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Covalent association of polyaza macrocyclic units to the electroactive tetrathiafulvalene moiety: synthesis and structural analysis

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Abstract

The synthesis of new macrocyclic receptors associating the electroactive tetrathiafulvalene unit (TTF) to different polyaza ligands is described. The structure of these receptors varies by the size of the coordinating unit (polyaza chains of various lengths), and by the nature of the latter, since a macrocyclic cyclam or a diazatetraoxa macrocycle derivative has been also introduced. The X-ray diffraction study on a single crystal of one of these receptors, demonstrates the electroactive TTF framework to be planar enough to present the expected reversible electrochemical behaviour. A preliminary study of the coordination ability of these polyazaTTF receptors is also given. ***To cite this article: G. Trippé et al., C. R. Chimie 6 (2003).***

Résumé

La synthèse de nouveaux récepteurs macrocycliques, associant l'unité électroactive tétrathiafulvalène (TTF) à divers ligands polyazotés, est décrite. Ces récepteurs varient tant par la taille de l'unité complexante (chaînes polyazotées de différentes longueurs), que par sa nature, un dérivé macrocyclique du cyclame ou un macrocycle diazatétraoxa ayant également été introduit. La structure par diffraction des rayons X sur monocristal d'un de ces récepteurs montre la conservation d'un caractère suffisamment plan de l'entité électroactive TTF, permettant de conserver les caractéristiques électrochimiques réversibles attendues pour ce dernier. Enfin, une étude préliminaire des propriétés complexantes de ces récepteurs polyazotés est également fournie. ***Pour citer cet article : G. Trippé et al., C. R. Chimie 6 (2003).***

Keywords: macrocyclic receptors; tetrathiafulvalene; macrocyclic cyclam derivative; diazatetraoxa macrocycle; X-ray diffraction; electrochemical behaviour; electroactive receptors

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Mots clés : récepteurs macrocycliques ; tétrathiafulvalène ; dérivé macrocyclique du cyclame ; macrocycle diazatétraoxa ; diffraction des rayons X ; comportement électrochimique ; récepteurs électroactifs

1. Introduction

The tetrathiafulvalene (TTF) moiety is well known as an electroactive organic core with applications in various fields of materials chemistry [1], including electroconducting organic metals (charge-transfer complexes and cation-radical salts), organic ferromagnets, molecular electronics, NLO-phores... Recently, it has also appeared as an important building block in supramolecular chemistry [1].

In this context, much effort has been devoted in the recent years for the preparation of TTF-based hybrid systems exhibiting synergy between electrical conductivity and magnetic interactions [2]. The goal, in this case, is to get crystalline solids for which conducting electrons involved in the π-stacking of TTF units, could interact with localized spins (d electrons of transition metals). In order to optimise the exchange between the mobile electrons and the localized spins in the solid, one may design a system allowing a close proximity of the metal (d electrons) to the electroactive TTF core. One way to achieve such a prerequisite is to covalently associate the TTF framework to a coordinating subunit prone to complex a metal. Among the possible receptors suitable for the complexation of transition metals, polyaza-macrocycles [3], and notably cyclam derivatives (1,4,8,11-tetraazacyclotetradecane) [4], are known to be particularly efficient. Taking advantage on our recent results concerning the preparation of redox-switchable ligands [5, 6], we have extended the synthesis to new redox systems associating the TTF framework (as a tetraalkylsulfanyl-TTF or a bis(pyrrolo)TTF unit) to various polyaza-macrocycles, including a cyclam derivative or a diazatetraoxa cyclooctadecane moiety. The X-ray structural determination of one aza-macrocycle is also depicted.

2. Results and discussion

2.1. Synthesis

The target macrocyclic compounds of the tetraalkylsulfanylTTF series (compounds **3–5**), were prepared [6] starting from the bis(2-cyanoethylsulfanyl)-3,7-bis(methylthio)tetrathiafulvalene **1**[7] ([*Z*+*E*] isomers with respect to the rigid TTF framework) (Fig. 1). Unfortunately, all attempts of *N*-tosyl or *N*-triflate cleavages were unsuccessful. On the other hand, reaction of compound **1** under basic medium with an excess of a ω–diodo polyethyleneglycol chain, led to **6a** and **6b**. The introduction of the polyaza-macrocyclic unit was carried out by using 5,12-dioxocyclam **7**, since such macrocycles are known to bind efficiently transition metals [8]. Compound **7**, prepared by condensation of ethylene diamine on methyl acrylate [9], allows an original control in the regioselectivity of the bis addition, since two of the four nitrogen atoms are involved in an amide bond, and therefore have lost their nucleophilic character. This protection mode permits to selectively functionalise the tetraazamacrocycle on the two remaining amino groups [10].

