Stable Macrocyclic and Tethered Donor−Acceptor Systems. Intramolecular Bipyridinium and Tetrathiafulvalene Assemblies

Klaus B. Simonsen,† Kyukwan Zong, Robin D. Rogers,* and Michael P. Cava*

Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487

Jan Becher*

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

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A series of compounds has been prepared in which a tetrathiafulvalene (TTF)-derived donor is covalently tethered or bridged to one or more bipyridinium (viologen) acceptors. The relative degree of charge transfer observed in this series is discussed as a function of structure. The greatest CT effect is seen in the cyclophanes **9a**−**c** and **13**.

Introduction

The incorporation of electroactive components into supramolecular and macrocyclic assemblies is currently a challenge in the fields of synthetic chemistry and material science. Furthermore the investigation of the electronic interaction in such systems enables the chemist to understand and explain charge transfer interactions.[1] Since the discovery of organic metals[2] derived from the two-electron donor tetrathiafulvalene (**1**, TTF),[3] and the proposal by Wudl et al. in 1977 that molecules containing two-electron donor units might allow formation of charge transfer complexes of higher dimensionality,[4] numerous bis and oligo TTF's have been prepared and their redox behavior investigated.[5] In the previous examples, the right geometry and connection of the donor portion are essential for intramolecular interactions. Macrocyclic systems containing two TTF units have also been prepared.[6] Cyclophanes containing two electron acceptors derived from 4,4′-bipyridinium dication **2** have been synthesized by Hünig et al., and their intra and intermolecular interactions were extensively investigated.[7] But it was only after Stoddard et al. reported the self assembly of dibenzyl-4,4′-bipyridinium **3** and showed the strong effect of noncovalent interaction in this synthesis that such molecules evoked much attention,[8] since the synthesis relies upon the molecular recognition between the π-electron deficient 4,4′-bipyridinium dication and systems containing π-electron rich aromatic rings. In particular, the $\pi-\pi$ interaction and the stacking of the donor and acceptor systems have made it possible to design and construct a variety of mechanically interlocked systems, such as catenanes and rotaxanes.[9] The tetracationic cyclophane **3** is a versatile host molecule for electron rich systems, such as TTF, and a complex between **3** and TTF has been isolated and characterized.[10] Furthermore, a molecular shuttle incorporating a TTF unit as the electron donor unit has also been reported.[11]

The literature is limited on systems containing macrocyclic donor−acceptor systems which are covalently attached. The work by Staab et al., in which a number of donor−acceptor cyclophanes were investigated, is a prominent example.[12]

Covalently linked π-electron systems have received considerable attention in the field of solid state investigations. Preorganized donor−acceptor systems and their complex superstructure have been especially investigated over the last decade.[13]

The recent development of TTF-based buildings blocks derived from tetramercaptotetrathiafulvalene **4**[14] has made it possible to synthesize a variety of supramolecular assemblies, such as macrocyclic tetrathiafulvalenes,[15] oligomeric tetrathiafulvalenes,[5d] and macrobicylic tetrathiafulvalenophanes.[16] The construction of tetrathiafulvalene-based pseudocatenanes derived from tetrathiaful-

† Visiting scholar from Odense University, Denmark.

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(1) Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

(2) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355.

(3) (a) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Rep.* **1987**, *7*, 155. (b) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1993**, *14*, 245.

(4) Kaplan, M. L.; Haddon, R. C.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1977**, 388.

(5) (a) Jørgensen, K.; Lerstrup, K. A.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684. (b) Sudmale, I. V.; Tormos, G. V.; Khodorkovsky, V. Y.; Edzina, A. S.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1993**, *58*, 1355. (c) Marshallsay, G. J.; Hansen, T. K., Moore, A. J.; Bryce, M. R.; Becher, J. *Synthesis* **1994**, 926. (d) Lau, J.; Simonsen, O.; Becher, J. *Synthesis* **1995**, 521. (e) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.

(6) (a) Ippen, J.; Tao-pen, C.; Starker, B.; Schweitzer, D.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 67. (b) Bertho-Thoraval, F.; Robert, A.; Souizi, A.; Boubekeur, K.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1991**, 843.

(7) Geuder, W.; Hünig, S.; Suchy, A. *Tetrahedron* **1985**, *42*, 1665.

(8) (a) Philp, D.; Stoddart, J. F. *Synlett* **1991**, 445. (b) Ashton, P. R.; Perez-Garcia, L.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 571. (c) Armspach, D.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Godi, A.; Moore, C. P.; Prodi, L.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Wear, T. J.; Williams, D. J. *Chem. Eur. J.* **1995**, *1*, 33 and references therein.

(9) Amabilino, D. B.; Anelli, P.-L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínes, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142 and references cited therein.

(10) Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Chem. Soc., Chem. Commun.* **1991**, 1584.

(11) Ashton, P. R.; Bissell, R. A.; Spencer, N.; Stoddart, J. F.; Tolley, M. S. *Synlett* **1992**, 923.

(12) Staab, H. A.; Gabel, G.; Krieger, K. *Chem. Ber.* **1983**, *116*, 2827.

