.



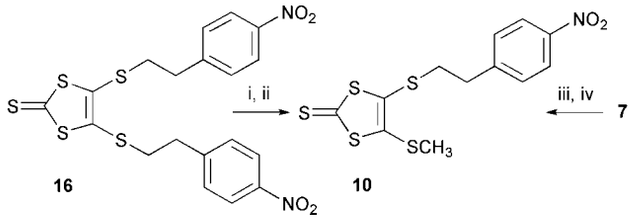
Scheme 2 Step-wise monodeprotection–realkylation protocol.

broad multiplet, whereas the β-protons are split into two broad multiplets (Table 3). The dumbbell SCH_3 and SCH_2 protons each resonate as two multiplets. One SCH_3 multiplet was shifted downfield by 0.22 ppm relative to the other, which is indicative of interactions with the cyclic acceptor.[5] The separated signals indicate slow shuttling motions of the



Reactants	Products (%)
6, **10**	**14** (43%)
12, **7**	**14** (33%)
8, **11**	**15** (28%)
9, **13**	**15** (28%)

Scheme 3 *Reagents and conditions*: i, $Hg(OAc)_2$, $CHCl_3$–CH_3CO_2H, room temp., 90 min, 87% (**12**), 70% (**13**); ii, $P(OEt)_3$, PhMe, 120 °C, 2 h.



Scheme 4 *Reagents and conditions*: i, 1 equiv. $CsOH·H_2O$–CH_3OH, DMF, room temp., 1 h; ii, CH_3I (excess), room temp., 5 h, 42%; iii, 1 equiv. $CsOH·H_2O$–CH_3OH, CH_3CN, room temp., 1 h; iv, 2-(4-nitrophenyl)ethyl bromide, CH_3CN, room temp. 1 h, 92%.

cyclic acceptor along the dumbbell on the ^{1}H NMR timescale (500 MHz).

Also for **28** two SCH_3 multiplets were observed, positioned at 2.31–2.45 and 2.55–2.64 ppm, respectively (Fig. 4). These two sets of SCH_3 protons were still present when cooling the sample to 213 K in $(CD_3)_2CO$ and can be assigned to uncomplexed and complexed SCH_3 groups, hence corresponding to encirclement of either the diester-TTF or the tetramercaptothio-TTF. The ratio between these two rotaxanes was estimated to *ca.* 8 : 10 at room temperature in CD_3CN (500 MHz). The exchange was still slow on the ^{1}H NMR timescale (250 MHz) upon heating to 338 K. Thus, a kinetical barrier prevents the conversion of rotaxane **28b** into the supposedly more stable **28a** in which the tetramercapto-TTF donor is encircled. The isomerically pure pyrrolo-TTF rotaxane **29** gave a simple ^{1}H NMR spectrum with sharp signals for the cyclophane protons.

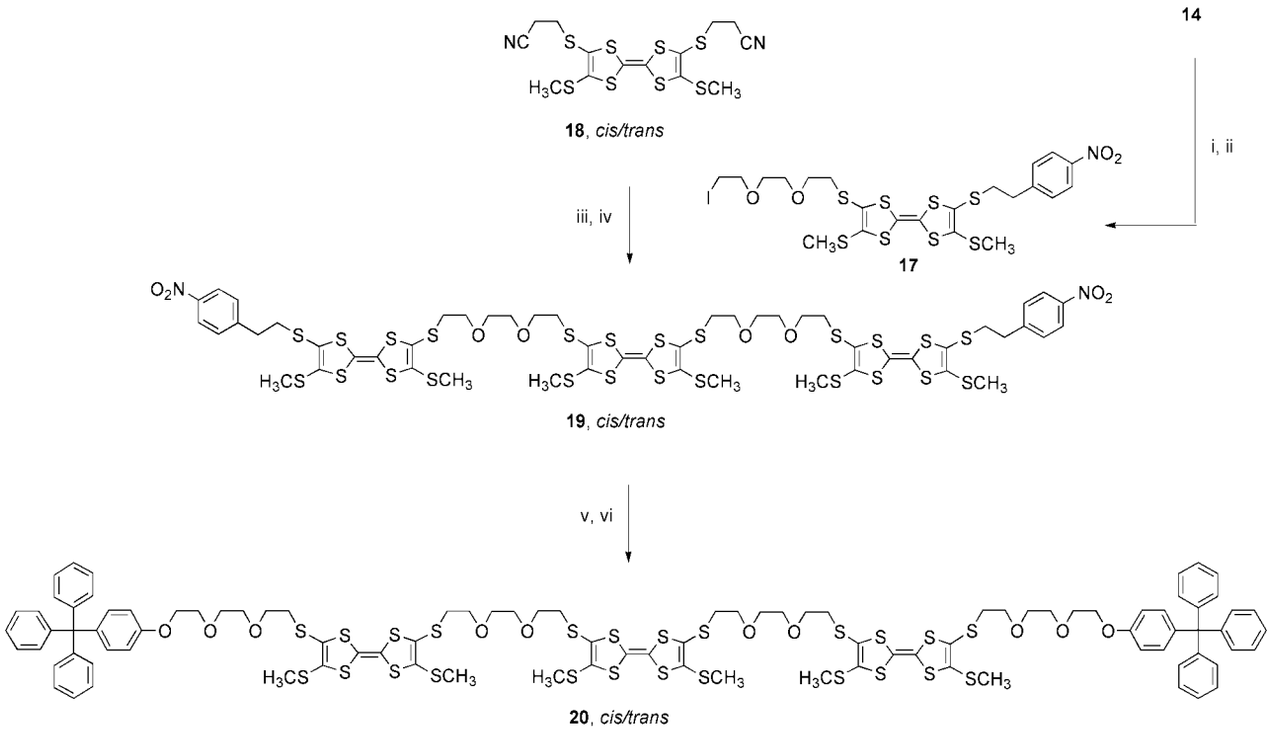
Conclusions

A strategy for preparing linear oligo-TTFs has been developed using two different thiolate protection groups. From these, rotaxanes were prepared and investigated, in both solution and in the gas phase. In the gas phase we observe electron transfers to the cyclic acceptor accompanied by its fragmentation. Future rotaxane systems based on a pyrrolo-TTF[10] and another donor seem very promising owing to the strong complexation between this TTF and the cyclic acceptor. Moreover, such systems will be devoid of *cis–trans* isomerism and hence more easy to characterise and study.