Since no good results were obtained by using high dilution conditions, dioxocyclam **7** and TTF derivative **6a** (or **6b**) were subjected to a [1+1] cyclocondensation under high pressure conditions (10 kbar, 72 h) [11]. The tedious isolation of the different macrocycles *in fine* necessitated the use of a preparative scale size exclusion chromatography (Sephadex LH20) to afford the target TTF cryptands **8a** and **8b** in 10% yield. The complete structural characterization of compounds **8a** and **8b** could be carried out thanks to two-dimensional NMR spectroscopy (DQF COSY, HMQC and HMBC). It is interesting to note that the *Z* and *E* isomers (if both isomers are formed), are not distinguishable, contrary to the case of macrocycles **3–5**[6].

In the case of the bis(pyrrolo)TTF series (compounds **12a,b**), the coordination unit introduced was a N_2O_4 macrocycle (Fig. 2); grafting of a N_2O_4 macrocyclic unit to tetraakylsulfanyl-TTF has already been described [12]. Therefore, targets **12a,b** were obtained according to a three steps strategy from naked bis(pyrrolo)TTF **9** [13]. Alkylation of both pyrrolo nitrogen atoms of **9** [5d] produced chlorinated intermediates **10a,b,** which were then submitted to a Cl/I exchange. The final step involved a cyclocondensation under high-dilution conditions between iodide inter-