(13) (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Otsuki, J.; Oya, T.; Lee, S.-H.; Araki, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2193. (c) For a monopyridinium-TTF molecule, see: Goldenberg, L. M.; Becker, J. V.; Levi, O. P.-T.; Khodorkovsky, V. Yu.; Bryce, M. R.; Petty, M. C. *J. Chem. Soc., Chem. Commun.* **1995**, 475.

(14) (a) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. H.; Becher, J. *Synthesis* **1994**, 809. (b) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407.

(15) Becher, J.; Lau, J.; Leriche, P.; Mørk, P.; Svenstrup, N. *J. Chem. Soc., Chem. Commun.* **1994**, 2715.

(16) Blanchard, P.; Svenstrup, N.; Becher, J. *J. Chem. Soc., Chem. Commun.* **1996**, 615.

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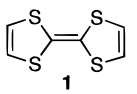
valene **4** and **3** by self-assembly has been achieved using the same strategy, and these systems show some interesting properties of the fulvalene double bond.[17] The central double bond in such a self-assembled system is prevented from undergoing facile *cis*/*trans* isomerization.

Although efficient and useful for many synthetic purposes, the tetramercaptotetrathiafulvalenes **4** are modest π-electron donors, and the search for good charge transfer systems must be found in systems containing a donor with a lower redox potential. Recently a practical preparation of the pyrrolo-annelated tetrathiafulvalene **5**, bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene, has been reported.[18] This novel tetrathiafulvalene has the potential for incorporation into macrocyclic systems containing an excellent π-donor.

To understand and explain the charge transfer interaction between two electroactive components, two questions need to be answered: (i) does the intramolecular charge transfer interaction occur because the two redox active units are forced together by conformation or (ii) are the charge transfer interactions just an interaction between two isolated π-systems without any influence from the fixation. In order to obtain more insight into the structural conditions necessary for π-interactions between two different electroactive systems, we chose to investigate systems in which the donor and acceptor units were tethered *via* a chain either in a rigid conformation, *e.g.* a macrocycle, or in an open conformation where the two systems are linked together by a bridge. Here we report the synthesis of macrocyclic donor−acceptor assemblies containing a donor unit derived from the tetrathiafulvalenes **4** or **5**, and the acceptor unit based on the 4,4′-bipyridinium dication **2**. This acceptor was chosen because it is accessible from the precursor 4,4′-bipyridyl, which has two potential attachment sites and possesses D_{2h} symmetry complementary to the donor **5**. Systems in which the donor and acceptor were linked together by a alkyl bridge were synthesized and compared with the related macrocyclic systems.



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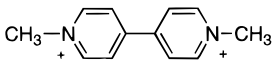

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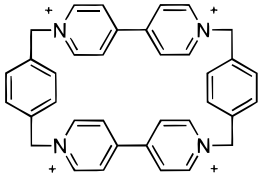

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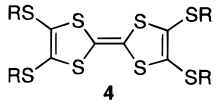

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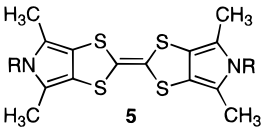

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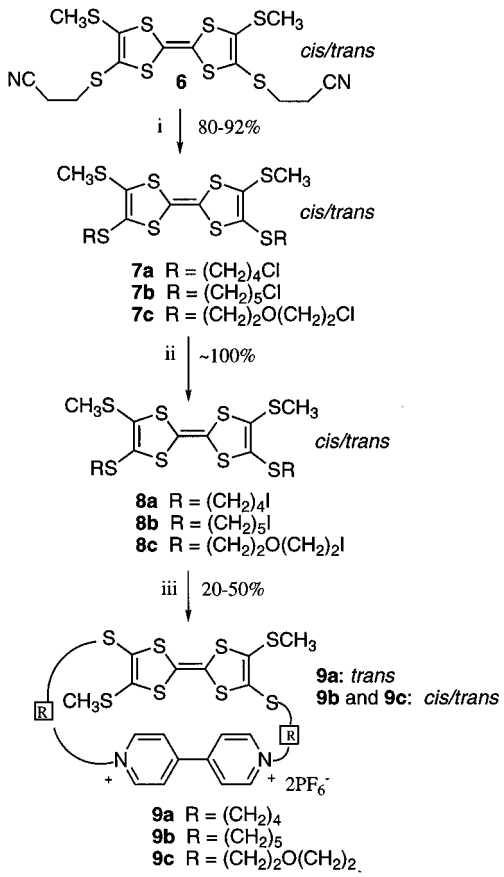
Results and Discussion

Synthesis. Synthesis of the Macrocyclic Donor−Acceptor Systems 9a−c and 13. The precursors for the macrocycles **9a−c**, the bisiodo TTFs **8a−c** were prepared in two steps from 2,6(7)-bis[(2-cyanoethyl)thio]-3,7(6)-bis(methylthio)tetrathiafulvalene **6**.[15] Thus, compound **6** in *N*,*N*-dimethylformamide was treated with a solution of cesium hydroxide in methanol and realkylated with the appropriate electrophile: 1-bromo-4-chlorobutane, 1-bromo-5-chloropentane and 2-(2-chloroethoxy)-ethanol tosylate.[19] The bis-chloro TTF **7a−c** was isolated in good yields after chromatography and transformed into the bis-iodo TTF **8a−c** using 20 equiv of sodium iodide in acetone, as outlined in Scheme 1.

