Aza-Crown Tetrathiafulvalene Derivatives: Synthesis, X-ray Structure, and Metal Complexation Study

Franck Le Derf[a], Marc Sallé*[a], Nicolas Mercier[a], Jan Becher[b], Pascal Richomme[a], Alain Gorgues*[a], Jesus Orduna[c], and Javier Garín[c]

Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers[a],
2, Boulevard Lavoisier, F-49045 Angers, France

Department of Chemistry, Odense University[b],
Campusvej 55, DK-5230 Odense M, Denmark

Departamento de Química Orgánica, ICMA, Universidad de Zaragoza, CSIC[c],
E-50009 Zaragoza, Spain

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The synthesis of new aza-macrocyclic tetrathiafulvalene (TTF) derivatives is described, with a view to limiting the structural distortion of the redox-active TTF moiety and to favour metal complexation. An X-ray diffraction determination of one of these crown systems is provided. The electrochemical properties of these redox-active macrocyclic ligands are studied by cyclic voltammetry. Their complexing ability towards silver ions is evaluated by FAB mass spectrometry.

Introduction

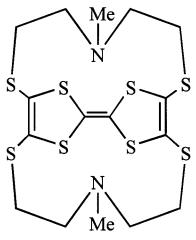
The synthesis and chemistry of macrocyclic receptor molecules containing redox site units (e.g. metallocenes) has been substantially developed over the past few years.[1] The main interest in these molecular receptors lies in their potential use as sensors for the detection of a wide range of organic and inorganic ions.

In this context, we have focused on the use of the π-electron-donating system tetrathiafulvalene (TTF) as the redox-active unit. Indeed, the well-known redox properties of the TTF moiety in combination with the complexing ability of crown ethers may lead to modulation of the trapping properties depending on the oxidation state of the redox-active unit.

Recently, some crown-annelated TTF derivatives constructed according to various strategies have been described.[2][3] The metal-binding abilities of some of these macrocyclic receptors were evaluated by UV/Vis spectrophotometry and cyclic voltammetry, although these studies[3d] were limited to derivatives bearing an O-crown ether moiety on the extremity of the TTF framework.

On the other hand, though the ability of polyaza-macrocyclic ligands to complex transition and non-transition metal cations is well established, very few studies have addressed the synthesis of aza-crown-annelated TTF analogues, and we are aware of only one example [molecule **A** (Figure 1)] incorporating an aliphatic aza chain.[3l] In this case, the aza-crown part is located along the long axis of the redox-active TTF core, which corresponds to a better situation for optimizing interactions between the metallic guest and the electrochemically active TTF core. However, due to the relatively short lateral nitrogen chains in these receptors, the redox-active TTF part (i.e. in **A**) is severely bent, leading to a loss of the classical redox properties of the TTF core, with electrochemical oxidation becoming irreversible and/or more difficult to achieve (higher oxidation potentials). Therefore, we have designed the alternative polyaza-macrocyclic TTF systems **5**–**7**, which have (i) the crown complexing part in close proximity along the TTF core, and (ii) a sufficiently large cavity in order to minimize the structural distortions of the TTF moiety previously observed with small crown systems. Macrocyclic TTFs **5**–**7** have been prepared according to a new general synthetic pathway, which is based on the pre-assembly of the bis-functionalized TTF core, followed by cyclocondensation under high-dilution conditions.

Figure 1. Molecule **A**



Results

In this study, the bis(3-bromopropyl)-TTF derivative **4** was used as the key intermediate en route to the aza-crown TTFs **5**–**7** (Scheme 1).

Both thiolate functionalities of compound **1**,[4] obtained as an (*E*/*Z*) isomeric mixture, were deprotected under basic conditions (*t*BuOK) and further functionalized with