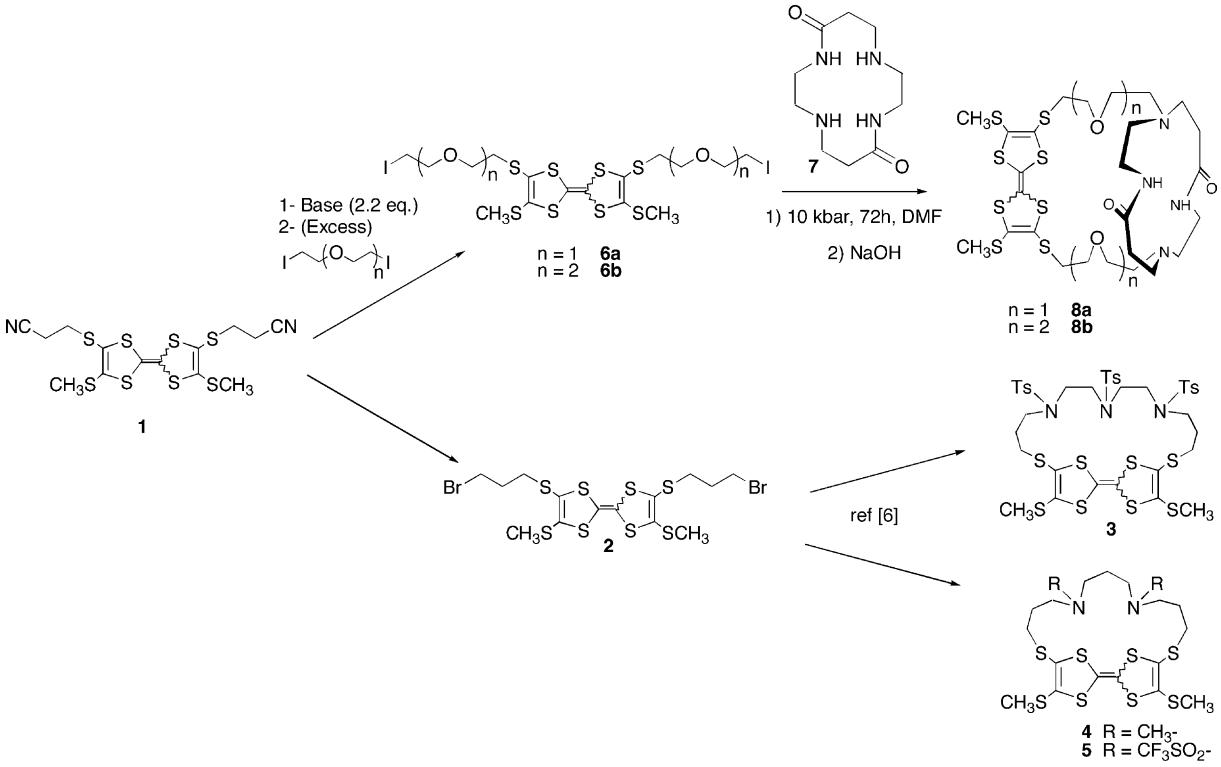

Fig. 1. Preparation of the target macrocyclic compounds of the tetraalkylsulfanylTTF series (**3–5**) starting from the bis(2-cyanoethylsulfanyl)-3,7-bis(methylthio)tetrathiafulvalene **1** ([*Z*+*E*] isomers with respect to the rigid TTF framework).

mediates **11a,b**, and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane.

2.2. X-ray structural determination, electrochemical properties and complexation studies

Slow diffusion of pentane in a dichloromethane solution of macrocycle **5** afforded single crystals suitable for an X-ray diffraction study. The diaza-crown TTF **5** appears in the [*Z*] configuration (Fig. 3), with a packing mode showing a segregation between the electroactive TTF unit and the diaza fragment along the *a* axis (Fig. 4). The TTF skeleton in **5** [*Z*] appears partially distorted, with a bending angle of 21° from the planarity (Fig. 3). This distortion is of course reminiscent of the structural constraints imposed by the lateral

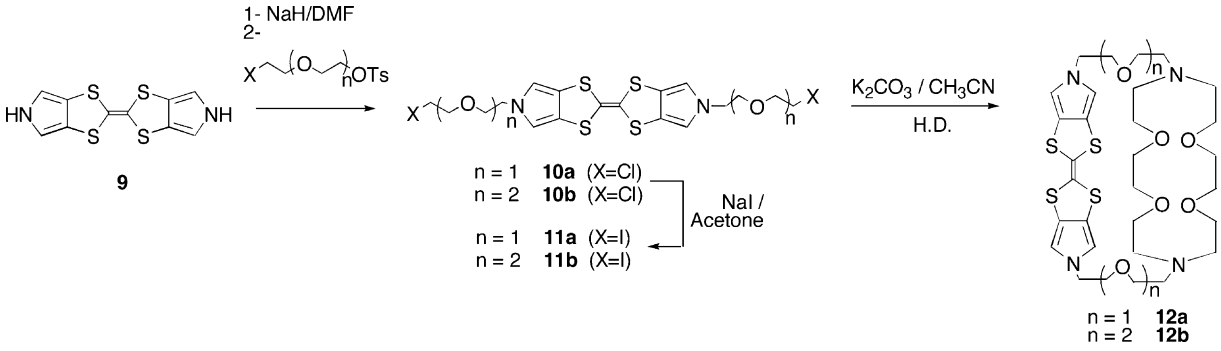

Fig. 2. Synthesis of **12a,b** from **9**.

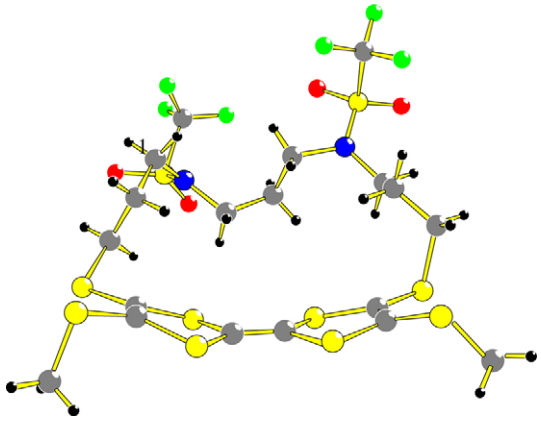

Fig. 3. X-ray structure of (*Z*)-**5**.