Scheme 1



(i) 1: $CsOH{\cdot}H_2O$ in MeOH, DMF, 2: XR (**7a-b** X=Br, **7c** X=OTs);
(ii) NaI, acetone;
(iii) 4,4' bipyridyl, MeCN and heat, ion exchange with NH_4PF_6.

Refluxing a solution containing equimolar amounts of **8a−c** and 4,4′-bipyridyl in acetonitrile for 4−8 d gave the corresponding macrocycles **9a−c**. The yields in the macrocyclization step are quite good even without using high dilution reaction conditions, which may be due to a template effect from the formation of a CT-complex.

The purification of these dication salts was achieved by chromatography using a mixture of methanol, 2 M aqueous ammonium chloride, and nitromethane in the ratio 5:2:1. This mixture gave well-defined green bands which were isolated and concd *in vacuo* to green solids. The solids obtained were dissolved in a minimum amount of water, and addition of a saturated aqueous solution of ammonium hexafluorophosphate caused the precipitation of the bis(hexafluorophosphate) macrocycles **9a−c** in moderate yields (20−48%). Recrystallization from acetonitrile/ether or acetone/ether gave **9a−c** as green needles, which are very stable in air at rt.

The structure of **9a** (as the acetonitrile solvate) was confirmed by X-ray crystallography (Figure 1). Several unusual aspects of this structure are noteworthy. First

(17) (a) Li, Z.-T.; Stein, P. C.; Svenstrup, N.; Lund, K. H.; Becher, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2524. (b) Li, Z.-T.; Becher, J. *J. Chem. Soc., Chem. Commun.* **1996**, 639.

(18) (a) Chen, W.; Cava, M. P.; Takassi, M. A.; Metzger, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 7903. (b) Zong, K.; Chen, W.; Cava, M. P.; Rogers, R. D. *J. Org. Chem.* **1996**, *61*, 8117.

(19) Butler, C. L.; Renfrew, A. G.; Cretcher, L. H.; Souther, B. L. *J. Am. Chem. Soc.* **1937**, *59*, 227.

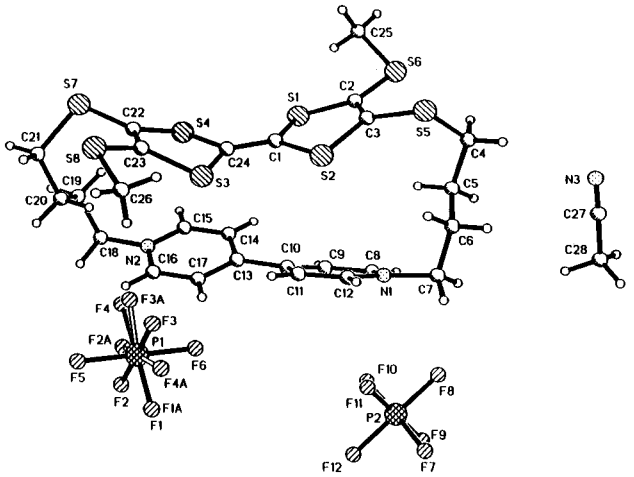


Figure 1. Cyclophane **9a**·CH_3CN.

Table 1. Crystal Data and Structure Refinement for Cyclophane 9a[a]

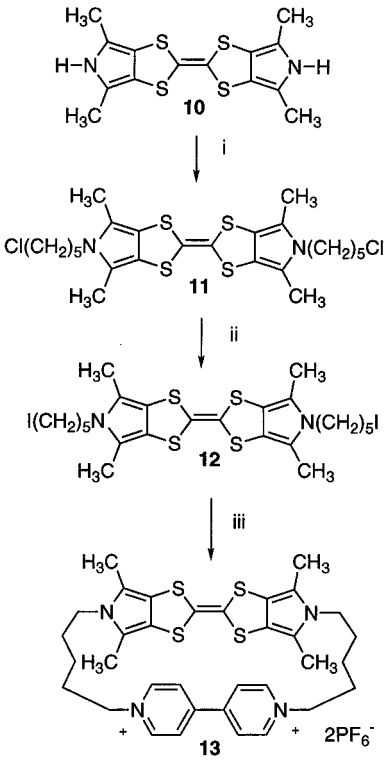
compound	cyclophane **9a**·CH_3CN
color/shape	green/plate
empirical formula	$C_{28}H_{33}F_{12}N_3P_2S_8$
formula weight	957.99
temperature	173(2) K
crystal system	monoclinic
space group	$P2_1/c$
unit cell dimensions	$a = 12.2617(1)$ Å $\alpha = 90°$
(8192 reflections	$b = 10.3713(1)$ Å $\beta = 93.140(1)°$
in full range)	$c = 30.4708(1)$ Å $\gamma = 90°$
volume	3869.15(5) Å^3
Z	4
density (calculated)	1.645 mg/m^3
absorption coefficient	0.630 mm^{-1}
diffractometer/scan	Siemens SMART/ CCD area detector
radiation/wavelength	Mo Kα (graphite monochrom)/0.71073 Å
$F(000)$	1952
crystal size	0.14 × 0.46 × 0.58 mm
range for data collection	1.34 to 23.00°
index ranges	$-13 \le h \le 13$, $-11 \le k \le 11$, $-28 \le l \le 33$
reflections collected	15740
independent/observed refls.	5392 ($R_{int} = 0.0450$)/ 4812 ($[I > 2\sigma(I)]$)
refinement method	full-matrix-block least-squares on F^2
computing	SHELXTL, ver 5
data/restraints/parameters	5386/0/495
goodness-of-fit on F^2	1.382
SHELX-93 weight parameters	0.0000, 14.6032
final R indices $[I > 2\sigma(I)]$	$R1 = 0.0681$, $wR2 = 0.1263$
R indices (all data)	$R1 = 0.0788$, $wR2 = 0.1345$
largest diff peak and hole	0.483 and −0.322 eÅ^{-3}