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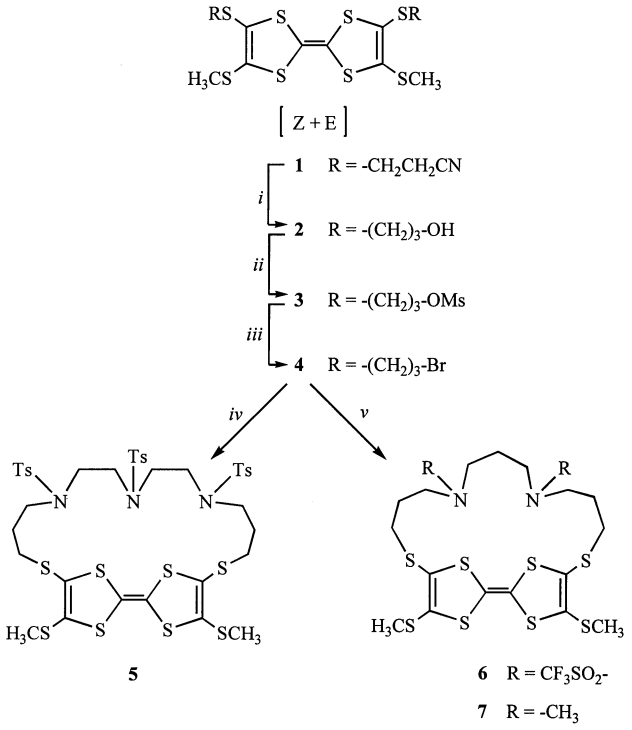
Scheme 1. (i) *t*BuOK, Br[CH_2]$_3$OH, DMF; (ii) MsCl, Et_3N, CH_2Cl_2; (iii) LiBr, Me_2CO; (iv) *N,N′,N′′*-tris(4-toluenesulfonyl)diethylenetriamine, K_2CO_3, DMF; (v) *N,N′*-bis(trifluoromethanesulfonyl)propylenediamine (for **6**) or *N,N′*-dimethylpropylenediamine (for **7**), K_2CO_3, DMF



bromopropanol to produce diol **2**. Treatment of **2** with methanesulfonyl chloride and subsequent halogenation of **3** with LiBr in refluxing acetone led to the key dibrominated intermediate **4** (81% overall yield from **1**). Finally, aza-crowns **5**−**7** were obtained by [1+1] cyclocondensations of **4** with the corresponding polyaza derivatives under high-dilution conditions (yields: **5**: 50%; **6**: 40%; **7**: 5%). These aza-crown TTF systems were obtained as mixtures of the (*Z*) and (*E*) isomers, the relative amounts of which were estimated by NMR to be (*E*)-**5**/(*Z*)-**5** ≈ 30:70, (*E*)-**6**/(*Z*)-**6** ≈ 35:65 and (*E*)-**7**/(*Z*)-**7** ≈ 50:50.

Attempts to achieve the deprotection of the *N,N′,N′′*-tritosyl-protected derivative **5** have as yet been unsuccessful. Removal of the classically used tosyl protecting group requires harshly acidic or reductive conditions,[5] e.g. 98% sulfuric acid or 48% HBr/AcOH, $LiAlH_4$, which are apparently incompatible with the redox part of macrocycle **5**, since only decomposition products are obtained. Although electrochemical reduction is commonly considered as a milder and more selective alternative, we unfortunately obtained decomposition products in this case as well.

Even though the triflate fragment has recently been used as an efficient, easily removable (Na/NH_3), *N*-protecting group, notably in the synthesis of polyaza-macrocycles,[6] attempts to deprotect compound **6** under these conditions were unsuccessful.

In an alternative synthesis, the *N*-methyl-substituted macrocycle **7** was obtained as an orange material. An X-ray structural determination[7] was performed on single crystals of the (*Z*) isomer, grown by slow evaporation of the solvents from a dichloromethane/pentane solution (Figure 2). The main crystallographic feature of (*Z*)-**7** is the partially distorted TTF unit. The bending essentially occurs around the S(1)−S(2) [and S(3)−S(4)] axis of each five-membered ring, and is associated with the structural constraints imposed by the lateral diaza-aliphatic chain. To the best of our knowledge, no other examples of related macrocyclic TTF derivatives bearing lateral polyaza, polythia, or polyoxa chains along the long axis of the TTF core, of the same size as in the case of **7**, have hitherto been described. However, some shorter, related poly(N, S, or O) macrocycles have been synthesized, with X-ray structural data being available in some cases.[3i][3l][8][9] Interestingly, the extent of the bending in (*Z*)-**7** is far less significant than in all of these systems, with dihedral angles of 16.7° and 23.2°, respectively, between planes defined by S(1)−S(2)−C(4) and S(1)−S(2)−C(6)−C(5) on the one hand, and S(3)−S(4)−C(3) and S(3)−S(4)−C(2)−C(1) on the other. This is related to the longer lateral chain in **7**. Furthermore, this better planarity (and therefore higher π-delocalization) can also be related to the intense orange colour observed for compound **7**, compared to the colourless or light-coloured constrained crown-TTF systems.[3i][3l][8a]

The redox properties of the crown-TTF derivatives **5**−**7** have been studied by cyclic voltammetry (in dichloromethane) (Table 1). Both of their oxidation processes are found to be reversible, with oxidation potentials (Ep_a1, Ep_a2) similar to those observed for the parent tetramethylsulfanyl-TTF (TMeSTTF).