diaza-chain. Such a value appears very similar to the one observed for compound **4**[6], which presents the same size for the lateral chain, but far less important than for other aza-crown TTF systems with shorter chains [14], for which a high bending angle value results in poor electrochemical characteristics (high oxidation potential (E^1_{ox} = 0.95 V vs /SCE) and irreversible redox processes). The weak distortion observed in the case of compound **5** should favour a good π-delocalization. Consequently, we can anticipate that all of these polyaza macrocyclic TTFs present large enough lateral chains to present good π-donating properties, which is confirmed by cyclic voltammetry experiments, where compounds **3–5, 8a, 8b** present two reversible redox processes with the usual E^1_{ox} and E^2_{ox} values for $(RS)_4$TTF derivatives (ca 0.56 V and 0.83 V vs AgCl/Ag respectively). Nevertheless, we could notice in the case of compounds **8a,b** a progressive passivation of the Pt working electrode upon scanning to potentials higher than 0.80 V, which could be attributed to an irreversible oxidation of the cyclam moiety. TTF-cryptands **12a,b** present as expected a higher π-donating ability as usually observed for bis(pyrrolo)TTF derivatives (ca E^1_{ox} = 0.33 V and E^2_{ox} = 0.79 V). Nevertheless, here again we could observe some passivation phenomena upon cycling potentials up to 1.00V.

Preliminary complexation studies led on these TTF macrocycles gave best results for TTF receptors **12a,b**, for which LSIMS measurements showed a good affinity for Groups-I and II cations, which was notably confirmed by UV–Vis titration experiments. Binding constants of ca log(*K*) = 3.0 to 4.1 (CH_2Cl_2/CH_3CN, 1:1) (Benesi–Hildebrand method) were obtained for complexation of Ca^{2+}, Sr^{2+} and Ba^{2+} by either **12a** or **12b**, without any evidence of selectivity. The 1:1 stoichiometry of the complexes was shown by occurrence

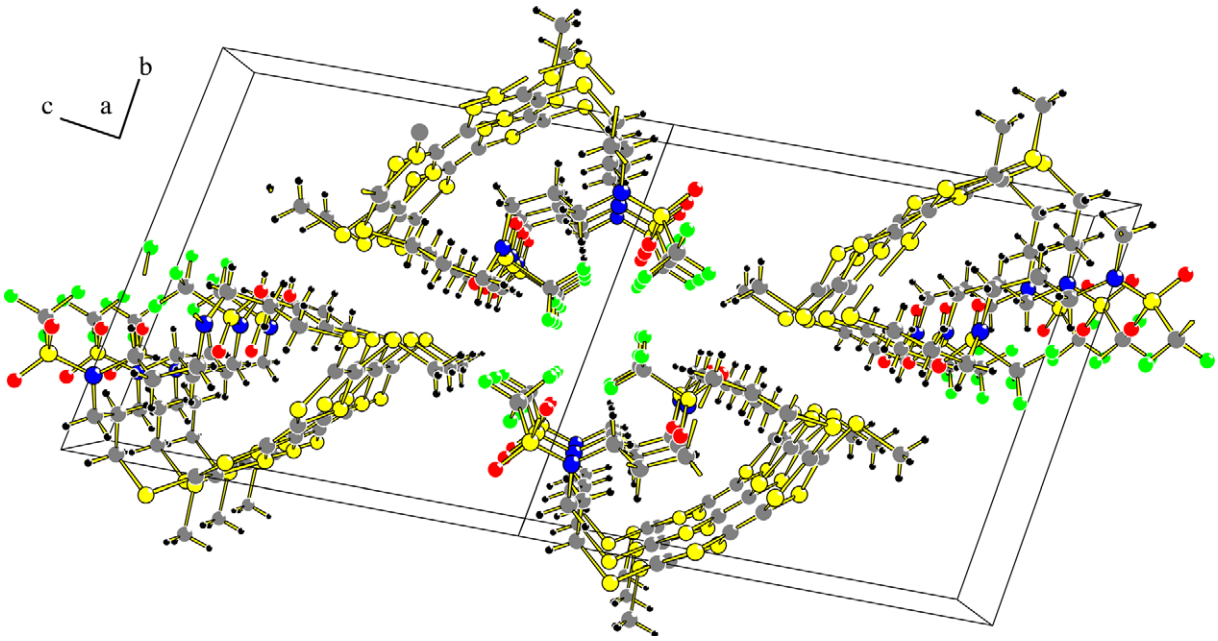

Fig. 4. Stacking mode of (*Z*)-**5** along the *a* axis.

of isobestic points (e.g., 264, 315, 324 nm in the case of **12a**/Sr^{2+}) and confirmed by the titration curves, which did not evolve anymore above 1 equiv of added cation.