[a] The authors have deposited atomic coordinates for cyclophane **9a** with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U. K.

of all, the tetramethylene bridges are attached to the TTF core in a *trans* configuration, resulting in a rather rigid molecule. In addition, the two dithiole rings of the TTF are slightly buckled, and the two pyridinium cation units are not coplanar. Basic crystal data are given in Table 1.

The length and flexibility of the linker between the TTF and the bipyridinium unit has a great influence upon the conformation of the products. Based on a CPK model, the butylene chain seems to be the shortest possible chain for making a macrocycle based on bipyridinium and thiatetrathiafulvalene units; this macrocycle

Scheme 2



(i) 1: NaH, DMF, 2: $Br(CH_2)_5Cl$; (ii) NaI, acetone, reflux; (iii) 4,4' bipyridyl, MeCN and heat, ion exchange with NH_4PF_6.

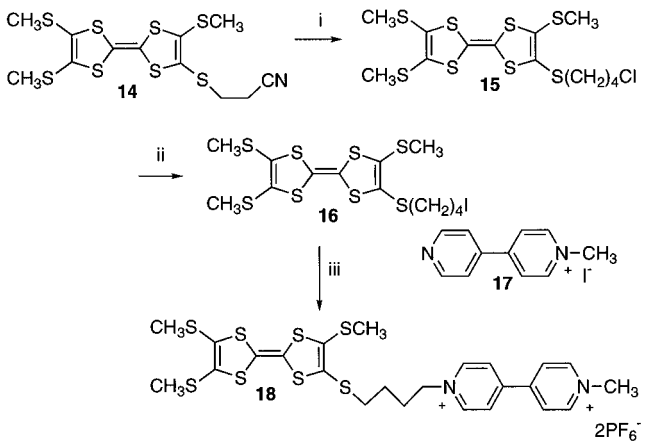
(**9a**) was isolated in 48% yield only as the *trans* isomer, as confirmed by X-ray, in contrast to the one to one ratio of *cis* and *trans* isomers in the starting material **8a**. With this linker, the two redox active portions are programmed to make an ideal donor−acceptor macrocycle. In the cases of the pentylene and diethylene glycol linkers, the macrocycles **9b**,**c** were isolated as a *cis*/*trans* mixture in the ratio of 1:2. These linkers are longer and more flexible, and the reactions affording **9b**,**c** had to be refluxed over a longer period (6−8 d) and gave the products only in moderate isolated yields (20−21%). The isolation of a *trans* TTF macrocycle using a suitable short linker has been reported previously by Robert et al.[20]

Following the methodology above, the macrocycle **13** was prepared using bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene **10** as the starting material.[18] Alkylation of **10** with 1-bromo-5-chloropentane in *N*,*N*-dimethylformamide using sodium hydride as the base afforded bis(2,5-dimethyl-*N*-(5-chloropentyl)pyrrolo[3,4-*d*])tetrathiafulvalene **11** in good yield. This was easily transformed to bis(2,5-dimethyl-*N*-(5-iodopentyl)pyrrolo[3,4-*d*])tetrathiafulvalene **12**, which was reacted with an equimolar amount of 4,4′-bipyridyl in refluxing acetonitrile for 4 d (Scheme 2). After chromatography and anion exchange, the bis(hexafluorophosphate) salt **13** was isolated and recrystallized from acetonitrile/ether to give **13** as small dark blue crystals (25%).

Synthesis of the Mono and Double Tethered Donor−Acceptor Systems 18, 22, 23, and 24. To fully understand the internal charge transfer interaction of the macrocyclic systems **9a**−**c**, two questions need to be answered: (i) does the intramolecular charge transfer interaction occur because the two redox active units are forced together by covalent bonds or (ii) are the charge

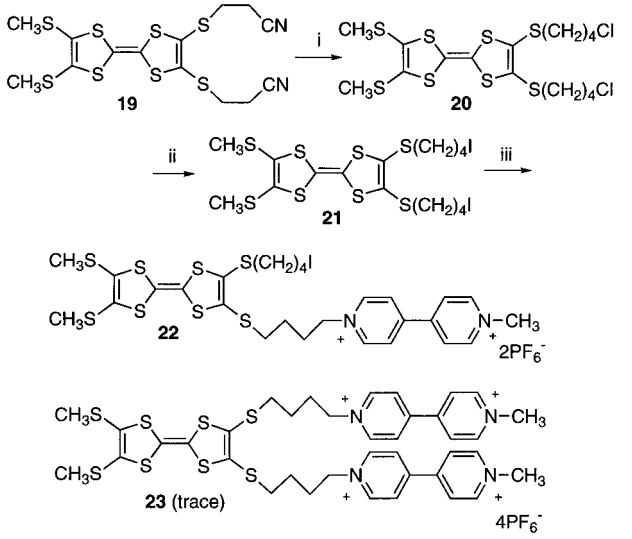
(20) Boubekeur, K.; Lenoir, C.; Batail, P.; Calier, R.; Robert, A.; LePaillard, M. P.; Lorcy, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1379.