Experimental

General methods

All reactions were carried out under an atmosphere of dry N_2. CH_3OH was distilled from Mg. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days before use. All reagents were standard grade and used as received. Analytical TLC was performed on Merck DC-Alufolien Kieselgel 60 F_{254} 0.2 mm thickness. Column chromatography was carried out using silica gel 60F (Merck, 9385, 230–400 mesh). Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC250, a Varian 300 or a Varian 500 spectrometer; all chemical shifts are referenced to Me_4Si; *J* values are in Hz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained on a Varian MAT 311 A instrument and a Kratos MS 60 RF, respectively. Plasma desorption (PD) mass spectra were carried out on a BioIon 10R time of flight mass spectrometer over 5×10^5 fissions (^{252}Cf). Electrospray (ES) mass spectra were recorded using a Finnigan MAT TSQ 700 triple quadrupole mass spectrometer [a] and an IonSpec Fourier Transform Mass Spectrometer [b]. The rotaxanes were electrosprayed from acetonitrile solutions. ESMS/MS experiments were performed on the TSQ using argon typically at a pressure of 0.7 mTorr. The ion of interest was selected by



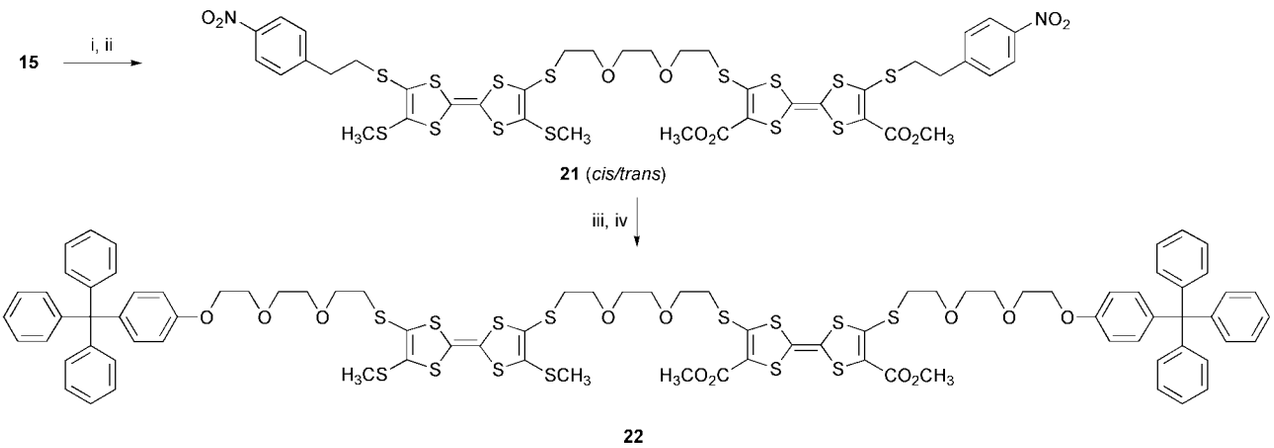
Scheme 5 *Reagents and conditions*: i, 1 equiv. $CsOH{\cdot}H_2O$–CH_3OH, DMF, room temp., 1 h; ii, $(CH_2OCH_2CH_2I)_2$, DMF, room temp., 5 h, 77%; iii, 2 equiv. $CsOH{\cdot}H_2O$–CH_3OH, DMF, room temp., 1 h; iv, 2 equiv. **17**, DMF, room temp., 5 h, 83%; v, 2 equiv. $CsOH{\cdot}H_2O$–CH_3OH, DMF, room temp., 1 h; vi, 2 equiv. **23a**, DMF, room temp., 5 h, 82%.

the first quadrupole, collisionally activated in the second (actually an octapole), and the products analysed by the third quadrupole. Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra were recorded using a Bruker Reflex instrument based on 200 shots, the matrix was dihydroxybenzene–CH_3OH 1 : 1. Electrochemical experiments were carried out with Bu_4NPF_6 as supporting electrolyte (0.1 M). Counter and working electrodes were made of Pt and the reference electrode was Ag/AgCl . The solvent was CH_3CN–CH_2Cl_2 9 : 1 unless otherwise indicated. All measurements were carried out at room temperature. UV-VIS spectra were recorded on a Shimadzu UV-160 instrument. Elemental analyses were performed at the Microanalytical Laboratory, University of Copenhagen and Atlantic Microlab, Inc., Georgia, USA.

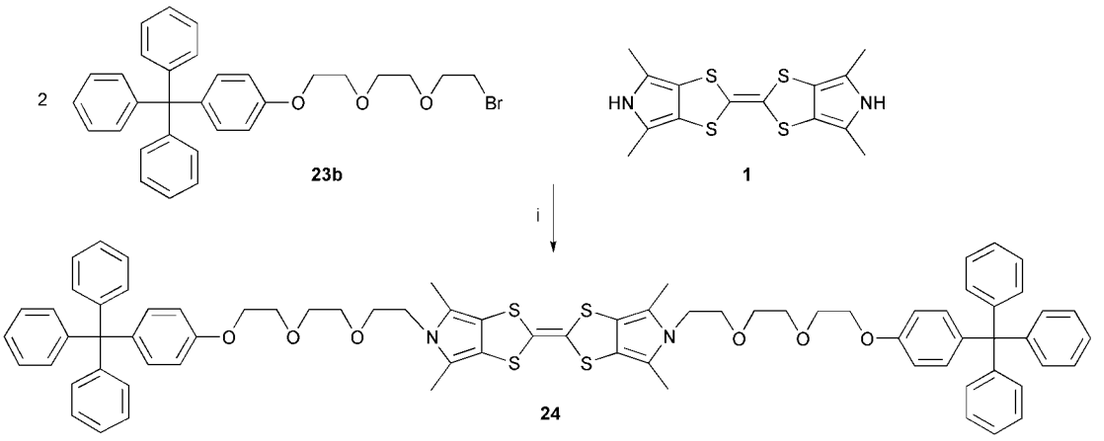
5-Methylthio-4-[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione 10

Method 1. To a solution of 4,5-bis[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione **16**[6] (1.00 g, 2.01 mmol), a solution of $CsOH{\cdot}H_2O$ (0.36 g, 2.11 mmol) in methanol (5 ml) was added dropwise *via* a syringe with stirring over 30 min. The solution was stirred for a further 30 min and CH_3I (1.43 g, 10.07 mmol) was added *via* a syringe and stirring was continued for an additional 5 h, whereupon the reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (100 ml) was added, and the organic solution washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether (bp 60–80 °C) 1 : 1), affording **10** (0.31 g, 0.85 mmol, 42%) as long yellow–orange needles. Mp 93–94 °C (from propan-2-ol).