In conclusion, we have synthesized a series of TTF receptors incorporating different polyaza macrocyclic receptors. The planarity of the π-system is sufficiently preserved in those systems, as shown by an X-ray structural determination, which allows them to exhibit the usual electrochemical behaviour of TTF derivatives. Some of these derivatives show good binding properties for alkaline-earth cations. Attempts to get single crystals of a complex associating one of these polyaza receptors to various transition metals are under investigation.

3. Experimental section

^{1}H-NMR (500.13 MHz) and ^{13}C-NMR (125.75 MHz) spectra were recorded on a BRUKER Advance DRX 500 spectrometer. Chemical shifts (δ) are expressed in ppm related to the tetramethylsilane (TMS) signal and *J* values in Hz. FAB and ESI mass spectra were achieved on a Jeol JMS 700 B/ES and MALDI–TOF spectra on a Bruker Biflex III. Cyclic voltammetry experiments were carried out on a potentiostat–galvanostat EG&G PARK models 273 or 273A, with solvents and electrolytes of electrochemical grades. For synthesis, anhydrous solvents were obtained by distillation on the appropriate drying agent (sodium/benzophenone for THF, sodium for toluene, P_2O_5 for dichloromethane, CaH_2 for acetonitrile).

*3.1. (Z/E)-2,6(7)-Bis(5-iodo-3-oxa-1-pentylsulfanyl)-3,7(6)-bis(methylsulfanyl) tetrathiafulvalene **6a***

Sodium methylate (8.5 ml at 2.26 M, 2.2 equiv, 19 mmol) was added slowly under N_2, to tetrathiafulvalene derivative **1** (4.0 g, 1 equiv, 8.6 mmol) in dry DMF (100 ml). The solution was stirred during 15 min and afterwards, bis(2-iodoethyl) ether (45 g, 8 equiv, 138 mmol) was added quickly. After stirring overnight, the solvent was removed in vacuo. The red residue was dissolved in dichloromethane, washed with water, dried over magnesium sulphate and concentrated in vacuo. The compound was purified by chromatography on a silica gel column (petroleum ether/dichloromethane 50:50) to furnish a red solid (74%, 4.8 g). ^{1}H NMR ($CDCl_3$): 2.45 (s, 6H, SC*H*$_3$); 3.01 (t, 4H, 6.6 Hz, SC*H*$_2$CH$_2$); 3.27 (t, 4H, 6.9 Hz, C*H*$_2$I); 3.71 (t, 4H, 6.6 Hz, SCH$_2$C*H*$_2$); 3.76 (t, 4H, 6.9 Hz, C*H*$_2$CH$_2$I). ^{13}C NMR ($CDCl_3$): 2.4 (*C*H$_2$I); 19.1 (S*C*H$_3$); 35.4 and 35.4 (S*C*H$_2$); 69.5 and 71.7 (O*C*H$_2$); 110.8 and 110.9 (central *C*=*C*); 124.0, 124.2, 131.2 and 131.4 (lateral *C*=*C*); MS (PDMS): 756.

*3.2. (Z/E)-2,6(7)-Bis(8-iodo-3,6-dioxa-1-octylsulfanyl)-3,7(6)-bis(methylsulfanyl) tetrathiafulvalene **6b***