Scheme 3



(i) 1: $CsOH{\cdot}H_2O$ in MeOH, DMF, 2: $Br(CH_2)_4Cl$; (ii) NaI, acetone, reflux; (iii) **17**, MeCN and heat, ion exchange with NH_4PF_6.

Scheme 4



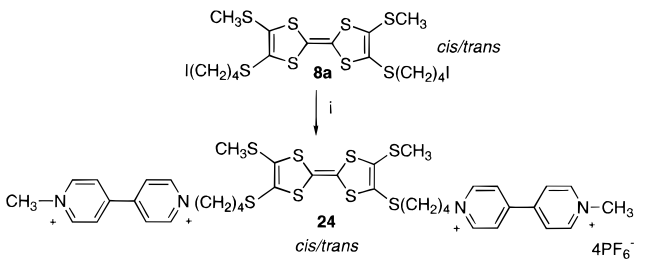
(i) 1: $CsOH{\cdot}H_2O$ in MeOH, DMF, 2: $Br(CH_2)_4Cl$; (ii) NaI, acetone, reflux; (iii) **17**, DMF and heat, ion exchange with NH_4PF_6.

transfer interactions just an interaction between an isolated TTF and a bipyridinium unit. To explore these possibilities, a number of compounds containing one tetrathiafulvalene and one bipyridinium unit were synthesized by connecting the two redox active units by one chain, thus allowing the systems to adopt an open conformation. Such a structure gives the donor−acceptor systems more degrees of freedom, and the two electroactive units do not necessarily have to interact intramolecularly in the solid state.

Starting from 2-[(2-cyanoethyl)thio]-3,6,7-tris(methylthio)tetrathiafulvalene **14**[14b] and 2,3-bis[(2-cyanoethyl)-thio]-6,7-bis(methylthio)tetrathiafulvalene **19**[14b] and 1-bromo-1-chlorobutane, and using the same conditions reported above, the TTF chlorides **15** and **20** were obtained, which were converted to the mono- and bis(4-iodobutylthio)-tetrathiafulvalenes **16** and **21**, respectively, in overall good yields (Schemes 3 and 4).

The iodo compounds **16** and **21** were refluxed with excess of 1-methyl-4-(4′-pyridyl)pyridinium iodide **17**[20] for 4 d in acetonitrile (Schemes 3 and 4). The resulting red precipitates (the diiodo salts) were chromatographed in the same solvent mixture reported above, when **18**, **22**, and **23** appeared as green bands on the column. These fractions were collected and addition of a saturated solution of ammonium hexafluorophosphate causes the

Scheme 5



(i) **17**, MeCN and heat, ion exchange with NH_4PF_6.

Table 2. 360 MHz ^{1}H-NMR Data (δ, ppm) of 2, 9a−c, and 13 (PF_6 salts) in DMSO-d_6[a]

compd	H2 and H2′ *cis*	H2 and H2′ *trans*	H3 and H3′ *trans*	H3 and H3′ *cis*
2	9.25		8.72	
9a	−	9.44	8.82	−
9b	9.42	9.39	8.89	8.83
9c	9.41	9.35	8.90	8.84
13	8.96		8.50	

[a] At 300 K all pyridinium protons give doublets with J app 6.8 Hz. The *cis*/*trans* ratios for both **9b** and **9c** are approximately 1:4.

dication salts **18** and **22** and the tetracationic salt **23** to precipitate as dark yellow/orange solids in 46%, 19%, and 3% yields, respectively. The trace of **23** was first explained by the low solubility of the diiodo salt **22**·2I in acetonitrile, preventing further reaction to the tetracation **23**·4I$^-$. To prevent this and to prepare **23** in more acceptable yield, the same reaction was carried out in *N*,*N*-dimethylformamide at 60 °C for 4 d. In this case there was no precipitation, but again **23** was only isolated as a minor product (2%). The formation of **23** in trace amounts was attributed to electronic and/or steric repulsion of the preformed dication **22**, preventing nucleophilic attack of another pyridine unit.

To synthesize double tethered donor−acceptor assemblies containing one tetrathiafulvalene unit and two bipyridinium units for comparison with the monotethered systems **18** and **22**, compound **24** was prepared (Scheme 5) by the methodology used above: thus, 1 equiv of 2,6-(7)-bis(4-chlorobutyl)-3,7(6)-bis(methylthio)tetrathiafulvalene **8a** was refluxed in acetonitrile with 2.5 equiv of 1-methyl-4-(4′-pyridyl)pyridinium iodide **17** for 5 d. After purification and anion exchange, the tetracationic salt **24** was obtained as a dark orange solid.