This observation can be compared with the electrochemical behaviour of shorter crown-annelated TTF derivatives, for which the first oxidation step is either irreversible or is found at much more anodic Ep_a values,[3i][3l][8a] due to distortion of the central TTF core.

MO calculations performed by geometry optimization at the PM3 level on macrocycle **7** starting from X-ray structural data, give a HOMO energy of −8.08 eV, which can be taken as further evidence for a lower ionization potential in the case of **7** as compared to other shorter aza-crown ethers (E_{HOMO} = −8.74 eV in the case of molecule **A**[3i] and −7.99 eV in the case of TTF itself, calculated at the PM3 level).

The efficiency of fast-atom bombardment (FAB) mass spectrometry in studying the binding properties of host molecules is well established.[1c][10] Using this technique (FAB positive ionization mode), in *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix, we were able to evaluate the Ag^+ binding constants of the aza-crown TTF systems **5**−**7**, which were studied as their (*E*/*Z*) mixtures. This method[10] first involves the experimental measurement of the peak intensity of the host-guest complex, normalized to the *m*/*z* = 307 peak of the *m*-NBA matrix, while the metal ion concentration is progressively increased. Then, calculations are performed in order to find the stability constant that best fits the experimental results.

While no significant evidence of Ag^+ complexation was observed in the case of ligands **6** and **7**, the addition of a

Figure 2. X-ray structure of aza-crown-TTF (*Z*)-**7**

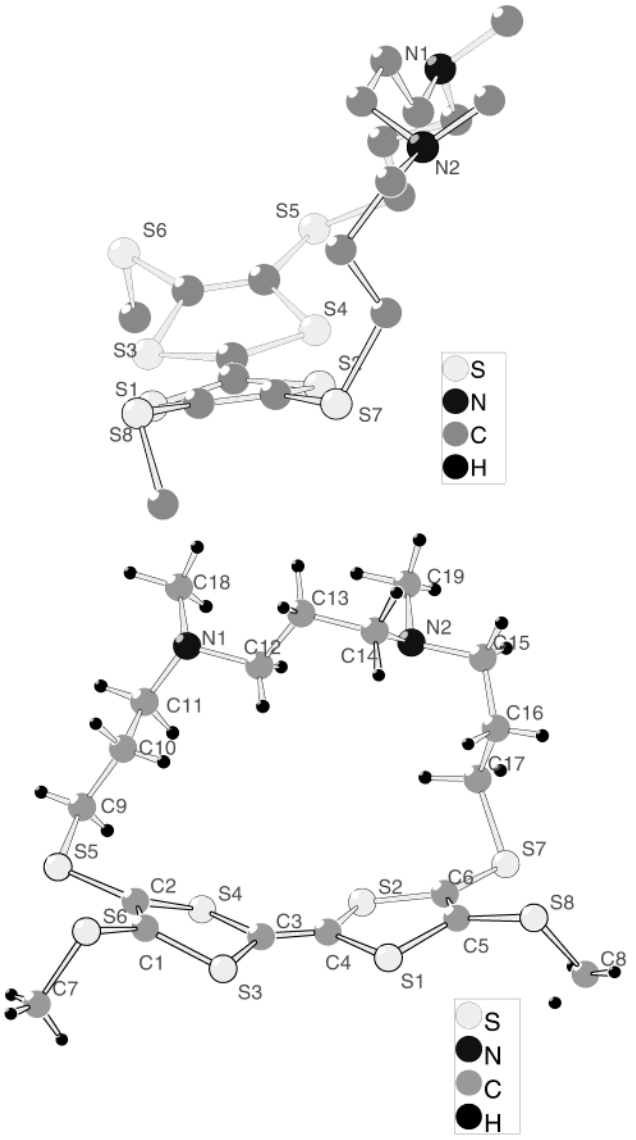


Table 1. Oxidation potentials ($Ep_a i$) of crown-annelated TTF systems **5**–**7**; Bu_4NPF_6 (0.1 mol·dm^{-3}) in CH_2Cl_2, 100 mV·sec^{-1}, vs. SCE