Caesium hydroxide monohydrate (1.8 g, 2.5 equiv, 10.8 mmol) in dry methanol was added under N_2 to tetrathiafulvalene derivative **1** (2.0 g, 1 equiv, 4.3 mmol) in distilled THF (150 ml). The solution was stirred during 15 min and afterwards, 2,2'-(oxydiethylenoxy)-1,1'-diiodoethane (15.9 g, 5 equiv, 21.5 mmol) was added. The caesium iodide immediately precipitated. The red reaction mixture was stirred for 1 h. The solvent was removed in vacuo and the red residue was dissolved in dichloromethane. The organic phase was washed with water, dried over magnesium sulphate and concentrated in vacuo. Purification of **6b** was carried out by chromatography on a silica gel column (petroleum ether/dichloromethane: 25/75 and dichloromethane), to produce a red oil (80% yield, 2.90 g). ^{1}H NMR ($CDCl_3$): 2.44 (s, 6H, SC*H*$_3$); 3.00 (t, 4H, 6.7 Hz, SC*H*$_2$CH$_2$); 3.27 (t, 4H, 6.6 Hz, C*H*$_2$I); 3.59–3.79 (t, 16H, OC*H*$_2$); ^{13}C NMR ($CDCl_3$): 3.6 (*C*H$_2$I); 36.0 and 36.1 (S*C*H$_2$); 70.7, 70.8, 71.1 and 72.6 (O*C*H$_2$); 111.2 and 111.3 (central *C*=*C*); 124.9, 125.0, 131.4 and 131.5 (lateral *C*=*C*). MS (FAB): 844.

*3.3. 1,8-(2,7-Diethyloxysulfanyltetrathiafulvaleno)-5,12-dioxocyclam **8a***

Tetrathiafulvalene derivative **6a** (378 mg, 1 equiv, 0.5 mmol) and 5,12-dioxocyclam **7**[9] (114 mg, 1 equiv, 0.5 mmol) in solution in DMF (18 ml) were reacted for three days under a pressure of 10 kbar. The solvent was removed in vacuo and the orange residue was dissolved in chloroform. A solution of sodium hydroxide in water (3 equiv) was added and the mixture was stirred for one day. The organic phase was washed with water, dried over magnesium sulphate and concentrated in vacuo. Purification was carried out thanks to the successive following treatments: column

chromatography (dichloromethane/methanol 100:5) over alumina deactivated with water (5%), silica gel chromatography – acetone/ NH_4PF_6 (0 to 4%) –, solubilisation in methanol, and finally gel permeation chromatography on Sephadex (LH20) (dichloromethane/methanol 90:10). Compound **8a** appears as an orange oil (10% yield, 36 mg). ^{1}H NMR ($CDCl_3$): 2.38 (m, 4H, CH_2CO); 2.46 (s, 6H, CH_3S); 2.62 (m, 4H, C$H_{2\ (9)}$); 2.72 (m, 8H, C$H_{2\ (8)}$ and C$H_{2\ (12)}$); 2.92 (m, 4H, SCH_2); 3.38 (m, 4H, C$H_{2\ (10)}$); 3.53–3.74 (m, 8H, CH_2O); 8.64 (s, 2H, N*H*); HRMS (ESI+) $C_{26}H_{40}N_4O_4S_8$: obs.: 751.0735 $(M+Na)^+$, th.: 751.0713.

*3.4. 1,8-(2,7-Triethyloxysulfanyltetrathiafulvaleno)-5,12-dioxocyclam **8b***

Compound **8b** was prepared according to the same methodology as for **8a**. Orange oil, 10% yield. ^{1}H NMR ($CDCl_3$): 2.38 (m, 4H, CH_2CO); 2.43 (s, 6H, CH_3S); 2.63 (m, 4H, C$H_{2\ (11)}$); 2.72 (m, 4H, C$H_{2\ (10)}$); 2.74 (m, 4H, C$H_{2\ (14)}$); 2.97 (m, 4H, SCH_2); 3.38 (m, 4H, C$H_{2\ (12)}$); 3.54–3.68 (m, 16H, CH_2O). 8.63 (s, 2H, N*H*); ^{13}C NMR ($CDCl_3$):19.1 and 19.2 (S*C*H_3); 32.6 (*C*H_2CO); 34.8 (S*C*H_2); 38.2 (*C*H_2NHCO); 50.4 (N*C*$H_{2\ (14)}$); 51.9 (N*C*$H_{2\ (10)}$); 53.0 (N*C*$H_{2\ (11)}$); 68.4, 70.0, 70.2, 70.2, 70.4, 70.5, 70.6 and 70.7 (*C*H_2O); 110.5 (central *C=C*); 124.0, 124.1, 131.0 and 131.1 (lateral *C=C*); 172.5 (*C*O); MS (MALDI-TOF) $C_{30}H_{48}N_4O_6S_8$: 816 ($M^{+\bullet}$).