^{1}H NMR Spectroscopy. The ^{1}H-NMR spectra of the mono and double tethered compounds **18** and **22**−**24** are almost identical, and the pyridinium protons appears in the same region as for other bipyridinium systems. These systems obviously prefer an open conformation, indicating that neither the two quaternized nitrogens nor the interactions of the two π-systems have an effect on the NMR spectrum.

The spectra are different for the macrocylic systems **9** and **13**, in which the two π-systems are covalently linked together in a closed conformation.

The bipyridinium protons for compound **9** and **13** are listed in Table 2, together with the chemical shift of the isolated bipyridinium compound **2**. The pyridine protons of **9** are shifted downfield when compared to **2**, whereas the corresponding protons of **13** are shifted upfield. This effect in **13** is a consequence of the strong charge transfer in this system, making the viologen portion less electron deficient and hence moving the resonances for the protons upfield. In the case of compound **9**, the charge

Table 3. Charge-Transfer Abosrption Maxima for Tethered Donor−Acceptor Systems

compd	solvent	λ_{max}	ϵ
9a	MeCN	673	650
9a	DMSO	626	620
9b	MeCN	650	160
9c	MeCN	666	180
18	MeCN	701	85
18	DMSO	624	70
22	MeCN	680	85
24	MeCN	695	77
13	MeCN	640	403

transfer interactions are not as dominant and are overcome by the deshielding effect of the tetrathiafulvalene portion sitting above the bipyridinium system. Whereas compound **9a** was isolated only in the *trans* conformation, the two other macrocycles **9b**,**c** were isolated as a mixture of *cis* and *trans* isomers, as listed in Table 2. In the latter case the linkers between the two π-systems are longer and more flexible, which allows for the formation of both isomers. In these cases, the protons on the linker are comparable to those in the tethered systems **18** and **22**−**24**, indicative of free rotation for the linker methylenes in these compounds.

The spectrum is more complicated when the linker is short (C4); in this case the small size of the macrocycle **9a** dramatically diminishes the internal mobility of the system with respect to the linker chain. The isolation of only the *trans* isomer in this case also illustrates the rigid conformation of this system. As a consequence, the protons on the bridged carbon are not identical. The two protons on C7 (and C18, crystallographic numeration) next to the nitrogen are no longer identical and give rise to a doublet of triplets at 4.89 and 4.69 ppm due to geminal coupling (J = 13 Hz) and coupling to the two protons on C6 (C19) (J = 5.5−5.0 Hz). The protons next to the sulfur (C4 and C21) are also split due to geminal coupling and appear as doublet of triplets at 3.08 and 2.70 ppm (J = 13.6−13.4 and 5.6−5.9 Hz). The protons on C5 (C20) give rise to two multiplets at 1.57 and 1.14 ppm, due to geminal coupling to each other and different coupling to all the neighbor protons on C4 and C6 (C19 and C21). C6 and C19 show up at 2.04 as a multiplet and are the only methylene groups in which the two protons are identical.

The temperature-dependent ^{1}H-NMR spectra of compound **9a** from 300−380 K gives some interesting details about the lack of internal mobility in this rigid macrocycle. The signals of all the nonequivalent protons on C4 (C21), C5 (C20), and C7 (C18) remain more or less unchanged over the temperature range and no coalescence temperature could be reached, indicating that the activation energy for the rotation around a carbon−carbon single bond in this rigid system is very high.

UV−vis. The UV−vis spectra of the macrocycles **9a**−**c** and **13** and the tethered systems **18** and **22**−**24** were carried out in acetonitrile and all compounds gave nice green solutions. All of the donor−acceptor systems showed very broad charge transfer bands around 500−850 nm with a maximum about 620−700 nm (Table 3). The CT band is clearly strongest for the highly strained **9a** (ϵ = 650) but still considerable (160−180) for the larger macrocyclic analogs **9b** and **9c**. The slightly higher value of ϵ for **9c** as compared to **9b** may be due to minor internal conformational differences. A very strong CT band (ϵ = 403) was also observed in the case of **13**, although it was less intense than in the case of **9a**, for reasons which are not evident.

Table 4. Half-Wave Potentials, $E_{1/2}$, for the Donor−Accepter Systems (vs SCE) in Acetonitrile at 100 mV/s

compd	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
2·2PF_6	−0.84	−0.41	−	−
2 + **8b**	−0.84	−0.42	0.51	0.76
8a	−	−	0.51	0.76
8b	−	−	0.51	0.76
8c	−	−	0.46	0.71
9a	−0.85	−0.36	0.58	0.82
9b	−0.85	−0.37	0.54	0.78
9c	−0.86	−0.40	0.51	0.76
12	−	−	0.29	0.69
13	−0.84	−0.36	0.45	0.76
16	−	−	0.50	0.75
18	−0.83	−0.39	0.52	0.77
21	−	−	0.50	0.76
22	−0.83	−0.39	0.53	0.78
23	−0.84	−0.39	0.53	0.78
24	−0.85	−0.38	0.53	0.78

Although weaker relative to the macrocylic systems, the CT band is also present in the tethered donor−acceptor systems, indicating some CT interaction even in dilute solutions. The tethered systems **18** and **22**−**24** are all dark orange or dark yellow in the solid state, but in polar solvents the solutions are green. This suggests a charge transfer interaction in solution, whereas in the solid state the two π-portions tend to stack separately. The crystallization energy apparently overcomes the charge transfer tendency and becomes dominant. The chameleon properties of the open tethered systems **18** and **22**−**24** are unusual, in that charge transfer interactions normally are observed in the solid state rather than in solution. The possibility that intermolecular charge transfer effects may play a part in these systems was discounted by examination of an MeCN solution (2.4 mM) of tetrathiomethyl-TTF (**4**, R = Me) and the PF_6^- salt of the bipyridinium cation **2**: no charge-transfer band in the 600−700 nm region was observed.