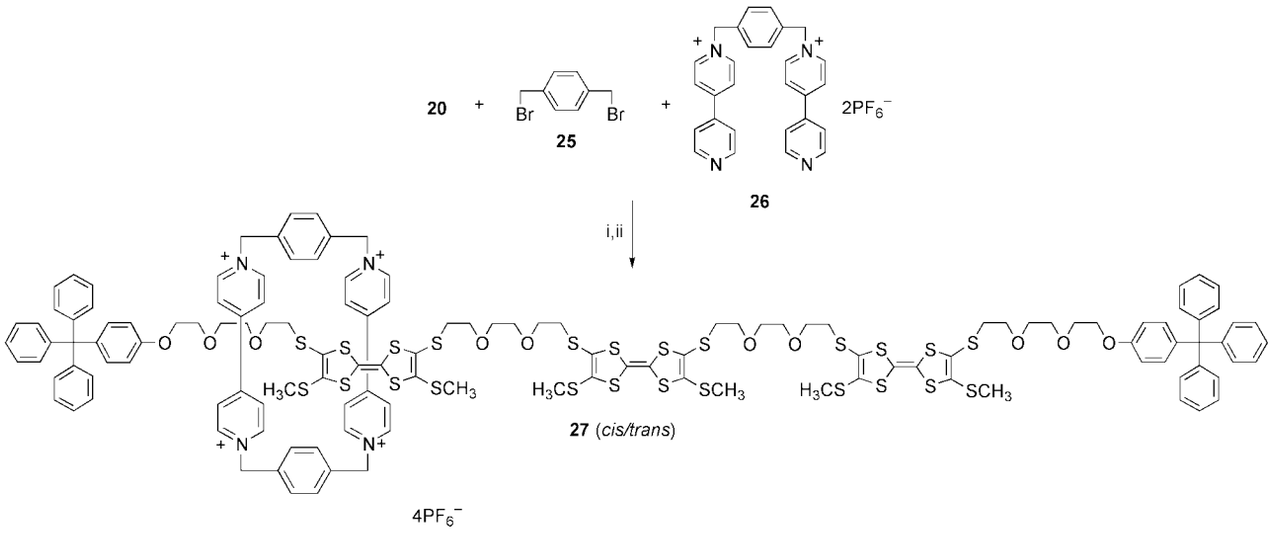
Method 2. To a solution of 4-(2-cyanoethylthio)-5-methylthio-1,3-dithiole-2-thione **7** (1.00 g, 3.77 mmol) in CH_3CN (50 ml), a solution of $CsOH{\cdot}H_2O$ (0.70 g, 4.14 mmol) in methanol (10 ml) was added dropwise with stirring over 30 min. The solution changed colour from yellow to red and was stirred for 30 min. A solution of 2-(4-



Scheme 6 *Reagents and conditions*: i, 1 equiv. $CsOH{\cdot}H_2O$–CH_3OH, DMF, room temp., 1 h; ii, 1 equiv. **17**, DMF, room temp., 5 h, 85%; iii, 2 equiv. $CsOH{\cdot}H_2O$–CH_3OH, DMF, room temp., 1 h; iv, 2 equiv. 1-{2-[2-(2-iodoethoxy)ethoxy]ethoxy}-4-(triphenylmethyl)benzene), DMF, room temp., 5 h, 65%.



Scheme 7 *Reagents and conditions*: i, NaH (excess), DMF, 81%.



Scheme 8 *Reagents and conditions*: i, **20**, **25** and **26**, DMF, room. temp., 10 kbar, 4 d; ii, NH_4PF_6, 20%.

nitrophenyl)ethyl bromide (1.06 g, 4.61 mmol) in CH_3CN (20 ml) was added in one portion. After stirring for 1 h, the reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (75 ml) was added, and the organic solution washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was then removed *in vacuo*. Recrystallisation of the product from propan-2-ol gave **10** (1.26 g, 3.49 mmol, 92%) as long yellow–orange needles. Mp 93–94 °C; δ_H ($CDCl_3$) 2.52 (s, 3H; SCH_3), 3.12 (m, 4H; SCH_2CH_2Ar), 7.40 (d, 2H, *J* 8.7; Ar 2,6-*H*), 8.19 (d, 2H, *J* 8.6; Ar 3,5-*H*); δ_C ($CDCl_3$) 18.96, 35.69, 36.87, 123.93, 129.55, 130.40, 140.98, 146.44, 147.05, 210.66; MS (EI): *m*/*z* (%): 361 (M^+, 100); Found: C, 39.84; H, 3.05; N, 3.76; $C_{12}H_{11}NO_2S_5$ requires C, 39.87; H, 3.07; N, 3.87%.