*3.5. Synthesis of bis(pyrrolo)TTF derivatives **10a,b***

A suitable ω-chlorinated derivative (3 mmol) was added to bis(pyrrolo)tetrathiafulvalene **9** (282 mg, 1 mmol) in dry degassed DMF (50 ml). The mixture was cooled to 0 °C. Sodium hydride (washed with petroleum ether) (3 mmol) was added in one portion. The reaction mixture was stirred 1 h at 0°C and then 2 h at room temperature. The suspension was filtered over Celite and the solvent was removed in vacuo. The residue dissolved in dichloromethane was washed with brine, dried over magnesium sulphate and concentrated in vacuo. The yellow oil was purified by chromatography (SiO_2+ 4% triethylamine, petroleum ether/dichloromethane 1:1).

*3.6. Bis-(*N*-(5-chloro-3-oxa-1-pentyl)pyrrolo[3, 4, d]tetrathiafulvalene **10a***

Yellow powder, 61% yield. m.p.: 120°C. ^{1}H NMR ($CDCl_3$): 3.56–3.73 (m, 12H, CH_2O and CH_2Cl); 3.99 (t, 5.4 Hz , 4H, CH_2N); 6.51 (s, 4H, C$H_{pyrrole}$). ^{13}C NMR ($CDCl_3$): 43.1 (*C*H_2Cl); 50.9 (*C*H_2N); 71.5, 71.7 (*C*H_2O); 113.1 (*C*$H_{pyrrole}$); 119.5 (*C=C*); 120.6 (C=$C_{fulvene}$). MS (EI) $C_{18}H_{20}Cl_2N_2O_2S_4$: 493.98 ($M^{+\bullet}$).

*3.7. Bis-(*N*-(9-chloro-3,6-dioxa-1-octyl)pyrrolo[3, 4, d]tetrathiafulvalene **10b***

Yellow oil, 57% yield. ^{1}H NMR ($CDCl_3$): 3.56–3.73 (m, 20H, CH_2O and CH_2Cl); 3.98 (t, 4H, CH_2N); 6.51 (s, 4H, C$H_{pyrrole}$). ^{13}C NMR ($CDCl_3$): 43.8 (*C*H_2Cl); 50.8 (*C*H_2N); 70.7, 70.9, 71.4 and 71.7 (*C*H_2O); 113.9 (*C*$H_{pyrrole}$); 118.5 (*C=C*); 119.8 (*C=C*$_{fulvene}$).

MS (PDMS) $C_{22}H_{28}Cl_2N_2O_4S_4$: 582.6.

*3.8. Synthesis of bis(pyrrolo)TTF derivatives **11a,b***

Compounds **10a** or **10b** were refluxed for two days in acetone with a large excess of sodium iodide. The solvent was removed in vacuo and the residue was dissolved in dichloromethane. The organic phase was washed with an aqueous solution of sodium thiosulphate, with water, dried over magnesium sulphate and concentrated in vacuo. Compounds **11a,b** were used without further purification.

*3.9. Bis-(*N*-(5-iodo-3-oxa-1-pentyl)pyrrolo[3, 4, d]tetrathiafulvalene **11a***

Yellow powder, 89% yield, m.p.: 93°C. ^{1}H NMR ($CDCl_3$): 3.21 (t, 6.6 Hz, 4H, CH_2I); 3.64–3.71 (m, 8H, CH_2O); 3.99 (large s, 4H, CH_2N); 6.52 (s, 4H, C$H_{pyrrole}$). ^{13}C NMR ($CDCl_3$): 2.9 (*C*H_2I); 51.0 (*C*H_2N); 71.1, 72.2 (*C*H_2O); 113.1 (*C*$H_{pyrrole}$); 119.5 (*C=C*); 120.6 (*C=C*$_{fulvene}$).

MS (EI) $C_{18}H_{20}I_2N_2O_2S_4$: 678.