Although most CT measurements were made on MeCN solutions, compounds **9a** and **18** were run in both MeCN and the more polar DMSO, as shown in Table 3. An appreciable hypsochromic shift and a slight decrease in the absorption maximum was observed in both cases in the more polar solvent.

In the case of the macrocyclic systems **9a**−**c** and **13**, the compounds are green both in solution and in the solid state, but here the two π-systems are held together in a rigid conformation and cannot come apart.

Electrochemistry. The redox behaviors of the new donor−acceptor systems were investigated by cyclic voltammetry (Table 4). All of the compounds exhibit four well defined one electron reversible redox waves, two from the tetrathiafulvalene (oxidation) and two from the viologen system (reduction). In order to explain the interaction between the tetrathiafulvalene and the viologen, the precursor compounds are also listed in Table 4.

As a reference, a CV was carried out on a solution containing equimolar amounts of **2** and **8b** using the same conditions (concentration, solvent, and electrolyte), the CV being recorded immediately after preparation and after 10 h; both measurements gave identical results, as listed in Table 4 (entry 2). The redox waves for both the oxidation of the TTF and the reduction of the viologen portion are identical with those of the two isolated measurements for **2** and **8b**, showing that no interaction at all takes place in the reference solution.

The cyclic voltammograms of the tethered systems **18**, **22**, **23**, and **24** show that the covalent attachment of the

two redox units changes (positive value) the potential (E^3, E^4) of the TTF portion by 20 mV, hence the generation of the radical cation and dication is made more difficult due to partial electron transfer from the donor to the acceptor system. The reduction of the bipyridinium portions, on the other hand, becomes more favorable by 20−30 mV because of the partial electron transfer from the TTFs. Although this difference is close to the reliability of the measurements, the change is consistent for all four compounds. A similar effect is also observed with some TTF-catenanes containing the "blue box".[17]

The reduction of the bipyridinium portion in **24** shows that the two viologen moieties are reduced at the same potentials, hence the CV gives two well defined redox waves which are twice as large as those for the TTF portion. The above observation suggests that the tethered systems prefer an open conformation in which the bipyridinium portions are distant from the TTF, and therefore only a minor charge transfer interaction is observed, as also observed by UV−vis.

When the two redox active units form part of a cyclophane, they are held in a close conformation, and for the compounds **9a**−**c** and **13** the changes in the redox pattern are significant. All potentials for the TTF portion (E^3 and E^4) exhibit a positive change, due to charge transfer interactions between the TTF and the bipyridinium dication, making the oxidation of the donor more difficult, but to a greater extent than for the tethered systems. The changes for **9a** ($\Delta E^3 = \Delta E^4 = 60$ mV) and **9b** ($\Delta E^3 = \Delta E^4 = 30$ mV) clearly show that the electron interactions increase as the ring becomes smaller and the two redox units become closer. Thus compound **9c** should be situated in between the previous two, as is actually observed ($\Delta E^3 = \Delta E^4 = 50$ mV).

The positive changes are much larger for the system containing the stronger donor **13**. The first potential is situated at 0.45 V ($\Delta E^3 = 160$ mV), whereas the second wave comes at 0.76 V ($\Delta E^4 = 70$ mV). The charge transfer is even more pronounced in this system, because the pyrrolo-annelated TTF is a much better donor than the tetrathio TTF, and therefore the partial electron transfer is larger for this system. The smaller change for the second oxidation (E^4) is caused by the electrostatic repulsion from the bipyridinium dication and the TTF radical cation, making the second oxidation less favorable. The reduction waves of the acceptor systems in these macrocycles are also shifted appreciably.

Conclusion

A comparison of the spectroscopic and electrochemical properties of a series of compounds derived from a tetrathiafulvalene (TTF) donor and one or two bipyridinium (BP) acceptors has been made. This series includes freely tethered TTF-BP as well as TTF-BP cyclophanes. As anticipated, the CT effects were greatest in cyclophanes **9a** and **13**, in which the donor and acceptor moieties are held rigidly in close proximity. The structure of **9a** contains an unusual *trans*- substituted TTF unit, as confirmed by X-ray crystallography.

Experimental Section

Electrochemistry. Cyclic voltammograms were performed in a single-compartment cell with a disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. For each measurement, a 0.1 M solution of the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAHFP) in acetonitrile (distilled), was employed with 0.1−0.5 mM of the substrate with a scan speed of 100 mV/s.

X-ray Crystallography. A green single crystal of compound **9a** was mounted on a fiber and transferred to the goniometer. The crystal was cooled to −100 °C during data collection by using a stream of cold nitrogen gas. The space group was determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table 1.

Disorder was resolved for one of the anions. F(1)−F(4) were found to be 85% occupied with an alternate orientation of these four atoms present at 15% occupancy.