5-Methylthio-4-[2-(4-nitrophenyl)ethylthio]-1,3-dithiol-2-one 12

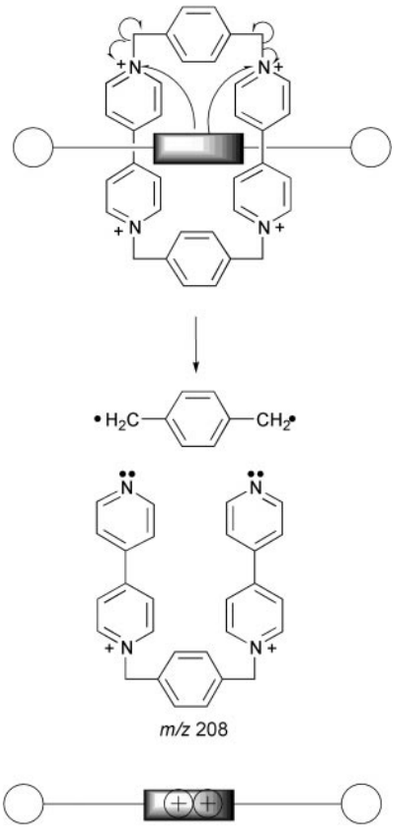
To a solution of 5-methylthio-4-[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione **10** (1.00 g, 2.77 mmol) in a mixture of $CHCl_3$ (45 ml) and AcOH (15 ml) was added Hg(OAc) (2.38 g, 7.47 mmol). After stirring for 90 min, the suspension was filtered through a short layer of Celite. The Celite was carefully washed with chloroform (3 × 50 ml). The combined filtrate was cautiously washed with aqueous $NaHCO_3$ (5 × 100 ml) and water (2 × 100 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue recrystallised from CH_3OH to give **12** (0.83 g, 2.41 mmol, 87%) as shining white needles. Mp 80–81 °C; δ_H ($CDCl_3$) 2.48 (s, 3H; SCH_3), 3.11 (m, 4H; SCH_2CH_2Ar), 7.39 (d, 2H, *J* 8.7; Ar 2,6-*H*), 8.18 (d, 2H, *J* 8.6; Ar 3,5-*H*); δ_C ($CDCl_3$) 19.26, 35.81, 36.90, 122.01, 123.86, 129.50, 131.60, 146.58, 147.00, 188.94; MS (EI): *m*/*z* (%): 345 (M^+, 75); Found: C, 41.84; H, 3.11; N, 4.05; S, 37.24; $C_{12}H_{11}NO_3S_4$ requires C, 41.72; H, 3.21; N, 4.05; S, 37.12%.

4′-(2-Cyanoethylthio)-5(4),5′-bis(methylthio)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene 14, *cis–trans*-mixture

Method 1. 4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiol-2-one **6** (1.54 g, 6.18 mmol) and 5-methylthio-4-[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione **10** (2.90 g, 8.03 mmol) were suspended in a mixture of $P(OEt)_3$ (30 ml) and toluene (15 ml). The mixture was heated under nitrogen to 120 °C causing the solid material to dissolve. The reaction mixture was heated for

Table 3 Selected ^1H NMR chemical shifts of rotaxanes (cyclophane region)

Compound	Solvent	H_α	H_β	C_6H_4	NCH_2
5	CD_3CN	9.00	7.89	7.72	5.68
27	CD_3COCD_3	9.65	8.67, 8.45	8.07	6.09
28	CD_3CN	9.07	8.08, 7.83	7.69	5.74
29	CD_3SOCD_3	9.39	7.94	7.90	5.76



Scheme 9 Possible fragmentations explaining the observed daughter ion peaks in ESMS/MS. The fragmentation of the cyclic acceptor is accompanied by electron transfers from the TTF(s).

2 h, before it was cooled to room temperature. The solvents were removed *in vacuo*. The residue was subjected to column chromatography (silica gel) with CH_2Cl_2 as the eluent. **14** (1.51 g, 2.68 mmol, 43%) was obtained as a red solid. Mp 135–137 °C; δ_H ($CDCl_3$) 2.45 (s, 3H; SCH_3), 2.50 (s, 3H; SCH_3), 2.75 (m, 2H; CH_2CN), 3.07 (m, 6H; SCH_2 and SCH_2CH_2Ar), 7.41 (d, 2H, *J* 8.6; Ar 2,6-*H*), 8.16 (d, 2H, *J* 8.6; Ar 3,5-*H*); MS (EI): *m*/*z* (%): 562 (M^+, 100); CV: $E^1_{1/2}=0.53$ V, $E^2_{1/2}=0.80$ V; Found: C, 40.48; H, 3.21; N, 4.84; $C_{19}H_{18}N_2O_2S_8$ requires C, 40.55; H, 3.22; N, 4.98%.

Method 2. 4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiole-2-thione **7** (0.77 g, 2.91 mmol) and 5-methylthio-4-[2-(4-nitrophenyl)ethylthio]-1,3-dithiol-2-one **12** were suspended in a mixture of $P(OEt)_3$ (30 ml) and toluene (15 ml). The mixture was heated under nitrogen to 120 °C causing the solid material to dissolve. The reaction mixture was heated for 2 h, before it was cooled to room temperature. The solvents were removed *in vacuo*. The residue was subjected to column chromatography (silica gel, (*i*) cyclohexane, (*ii*) CH_2Cl_2–cyclohexane 1 : 1) affording **14** (0.28 g, 0.50 mmol, 33%) as a red solid. Mp 135–136 °C.

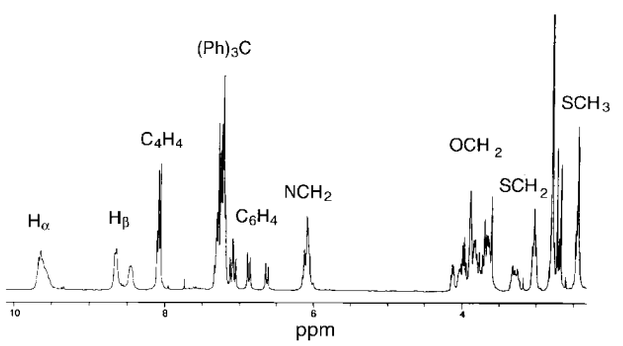


Fig. 5 ^{1}H NMR (250 MHz) spectrum of **27** in $(CD_3)_2CO$.

4′-{2-[2-(2-Iodoethoxy)ethoxy]ethylthio}-5(4),5′-bis(methylthio)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene 17, *cis–trans*-mixture

To a solution of 4′-(2-cyanoethylthio)-5(4),5′-bis(methylthio)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene **14** (0.80 g, 1.42 mmol) in DMF (100 ml), a solution of $CsOH\cdot H_2O$ (0.25 g, 1.49 mmol) in methanol (5 ml) was added dropwise with stirring over 30 min. The solution was stirred for 30 min, whereupon a solution of 1,2-bis(2-iodoethoxy)ethane (1.58 g, 4.26 mmol) in DMF (5 ml) was added in one portion. The solution was stirred for 5 h, and the solvents were removed *in vacuo*. The residue was extracted with CH_2Cl_2 (100 ml) and the organic phase washed with water and saturated aqueous NaCl solution. It was then dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography (silica gel) with CH_2CH_2–petroleum ether (bp 60–80 °C) (1 : 1) as the eluent. **17** (0.83 g, 1.10 mmol, 77%) was obtained as a red solid. Mp 50–52 °C; δ_H ($CDCl_3$) 2.50 (br s, 6H; SCH_3), 3.08 (m, 6H; SCH_2 and SCH_2CH_2Ar), 3.27 (m, 2H; ICH_2), 3.75 (m, 8H; OCH_2), 7.41 (d, 2H, *J* 8.6; Ar 2,6-*H*), 8.16 (d, 2H, *J* 8.4; Ar 3,5-*H*); MS (FAB): *m*/*z*: 751 (M^+); CV: $E^1_{1/2}=0.52$ V, $E^2_{1/2}=0.79$ V; Found: C, 35.25; H, 3.19; N, 1.87; $C_{22}H_{26}INO_4S_8$ requires C, 35.15; H, 3.49; N, 1.86%.