	5	**6**	**7**	TMeSTTF
Ep_a1	0.57	0.56	0.58	0.57
Ep_a2	0.93	0.79	0.84	0.91

solution of Ag^+ to aza-crown **5** resulted in the formation of a 1:1 complex, giving rise to a new peak (*m*/*z* = 1114) in the FAB mass spectrum (Figure 3). Therefore, this ligand is seen to exhibit good complexing properties, even as the *N*-tosyl-protected form. It is noteworthy that the addition of an excess of Ag^+ resulted in the complexation of only 70% of the total crown ether (Figure 4). This result, along with the 70:30 (*Z*/*E*) ratio determined from NMR experiments, indicates that Ag^+ is only complexed by the (*Z*) isomer. Calculation of the binding constant for (*Z*)-**5**-Ag^+ gives a log *K* value of 2.41.

Conclusion

Using a high-dilution technique, we have synthesized some unprecedentedly large aza-crown TTF systems in good yields. As a consequence of their size, which prevents distortion of the central TTF backbone, the electrochemical behaviour of these crown systems is similar to that typically observed for TTF derivatives. The good complexing ability of (*Z*)-**5** for silver ions has been demonstrated by FAB mass spectrometry.

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Experimental Section

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker Avance DRX500 spectrometer operating at 500 MHz and 125.7 MHz, respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. − Cyclic voltammetry experiments were performed with a PAR model 273 potentiostat/galvanostat, under argon versus SCE, using Pt working and counter electrodes, and electrochemical grade solvents and supporting electrolytes. − Mass spectra were recorded with a VG-Autospec (Micromass, UK). EI mass spectra were obtained at 70 eV and accurate mass measurements were performed at 10000 resolution (peak width at 5% height) using PFK as internal reference. FAB mass spectra were obtained using the standard Cs^+ gun operating at 30 kV. − For the determination of absolute binding constants, the spectra of NBA solutions (2 μl) containing **5** (0.05 M) and various $AgCF_3SO_3$ concentrations were recorded.

(E/Z)-3,6(7)-Bis(3-hydroxypropylsulfanyl)-2,7(6)-bis(methylsulfanyl)tetrathiafulvalene (**2**): Compound **1** (2.33 g, 5 mmol), prepared according to ref.[4], was dissolved in dry DMF (50 ml) and degassed with N_2 for 15 min. Potassium *tert*-butoxide (2.2 equiv.) was then added in one portion. After stirring for 15 min, 3-bromopropanol (1.53 g, 11 mmol) was introduced, and stirring was continued for an additional 45 min. The solvent was then removed in vacuo, and the resulting orange oil was dissolved in 50 ml of CH_2Cl_2, washed with water, and dried with Na_2SO_4. Subsequent chromatography on silica gel (CH_2Cl_2/AcOEt, 9:1), and evaporation of the solvent from the appropriate fractions afforded diol **2** (*E*/*Z* isomeric mixture) as an orange oil (2.26 g, 95% yield). − ^{1}H NMR ($CDCl_3$): δ = 3.77 (t, 4 H, CH_2OH), 2.93 (t, 4 H, SCH_2), 2.43 (s, 6 H, SCH_3), 2.37 (s, 2 H, OH), 1.89 (m, 4 H, CH_2). − IR: $\tilde{\nu}$ = 3370 cm^{-1}.

(E/Z)-3,6(7)-Bis[(3-methanesulfonyloxypropyl)-1-sulfanyl]-2,7(6)-bis(methylsulfanyl)tetrathiafulvalene (**3**): A cooled solution (0°C) of compound **2** (2.2 g, 4.6 mmol) and 5 ml of triethylamine in dichloromethane was treated dropwise under nitrogen with a solution of methanesulfonyl chloride (1.2 g) in dichloromethane (10 ml), with the temperature being maintained below 5°C. The reaction mixture was stirred for 1 h, washed with water (3 × 50 ml), and the organic phase was dried with sodium sulfate. The solvent was then evaporated in vacuo. Compound **3** was obtained as an orange solid after chromatography on silica gel (CH_2Cl_2) and precipitation with petroleum ether (2.61 g, 90%). − ^{1}H NMR ($CDCl_3$): δ = 4.38 (t, 4 H, CH_2O), 3.04 (s, 6 H, SO_2CH_3), 2.92 (t, 4 H, SCH_2), 2.44 (s, 6 H, SCH_3), 2.07 (m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 132.3, 132.2, 124.6 (lateral C=C), 67.6, 67.54