*3.10. Bis-(*N*-(9-iodo-3,6-dioxa-1-octyl)pyrrolo[3, 4, d]tetrathiafulvalene **11b***

Yellow oil, 86% yield. ^{1}H NMR ($CDCl_3$): 3.25 (t, 6.9 Hz, 4H, CH_2I); 3.55–3.75 (m, 16 H, CH_2O); 3.99

(large s, 4H, CH_2N); 6.52 (s, 4H, C$H_{pyrrole}$). ^{13}C NMR ($CDCl_3$): 3.7 (*C*H_2I); 54.5 (*C*H_2N); 70.2, 70.8, 71.4 and 72.6 (*C*H_2O); 113.9 (*C*$H_{pyrrole}$); 118.5 (*C*=*C*); 119.8 (*C*=*C* $_{fulvene}$). MS (EI) $C_{22}H_{28}I_2N_2O_4S_4$: 766.

3.11. Synthesis of N,N′*-Bis(pyrrolo) tetrathiafulvalene cryptands* ***12a,b***

A suspension of 4,13-diaza-18-crown-6 (76 mg, 0.29 mmol) and potassium carbonate (400 mg, 10 equiv, 2.9 mmol) in dry degassed acetonitrile (25 ml) was refluxed during 30 min. The mixture was diluted with acetonitrile (425 ml) and tetrathiafulvalene derivative **11a** or **11b** (1 equiv) was added. The reaction mixture was refluxed during five days. Then, the solvent was removed in vacuo. The residue was dissolved in dichloromethane, washed with water, dried over magnesium sulphate and concentrated in vacuo. The oil was purified by chromatography on a silica gel column (SiO_2 + 4% triethylamine, petroleum ether/dichloromethane 50:50 and dichloromethane/methanol 100:1).

3.12. Compound ***12a***

Yellow oil, 32% yield. ^{1}H NMR ($CDCl_3$): 2.58 (t, 4.8 Hz, 4H, CH_2N); 2.64 (t, 5.6 Hz, 8H, CH_2N); 3.33 (t, 5.6 Hz, 4H, CH_2O); 3.40 (t, 4.8 Hz, 8H, CH_2O); 3.48 (s, 8H, CH_2O); 3.57 (t, 4.3 Hz, 4H, CH_2O); 3.95 (t, 4.3 Hz, 4H, CH_2N); 6.49 (s, 4H, C*H*). ^{13}C NMR ($CDCl_3$): 51.1 (N*C*H_2); 54.5 (N*C*H_2); 55.6 (N*C*H_2); 69.7, 70.3, 70.3 and 70.7 (O*C*H_2); 112.6 (*C*$H_{pyrrole}$); 118.7 (*C*$_{Ar}$); 122.0 (*C*=*C*). HRMS (ESI+) $C_{30}H_{44}N_4O_6S_4$: obs.: 685.2192 $(M+H)^+$, th: 685.2222.

3.13. Compound ***12b***

Yellow oil, 41% yield. ^{1}H NMR ($CDCl_3$): 2.80 (large s, 4H, CH_2N); 2.88 (large s, 8H, CH_2N); 3.51–3.61 (m, 24H, CH_2O); 3.70 (s, 4H, CH_2O); 3.97 (s, 4H, CH_2N); 6.57 (s, 4H, C*H*). MS (ESI+) $C_{34}H_{52}N_4O_8S_4$: obs.: 773.2753 $(M+H)^+$, th 773.2746.

3.14. X-ray structure analysis of compound ***5***

Data were collected at 293 K on a Nonius MACH3 four-circle diffractometer, using MoKα graphite-monochromated radiation. The structural determination was achieved using the MolEN package.

Crystal Data for (Z)-5: orange plates, triclinic, $P\bar{1}$, a = 6.873(5) Å, b = 14.786(5) Å, c = 15.728(0), α = 99.89°, β = 94.89°, γ = 95.24°, V = 1559(8) Å^3, Z = 2, 2774 data with $I > 3\,\sigma(I)$, R = 0.057, Rw = 0.066, *GOF* = 1.807 (CCDC 198842).

4. Supplementary material

The supplementary material has been sent in electronic format to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as Cif files No. CCDC 198842, and can be obtained by contacting the CCDC.

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