Tris(tetrathiafulvalene) 19, *cis–trans*-mixture

To a solution of 4(5),4′-bis(2-cyanoethylthio)-5(4),5′-bis(methylthio)tetrathiafulvalene **18**[11] (0.21 g, 0.45 mmol) in DMF (75 ml), a solution of $CsOH\cdot H_2O$ (0.17 g, 0.99 mmol) in methanol (10 ml) was added dropwise with stirring over 30 min. After stirring for 30 min, a solution of 4′-{2-[2-(2-iodoethoxy)ethoxy]ethylthio}-5(4), 5′-bis(methylthio)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene **17** in DMF was added in one portion. The solution was stirred for 5 h, and the reaction mixture was then concentrated *in vacuo*. CH_2Cl_2 (100 ml) was added, and the organic solution washed with water, saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, (*i*) CH_2Cl_2, (*ii*) CH_2Cl_2–ethyl acetate 19 : 1), affording **19** (0.60 g, 0.75 mmol, 83%) as a dark red viscous oil. δ_H ($CDCl_3$) 2.48 (br s, 18H; SCH_3), 3.06 (m, 16H; SCH_3 and SCH_2CH_2Ar), 3.64 (m, 16H; OCH_2), 7.41 (d, 4H, *J* 8.5; Ar 2,6-*H*), 8.16 (d, 4H, *J* 8.8; Ar 3,5-*H*); MS (FAB): *m*/*z*: 1606 (M^+); CV: $E^1_{1/2}=0.48$ V, $E^2_{1/2}=0.80$ V; Found: C, 38.75; H, 3.51; N, 1.68; $C_{52}H_{58}N_2O_8S_{24}$ requires C, 38.83; H, 3.63; N, 1.74%.

Tris(tetrathiafulvalene) dumbbell 20, *cis–trans*-mixture

To a solution of **19** (0.26 g, 0.16 mmol) in DMF (50 ml) was added dropwise *via* a syringe, a solution of $CsOH\cdot H_2O$ (0.059 g, 0.35 mmol) in methanol (5 ml) with stirring over 30 min. The solution was stirred for 30 min. A solution of **23a**[1g] (0.23 g, 0.40 mmol) in DMF (10 ml) was added in one portion, and the reaction mixture was stirred for 5 h. The solvents were removed *in vacuo*. The residue was extracted with CH_2Cl_2 (50 ml), and the organic phase washed with water and saturated aqueous NaCl solution. It was then dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, (*i*) CH_2Cl_2, (*ii*) CH_2Cl_2–ethyl acetate 19 : 1), affording **20** (0.29 g, 0.13 mmol, 82%) as an orange oil. δ_H ($CDCl_3$) 2.43 (br s, 18H; SCH_3), 2.97 (m, 12H; SCH_2), 3.68 (m, 28H; OCH_2), 3.85 (m, 4H; ArOCH_2CH_2), 4.11 (m, 4H; ArOCH_2), 6.79 (d, 4H, *J* 9.0; Ar 3,5-*H*), 7.10 (d, 4H, *J* 8.9; Ar 2,6-*H*), 7.27 (m, 30H; C_6H_5);

MS (FAB): *m/z*: 2208 (M^+); CV: $E^1_{1/2}=0.48$ V, $E^2_{1/2}=0.79$ V; Found: C, 52.68; H, 4.56; $C_{98}H_{104}O_{10}S_{24}\cdot H_2O$ requires C, 52.80; H, 4.79%.

Tris(tetrathiafulvalene) rotaxane 27, *cis–trans*-mixture

A solution of **20** (0.271 g, 0.12 mmol), **26** (0.260 g, 0.37 mmol) and **25** (0.110 g, 0.42 mmol) in DMF (12 ml) was transferred to a high-pressure-reaction Teflon tube, which was then compressed (10 kbar) at room temperature for 4 d. The solvent was then removed *in vacuo* to give a residue, which was subjected to column chromatography on silica gel with first acetone and later acetone–NH_4PF_6 as eluent. Collection of the green fraction afforded a green solid after evaporation of the solvent *in vacuo*. CH_3NO_2 was added and the resulting solution washed with water and cyclohexane. The solvent was then removed to give **27** (0.081 g, 0.024 mmol, 20%) as a green solid. Mp 202–205 °C (decomp.); δ_H (CD_3COCD_3) 2.48 (m; SC*H*$_3$), 2.70 (m; SC*H*$_3$), 2.48–2.70 (18H), 3.00 (m; SC*H*$_2$), 3.35 (m; SC*H*$_2$), 3.00–3.35 (12H), 3.61–4.15 (m, 36H; OC*H*$_2$), 6.09 (m, 8H; NC*H*$_2$), 6.62 (br d, *J* 7.9; C_6H_5), 6.86 (br d, *J* 8.6; C_6H_5), 7.09 (br t, *J* 8.4; C_6H_5), 7.34 (m; C_6H_5), 6.62–7.34 (38H), 8.07(m, 8H; C_6H_4), 8.45 (m; β-*H*), 8.67 (m; β-*H*), 8.45–8.67 (8H), 9.65 (m, 8H; β-*H*); MS (ES): *m/z*: [a]: 682 $[M-4PF_6]^{4+}$, 737 $[\mathbf{20}]^{3+}$, 958 $[M-3PF_6]^{3+}$, 1105 $[\mathbf{20}]^{2+}$, 1510 $[M-2PF_6]^{2+}$, 2728 $[M-4PF_6]^{+}$, 2873 $[M-3PF_6]^{+}$, 3018 $[M-2PF_6]^{+}$, 3163 $[M-1PF_6]^{+}$; [b]: 682 $[M-4PF_6]^{4+}$, 718 $[M-3PF_6]^{4+}$, 754.5 $[M-2PF_6]^{4+}$, 958 $[M-3PF_6]^{3+}$; MS (MALDI): *m/z*: 682 $[M-4PF_6]^{4+}$, 909 $[M-4PF_6]^{3+}$, 958 $[M-3PF_6]^{3+}$, 1364 $[M-4PF_6]^{2+}$, 2728 $[M-4PF_6]^{+}$, 2873 $[M-3PF_6]^{+}$; MS/MS (ES): parent ion: *m/z*: 682, daughter ions: *m/z*: 104, 208, 260, 1105; CV: $E^1_{1/2}=0.52$ V, $E^2_{1/2}=0.81$ V; UV-VIS: $\lambda_{max}=788$ nm and $\varepsilon=496$ M^{-1} cm^{-1}.