Figure 3. FAB mass spectrum of ligand **5** plus 0.75 equiv. of $AgCF_3SO_3$

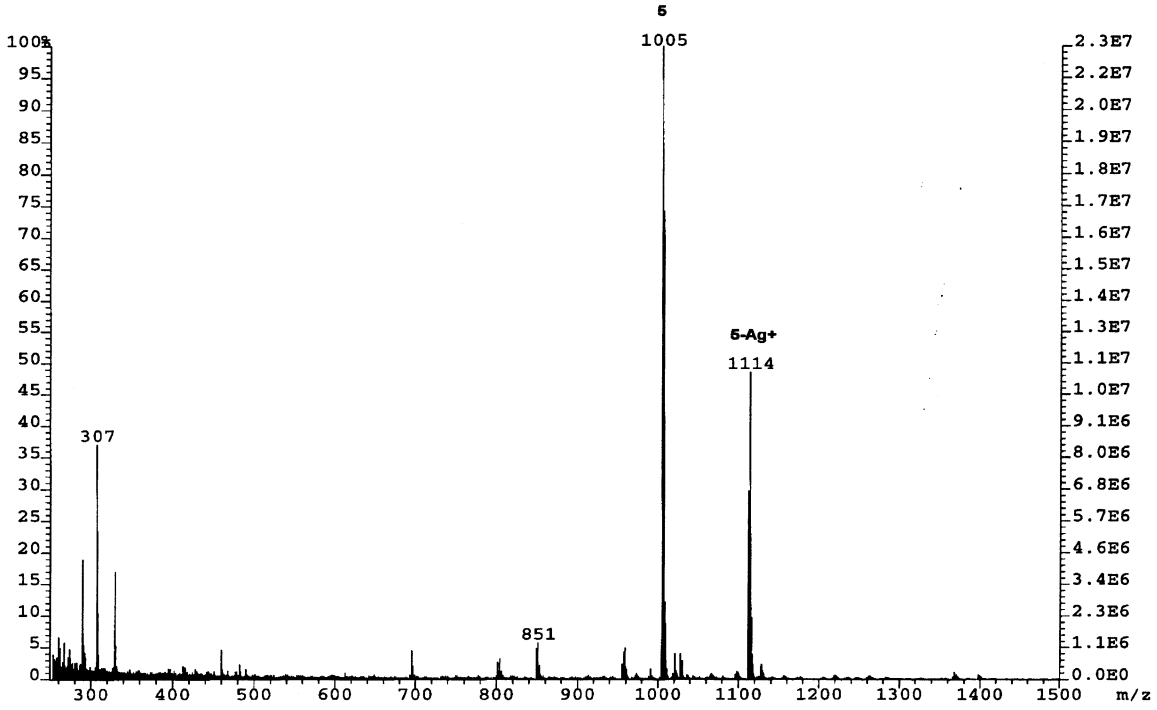
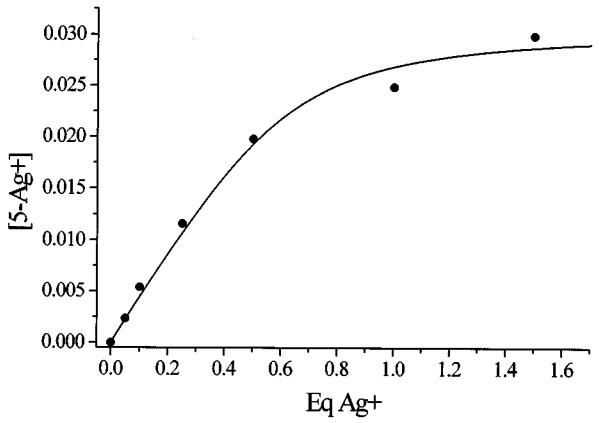


Figure 4. Plot of [(*Z*)-**5**-Ag^+] concentration versus added Ag^+ for a 0.05 M solution of **5** [0.035 M (*Z*)-**5**]



(CH_2O), 37.3 (SCH_2), 31.8 (CH_3SO_2), 28.8 (CH_2), 19.2 (SCH_3). − MS (EI): *m/z* = 632 [$M^{+\bullet}$].