4-Methoxycarbonyl-5-[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione 11

Method 1. A solution of caesium 5-methoxycarbonyl-1,3-dithiole-2-thione-4-thiolate[12] (2.00 g, 5.61 mmol) and 2-(4-nitrophenyl)ethyl bromide (1.55 g, 6.74 mmol) in acetone was refluxed for 2 h. The resulting solution was cooled to room temp. and concentrated *in vacuo*. The crude product was redissolved in CH_2Cl_2 (100 ml), washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, (*i*) CH_2Cl_2–petroleum ether (bp 60–80 °C) 1 : 1, (*ii*) CH_2Cl_2) affording **11** (1.40 g, 3.75 mmol, 66%) as yellow needles. Mp 146–147 °C (from propan-2-ol).

Method 2. To a solution of 5-methoxycarbonyl-4-mercapto-1,3-dithiole-2-thione[12] (10.00 g, 44.58 mmol) in DMF, (400 ml). NaOEt (1.03 g, in EtOH, 44.58 mmol) was added dropwise with stirring over 30 min. The solution was stirred for 30 min, whereupon a solution of 2-(4-nitrophenyl)ethyl bromide (12.31 g, 5.35 mmol) in DMF was added. Stirring was continued for an additional 5 h, and the reaction mixture was then concentrated *in vacuo*. CH_2Cl_2 (400 ml) was added, and the organic solution washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). The solvent was then removed and the residue purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether (bp 60–80 °C) 4 : 1), affording **11** (4.08 g, 10.92 mmol, 20%) as a yellow solid. Mp 146–147 °C (from propan-2-ol); δ_H ($CDCl_3$) 3.17 (m, 2H; ArC*H*$_2$), 3.28 (m, 2H; SC*H*$_2$), 3.86 (s, 3H; CO_2CH_3), 7.41 (d, 2H, *J* 8.8; Ar 2,6-*H*), 8.20 (d, 2H, *J* 8.7; Ar 3,5-*H*); δ_C ($CDCl_3$) 35.12, 35.77, 52.94, 122.21, 124.00, 124.13, 129.51, 145.78, 147.27, 158.90, 207.43; MS (EI): *m/z* (%): 373 (M^+, 100); Found: C, 41.77; H, 2.95; N, 3.79; S, 34.38; $C_{13}H_1NO_4S_4$ requires C, 41.81; H, 2.97; N, 3.75; S, 34.34%.

4-Methoxycarbonyl-5-[2-(4-nitrophenyl)ethylthio]-1,3-dithiol-2-one 13

To a solution of 4-methoxycarbonyl-5-[2-(4-nitrophenyl) ethylthio]-1,3-dithiole-2-thione **11** (2.00 g, 5.36 mmol) in a mixture of $CHCl_3$ (75 ml) and AcOH (25 ml) was added Hg(OAc) (4.61 g, 14.46 mmol). After stirring for 16 h the suspension was filtered through a short layer of Celite. The Celite was carefully washed with chloroform (100 ml). The combined filtrate was cautiously washed with aqueous $NaHCO_3$ and water, and dried ($MgSO_4$). The solvents were removed *in vacuo* and the residue recrystallised from CH_3OH to give **13** (1.34 g, 3.75 mmol, 70%) as bright-yellow needles. Mp 126–127 °C; δ_H ($CDCl_3$) 3.16 (m, 2H; ArC*H*$_2$), 3.27 (m, 2H; SC*H*$_2$), 3.86 (s, 3H; CO_2CH_3), 7.41 (d, 2H, *J* 8.6; Ar 2,6-*H*), 8.20 (d, 2H, *J* 8.6; Ar 3,5-*H*); MS (EI): *m/z* (%): 357 (M^+,100); Found: C, 43.67; H, 3.06; N, 3.92; S, 26.95; $C_{13}H_{11}NO_5S_3$ requires C, 43.69; H, 3.10; N, 3.92; S, 26.91%.

4′-(2-Cyanoethylthio)-5(4),5′-bis(methoxycarbonyl)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene 15, *cis–trans*-mixture

Method 1. 4-Methoxycarbonyl-5-[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione **11** (1.20 g, 3.21 mmol) and 4-(2-cyanoethylthio)-5-methoxycarbonyl-1,3-dithiol-2-one **8** (0.65 g, 2.47 mmol) were suspended in a mixture of freshly distilled $P(OEt)_3$ (30 ml) and toluene (15 ml) and heated to 120 °C. The mixture was stirred for 2 h and then allowed to cool to room temp. The product was precipitated with CH_3OH (50 ml), filtered off and washed with CH_3OH. Column chromatography (silica gel, CH_2Cl_2), afforded **15** (0.41 g, 0.69 mmol, 28%) as an orange–red solid. Mp 183–184 °C; δ_H (DMSO-d_6) 2.99 (m, 2H; C*H*$_2$CN), 3.17 (t, 2H, *J* 7.6; SCH_2CH_2Ar), 3.39 (m, 4H; SC*H*$_3$), 3.73 (s, 3H; CO_2CH_3), 7.59 (d, 2H, *J* 8.3; Ar 2,6-*H*), 8.18 (d, 2H, *J* 8.6; Ar 3,5-*H*); MS (EI): *m/z* (%): 586 (M^+,100); CV: $E^1_{1/2}=0.65$ V, $E^2_{1/2}=0.98$ V; Found: C, 43.26; H, 3.16; N, 4.65; S, 32.55; $C_{21}H_{18}N_2O_6S_6$ requires C, 42.99; H, 3.09; N, 4.77; S, 32.78%.

Method 2. 4-(2-Cyanoethylthio)-5-methoxycarbonyl-1,3-dithiole-2-thione **9** (1.16 g, 4.20 mmol) and 4-methoxycarbonyl-5-[2-(4-nitrophenyl)ethylthio]-1,3-dithiol-2-one **13** (1.00 g, 2.80 mmol) were suspended in a mixture of freshly distilled $P(OEt)_3$ (20 ml) and toluene (10 ml). The mixture was heated at 120 °C for 2 h and then allowed to cool to room temp. The product was precipitated with CH_3OH (50 ml), filtered off and washed with CH_3OH. Column chromatography (silica gel, CH_2Cl_2), afforded **15** (0.47 g, 0.80 mmol, 28%) as an orange–red solid. Mp 183–184 °C.

Bis(tetrathiafulvalene) 21, *cis–trans*-mixture

To a solution of 4′-(2-cyanoethylthio)-5(4),5′-bis(methoxycarbonyl)-4(5)-[2-(4-nitrophenyl)ethylthio]tetrathiafulvalene **15** (0.39 g, 0.66 mmol) in DMF (100 ml), a solution of $CsOH\cdot H_2O$ (0.12 g, 0.70 mmol) in methanol (5 ml) was added dropwise *via* a syringe with stirring over 30 min. After stirring for 30 min, a solution of 4′-{2-[2-(2-iodoethoxy)ethoxy]-ethylthio}-5(4), 5′-bis(methylthio)-4(5)-[2-(4-nitrophenyl)-ethylthio]tetrathiafulvalene **17** (0.55 g, 0.73 mmol) in DMF was added *via* a syringe. The solution was stirred for 5 h, whereupon the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (100 ml), and the organic phase washed with water and saturated aqueous NaCl solution. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography (silica gel) with CH_2Cl_2 as the eluent. **21** (0.66 g, 0.57 mmol, 85%) was obtained as an orange–red glass. δ_H ($CDCl_3$) 2.45 (br s, 6H; SC*H*$_3$), 3.11 (m; C*H*$_2$Ar), 3.30 (m; SC*H*$_2$), 3.11–3.30 (12H), 3.78 (m, 14H; CO_2CH_3 and OC*H*$_2$), 7.42 (m, 4H; Ar 2,6-*H*), 8.20 (m, 4H; Ar 3,5-*H*); MS

(FAB): *m/z*: 1156 (M^+); Found: C, 41.69; H, 3.67; N, 2.43; S, 38.62; $C_{40}H_{40}N_2O_{10}S_{14}$ requires C, 41.50; H, 3.48; N, 2.42; S, 38.77%.

Bis(tetrathiafulvalene) dumbbell 22, *cis–trans*-mixture

To a solution of **21** (0.64 g, 0.55 mmol) in DMF (75 ml) a solution of $CsOH{\cdot}H_2O$ (0.20 g, 1.19 mmol) in methanol (10 ml) was added dropwise with stirring over 30 min. The solution was stirred for 30 min. A solution of **23a**[1g] (0.80 g, 1.38 mmol) in DMF was added and the mixture was stirred for 5 h. The reaction mixture was concentrated *in vacuo*. CH_2Cl_2 (100 ml) was added, and the organic phase was washed with water, saturated aqueous NaCl solution, and dried ($MgSO_4$). The solvent was then removed and the residue was chromatographed on silica gel using CH_2Cl_2 as eluent, affording **22** (0.64 g, 0.36 mmol, 65%) as an orange–red oil. δ_H ($CDCl_3$) 2.43 (br s, 6H; SC*H*$_3$), 3.00 (m, 4H; SC*H*$_2$), 3.24 (m, 4H; SC*H*$_2$), 3.70 (m, 30H; OC*H*$_2$ and CO_2CH_3), 4.10 (m, 4H; C*H*$_2$OAr), 6.79 (d, 4H, *J* 8.8; Ar 2,6-*H*), 7.09 (d, 4H, *J* 8.9; Ar 2,6-*H*), 7.24 (m, 30H; C_6H_5); MS (FAB): *m/z*: 1758 (M^+); CV: $E^1_{1/2}=0.47$ V, $E^2_{1/2}=0.61$ V, $E^3_{1/2}=0.83$ V, $E^4_{1/2}=0.97$ V; Found: C, 57.32; H, 5.08; S, 24.73; $C_{86}H_{86}O_{12}S_{14}{\cdot}2.5\ H_2O$ requires C, 57.21; H, 5.08; S, 24.86%.