(E/Z)-3,6(7)-Bis(3-bromopropylsulfanyl)-2,7(6)-bis(methylsulfanyl)tetrathiafulvalene (**4**): A mixture of **3** (1.26 g, 2.0 mmol) and 870 mg (5 equiv.) of lithium bromide in acetone was refluxed for 12 h. The solvent was then evaporated and replaced by dichloromethane. The resulting solution was washed with water (3 × 50 ml), and then dried with sodium sulfate. Evaporation of the solvent in vacuo and subsequent chromatography on silica gel (CH_2Cl_2) afforded **4** (1.14 g, 95%) as a bright-orange solid following precipitation with methanol. − ^1H NMR ($CDCl_3$): δ = 3.57 (t, 4 H, CH_2Br), 2.95 (t, 4 H, SCH_2), 2.44 (s, 6 H, SCH_3), 2.15 (m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 131.8, 131.6, 124.6 (lateral C=C), 34.2 (SCH_2), 31.9 (CH_2Br), 31.5 (CH_2), 19.2 (SCH_3). − MS (EI): *m/z* = 602 [$M^{+\bullet}$]. − $C_{14}H_{18}Br_2S_8$: calcd. C 28.01, H 3.02, S 42.65; found C 28.81, H 3.07, S 43.93.

(E/Z)-2,7(6)-Bis(methylsulfanyl)-3,6(7)-[5,8,11-tris(4-toluenesulfonyl)-5,8,11-triaza-1,15-pentadeca-1,15-disulfanyl]tetrathiafulvalene (**5**), *(E/Z)-2,7(6)-Bis(methylsulfanyl)-3,6(7)-[5,9-bis(trifluoromethanesulfonyl)-5,9-diaza-1,13-trideca-1,13-disulfanyl]tetrathiafulvalene* (**6**), *and (E/Z)-3,6(7)-(5,9-Dimethyl-5,9-diaza-1,13-trideca-1,13-disulfanyl)-2,7(6)-bis(methylsulfanyl)tetrathiafulvalene* (**7**): Solutions were prepared consisting of (i) the dibromo derivative **4** (0.602 g, 1.0 mmol) in dry DMF (60 ml), and (ii) the appropriately substituted polyamine (1 mmol) [*N,N′,N″*-tris(4-toluenesulfonyl)diethylenetriamine[11] (0.506 g) for the preparation of compound **5**, *N,N′*-bis(trifluoromethanesulfonyl)propylenediamine[6] (0.361 g) for the preparation of **6**, and *N,N′*-dimethylpropylenediamine (Aldrich) (0.074 g) for the preparation of compound **7**] in dry DMF (60 ml). Under nitrogen, solutions (i) and (ii) were simultaneously added by means of a perfusor pump to 0.5 g of potassium carbonate in 200 ml of dry DMF at 90°C (high-dilution conditions), over a period of 12 h (5 ml/h). The reaction mixture was stirred for an additional 2 h, and then the solvent was removed in vacuo. The residue was dissolved in dichloromethane (50 ml), washed with water (3 × 50 ml), and the organic phase was dried with sodium sulfate. After evaporation of the solvent, the aza-crown was purified by chromatography on silica gel (**5**, **6**: toluene; **7**: CH_2Cl_2/MeOH, 9:1, + 1% Et_3N) and subsequent precipitation in methanol.

5: Orange solid (0.52 g, 50%). − ^1H NMR ($CDCl_3$) (*E/Z* = 30:70): δ = 7.71 (m, 6 H, ArH), 7.33 (m, 6 H, ArH), 3.40−3.15 (m, 12 H, NCH_2), 2.99−2.73 (m, 4 H, SCH_2), 2.45, 2.44, 2.43 (3 s, 9 H, $ArCH_3$), 2.37, 2.35 (2 s, 6 H, SCH_3), 1.90 (m, 4 H, $CH_2CH_2CH_2$). − ^{13}C NMR ($CDCl_3$): δ = 143.89, 143.73, 143.66, 135.69, 135.46, 135.44, 131.14, 130.02, 129.94, 129.89, 127.71, 127.65, 127.45, 127.33, 124.10, 121.57 (Ar and lateral C=C), 110.92 (central C=C), 50.92, 49.89, 49.31, 48.89, 48.72, 47.72, 46.63 (NCH_2), 32.99, 32.67 (SCH_2), 29.51, 28.15 ($ArCH_3$), 21.66, 21.61 ($CH_2CH_2CH_2$), 19.24, 19.21 (SCH_3). − MS (EI): *m/z* = 1005 [$M^{+\bullet}$]

− $C_{39}H_{47}N_3O_6S_{11}$: calcd. C 46.57, H 4.71, N 4.18; found C 45.76, H 4.59, N 3.91.

6: Yellow solid (0.32 g, 40%). − ^{1}H NMR ($CDCl_3$) (*E*/*Z* = 35:65): δ = 3.47 (m, 8 H, NCH_2), 2.76 (m, 4 H, SCH_2), 2.52, 2.47 (2 s, 6 H, SCH_3), 1.99 (m, 6 H, $CH_2CH_2CH_2$). − ^{13}C NMR ($CDCl_3$): δ = 132.3, 122.6, 122.3, 117.5 (lateral C=C), 119.8 (q, *J* = 329 Hz, CF_3), 115.8, 112.3 (central C=C), 48.0, 46.0 (NCH_2), 32.4, 31.5 (SCH_2), 29.6, 28.9, 28.4, 27.1 ($CH_2CH_2CH_2$), 19.3, 19.2 (SCH_3). − HRMS (EI): *m*/*z* = 777.8843 [$M^{+\bullet}$]; calcd. for $C_{19}H_{24}F_6N_2O_4S_{10}$ 777.8847.

7: Orange solid (0.03 g, 5%). − ^{1}H NMR ($CDCl_3$) (*E*/*Z* = 50:50): δ = 3.99 [m, 2 H, SCH (*E*)], 2.95 [t, 4 H, SCH_2 (*Z*)], 2.62−2.29 [m, NCH_2 (*Z*) + (*E*) and SCH (*E*)], 2.45 [s, 6 H, SCH_3 (*E*)], 2.41 [s, 6 H, SCH_3 (*Z*)], 2.23 (s, 6 H, NCH_3), 2.21 (s, 6 H, NCH_3), 1.92−1.43 [m, $CH_2CH_2CH_2$ (*Z*) + (*E*)]. − ^{13}C NMR ($CDCl_3$): δ = 131.9, 128.9, 125.9, 123.9 (lateral C=C), 114.4, 112.5 (central C=C), 56.5, 55.9, 54.6, 54.4 (NCH_2), 42.6, 42.2 (NCH_3), 34.2, 33.4 (SCH_2), 28.0, 27.1, 24.9, 23.0 ($CH_2CH_2CH_2$), 19.4, 19.3 (SCH_3). − HRMS (EI): *m*/*z* = 542.0174 [$M^{+\bullet}$]; calcd. for $C_{19}H_{30}N_2S_8$ 542.0175.

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[7] X-ray data for compound **7**: $C_{19}H_{30}N_2S_8$ (M_W = 542.98), triclinic *P*$\bar{1}$, *Z* = 2, *a* = 9.454(2), *b* = 12.370(3), *c* = 12.420(7) Å, α = 78.43(3), β = 71.75(2), γ = 71.18(2)°, *V* = 1297(1) Å^3, calculated density 1.39 g.cm^{-3}. A yellow-brown single crystal of the title compound was selected by optical examination and X-ray diffraction data were collected at 293 K with an Enraf-Nonius MACH3 four-circle diffractometer. The unit cell was determined from a set of 25 reflections randomly found in the θ range 13−16°. Closely related values of the *a* and *b* parameters and the β and γ angles are often indicative of a higher symmetry: a monoclinic cell was then deduced with *a* = 19.21, *b* = 15.674, *c* = 9.453 Å, α = 90.37, β = 114.2, γ = 90.23°. However, in this cell, the very different intensities of equivalent reflections confirms unambiguously the triclinic symmetry found initially. 6620 reflections were collected by the ω-scan technique in the θ range 2−28° [λ(Mo-K_α) = 0.71069 Å; $0 \le h \le 12$; $-15 \le k \le 15$; $-15 \le l \le 15$), of which 6247 were independent (*R* = 0.022). The $I/\sigma(I) > 3$ criterion led to 3894 reflections suitable for structure refinement. A starting set of non-hydrogen atomic coordinates was obtained from the direct methods (SIR). Refinement of the structure did not allow the location of hydrogen atoms, which were then fixed at 0.95 Å from the carbon atoms (Hydro program). Finally, refinement of all atomic coordinates, anisotropic thermal factors (H refined isotropically) led to *R* = 0.044, R_W = 0.054 (use of *F* magnitude, 382 parameters for 3894 reflections). All calculations were performed using the MolEN package.

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