Bis(tetrathiafulvalene) rotaxane 28, *cis–trans*-mixture

A solution of **22** (0.61 g, 0.35 mmol), **26** (0.73 g, 1.04 mmol) and **25** (0.311 g, 1.14 mmol) in DMF (12 ml) was transferred to a high-pressure-reaction Teflon tube, which was then compressed (10 kbar) at room temperature for 4 d. The solvent was then removed *in vacuo* to give a residue, which was subjected to column chromatography on silica gel with first acetone and later acetone–NH_4PF_6 as eluents. Collection of the green fraction afforded a green solid after evaporation of the solvent *in vacuo*. CH_3NO_2 was added and the solution washed with water and cyclohexane, the solvent was then removed to give **28** (0.35 g, 0.123 mmol, 35%) as a green solid. Mp 162–165 °C (decomp.); δ_H (CD_3CN) 2.45–2.31 (m; SC*H*$_3$), 2.55–2.64 (m; SC*H*$_3$), 2.31–2.64 (6H), 2.90–3.22 (m, 8H; SC*H*$_2$), 3.59–4.11 (m, 34H; OC*H*$_2$ and CO_2CH_2), 5.74 (m, 8H; NC*H*$_2$), 6.57 (m; Ar 2,6-*H*), 6.80 (d, *J* 8.8; Ar 2,6-*H*), 7.13 (m; Ar 3,5-*H*), 6.57–7.13 (8H), 7.30 (m, 30H; C_6H_5), 7.69 (m, 8H; C_6H_4), 7.83 (m; β-*H*), 8.08 (m; β-*H*), 7.83–8.08 (8H), 9.07 (m, 8H; β-*H*); δ_H ($(CD_3)_2CO$) 2.41–2.52 (m; SC*H*$_3$), 2.65–2.79 (m; SC*H*$_3$), 2.41–2.79 (6H), 3.23–3.55 (m, 8H; SC*H*$_2$), 3.64–4.12 (m, 34H; OC*H*$_2$ and CO_2CH_2), 6.00–6.12 (m, 8H; NC*H*$_2$), 6.45 (m; Ar 2,6-*H*), 6.84 (d, *J* 8.8; Ar 2,6-*H*), 7.13 (m; Ar 3,5-*H*), 6.45–7.13 (8H), 7.26 (m, 30H; C_6H_5), 8.05 (m, 8H; C_6H_4), 8.42 (m; β-*H*), 8.63 (m; β-*H*), 8.42–8.63 (8H), 9.61 (m, 8H; β-*H*); MS (ES): *m/z*: [a]: 570 $[M-4PF_6]^{4+}$, 760 $[M-4PF_6]^{3+}$, 808 $[M-\text{-}3PF_6]^{3+}$, 1212 $[M-3PF_6]^{2+}$, 1284 $[M-2PF_6]^{2+}$; [b]: 570 $[M-4PF_6]^{4+}$, 760 $[M-4PF_6]^{3+}$, 808 $[M-3PF_6]^{3+}$, 1212 $[M-3PF_6]^{2+}$, 1284 $[M-2PF_6]^{2+}$; MS (MALDI): *m/z*: 760 $[M-4PF_6]^{3+}$, 1139 $[M-4PF_6]^{2+}$, 2278 $[M-4PF_6]^{+}$, 2423 $[M-3PF_6]^{+}$, 2568 $[M-2PF_6]^{+}$; MS/MS (ES): parent ion: *m/z*: 569.5, daughter ions: *m/z*: 208, 260, 439.5, 879.2; CV: $E^1_{1/2}=0.53$ V, $E^2_{1/2}=0.63$ V, $E^3_{1/2}=0.77$ V, $E^4_{1/2}=0.96$ V; UV-VIS: $\lambda_{max}=748$ nm and $\varepsilon=1150\ M^{-1}\ cm^{-1}$.

Bis(pyrrolo)-TTF dumbbell 24

Bis(2,5-dimethylpyrrolo)-fused tetrathiafulvalene **1** (0.20 g, 0.59 mmol) in DMF (50 ml) was cooled on an ice bath before NaH (142 mg, 5.9 mmol) was added in small portions over a period of 5 min. The orange reaction mixture was stirred for 20 min before **23b**[13] (0.83 g, 1.56 mmol) was added in one portion. The reaction mixture was stirred for 3 h before it was poured on to brine–ice (400 ml). The yellow–brown precipitate was filtered off and washed with H_2O and CH_3OH. The crude product was subjected to column chromatography (basic Al_2O_3 deactivated with 2% H_2O, CH_2Cl_2–cyclohexane 20 : 3). Collection of the yellow band gave **24** (0.59 g, 81%) as a pale yellow solid. Mp 209–210 °C (from $CHCl_3$–CH_3OH); δ_H ($CDCl_3$) 2.15 (s, 12H; C*H*$_3$), 3.53–3.65 (m, 12H), 3.75 (t, 4H, *J* 4.8), 3.88 (t, 4H), 4.06 (t, 4H, *J* 4.3), 6.80 (d, 4H, *J* 9.0; OC_6H_4 2,6-*H*), 7.14 (d, 4H, *J* 8.8; OC_6H_4 3,5-*H*), 7.16–7.30 (m, 30H; C_6H_5); MS (PDMS): *m/z*: 1238.9 calcd. for $C_{76}H_{74}N_2O_6S_4$ 1239.7; CV (CH_3CN): $E^1_{1/2}=0.33$ V, $E^2_{1/2}=0.74$ V; Found: C, 68.23; H, 5.65; N, 2.06; $C_{76}H_{74}N_2O_6S_4$ requires C, 68.05; H, 5.56; N, 2.06%.

[2]Rotaxane 29

A solution of the dumbbell **24** (180 mg, 0.145 mmol), **26** (310 mg, 0.436 mmol) and **25** (127 mg, 0.480 mmol) in dry degassed DMF (12 ml) was transferred to a high-pressure-reaction Teflon tube, which was compressed (10 kbar) at room temperature for 3 d. The resulting green suspension was concentrated *in vacuo* and the residue applied on a column (SiO_2) as a suspension in CH_3CN and eluted with a mixture of CH_3OH–NH_4Cl (2 M)–CH_3NO_2–CH_3CN (14 : 4 : 2 : 5). The broad green band was collected and the solvents were removed *in vacuo.* The green residue was washed with H_2O (50 ml) and subsequently dissolved in CH_3OH (25 ml). A concentrated solution of NH_4PF_6 in CH_3OH was added until precipitation was complete. The precipitate was washed with H_2O and dried to give rotaxane **29** (88 mg, 26%). Mp (decomp.) over a wide range; δ_H (DMSO-d_6) 2.19 (s, 12H; C*H*$_3$), 3.65–3.75 (m, 16H), 3.98 (t, 4H), 4.06 (t, 4H), 5.76 (s, 8H, $ArCH_2$), 6.76 (d, 4H, *J* 9.1; OC_6H_4 2,6-*H*), 7.02 (d, 4H, *J* 8.9; OC_6H_4 3,5-*H*), 7.12–7.19 (m, 18H; C_6H_5 3,4,5-*H*), 7.26–7.31 (m, 12H; C_6H_5 2,6-*H*), 7.90 (s, 8H, C_6H_4), 7.94 (d, 8H, *J* 6.9; β-H), 9.39 (d, 8H, *J* 6.6; β-H); δ_C ($CDCl_3$) 11.91, 44.14, 63.26, 63.79, 66.87, 69.00, 69.86, 70.02, 70.07, 112.49, 113.49, 115.10, 118.91, 125.65, 126.04, 127.82, 130.51, 130.66, 131.70, 136.73, 138.72, 144.30, 145.39, 146.84, 156.30; CV (CH_3CN): $E^1_{1/2}=0.65$ V, $E^2_{1/2}=1.04$ V; Found: C, 56.72; H, 4.64; N, 3.78; $C_{112}H_{106}F_{24}N_6O_6P_4S_4{\cdot}1H_2O$ requires C, 57.04; H, 4.62; N, 3.56%.

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