The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2*U_{eqv}(C)$. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom ($B = 1.2*U_{eqv}(C)$). Refinement of nonhydrogen atoms was carried out with anisotropic temperature factors except for $F(1A)-F(4A)$ which were only 15% occupied.

2,6(7)-Bis[(4-chlorobutyl)thio]-3,7(6)-bis(methylthio)-tetrathiafulvalene 7a. Typical Procedure for 7a−c. Compound **6** (1.01 g, 2.2 mmol) was dissolved in dry DMF (50 mL) and degassed with N_2 for 15 min. A solution of $CsOH·H_2O$ (0.80 g, 4.7 mmol) in dry MeOH was added, and the reaction mixture was stirred for 30 min. 1-Bromo-4-chlorobutane (1 mL) was added, and the mixture was stirred for an additional 2 h. The solvent was removed *in vacuo*, and the resulting orange oil was chromatographed (silica, CH_2Cl_2/hexanes 4:1, $R_f = 0.6$) yielding 1.17 g of **7a** as a orange oil, which solidifies upon standing: mp 68−70 °C; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.56 (t, $J = 6.9$ Hz, 4H, CH_2Cl), 2.85 (t, $J = 6.8$ Hz, 4H, SCH_2), 2.43 (s, 6H, SCH_3), 1.93 (quintet, $J = 6.8$ Hz, 4H, CH_2), 1.80 (quintet, $J = 6.9$ Hz, 4H, CH_2); MS(EI) m/z: 542 (M^+, 100%). Anal. Calcd for $C_{16}H_{22}Cl_2S_8$ (541.73): C, 35.47; H, 4.09; S, 47.34. Found: C, 35.54; H, 4.13; S, 45.74. CV (CH_2Cl_2): $E_{1/2}$ = 0.51 V, 0.86 V.

2,6(7)-Bis[(5-chloropentyl)thio]-3,7(6)-bis(methylthio)-tetrathiafulvalene (7b). Chromatography (silica gel, CH_2Cl_2/hexanes 3:1, $R_f = 0.6$), yield 98%, orange oil; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.53 (t, $J = 6.6$ Hz, 4H, CH_2Cl), 2.81 (t, $J = 6.8$ Hz, 4H, SCH_2), 2.42 (s, 6H, SCH_3), 1.79 (quintet, $J = 7.0$ Hz, 4H, CH_2), 1.67 (quintet, $J = 6.9$ Hz, 4H, CH_2), 1.59 (quintet, $J = 7.0$ Hz, 4H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 129.92, 125.24, 125.16, 110.55, 44.71, 35.93, 32.03, 28.94, 25.69, 19.15; MS(EI) m/z: 568 (M^+, 100). Anal. Calcd for $C_{18}H_{26}Cl_2S_8$ (569.8): C, 37.94; H, 4.60; S, 45.01. Found: C, 38.06; H, 4.62; S, 45.07. CV (CH_2Cl_2): $E_{1/2} = 0.50$ V, 0.85 V.

2,6(7)-Bis[[2-(2-chloroethoxy)ethyl]thio]-3,7(6)bis-(methylthio)tetrathiafulva-lene (7c). Chromatography (silica, CH_2Cl_2/hexanes 4:1, $R_f = 0.5$), yield 62%, dark orange oil; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.74 (t, $J = 5.8$ Hz, 4H, OCH_2-CH_2Cl), 3.70 (t, $J = 6.5$ Hz, 4H, SCH_2CH_2O), 3.61 (t, $J = 5.7$ Hz, 4H, OCH_2CH_2Cl), 2.99 (t, $J = 6.6$ Hz, 4H, SCH_2CH_2O), 2.43 (s, 6H, SCH_3); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 131.30, 131.10, 124.09, 123.87, 110.79, 110.76, 71.13, 69.95, 42.60, 35.36, 19.11; MS(EI) m/z: 573 (M^+, 100). Anal. Calcd for $C_{16}H_{22}$-$Cl_2O_2S_8$ (573.7): C, 33.50; H, 3.86; S, 44.71. Found: C, 33.56; H, 3.89; S, 44.80. CV (CH_2Cl_2): $E_{1/2} = 0.49$ V, 0.82 V.

2,6(7)-Bis[(4-iodobutyl)thio]-3,7(6)-bis(methylthio)-tetrathiafulvalene (8a). Typical Procedure for 8a−c. A stirred solution of **8a** (1.07 g, 2.0 mmol) and NaI (5.5 g, 36.7 mmol) in dry acetone (100 mL) under N_2 was refluxed for 24 h. The solvent was removed *in vacuo*, and the crude product was redissolved in CH_2Cl_2 (75 mL), washed with H_2O (3 × 100 mL) and NaCl (100 mL), and dried (Na_2SO_4). Chromatography (silica gel, CH_2Cl_2:hexanes 4:1, $R_f = 0.5$) gave **8a** as an orange oil which solidifies upon standing, yield 1.38 g (97%): mp 54−55 °C; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.19 (t, $J = 6.8$ Hz, 4H, CH_2I), 2.82 (t, $J = 7.0$ Hz, 4H, CH_2S), 2.43 (s, 6H, SCH_3), 1.96 (quintet, $J = 7.1$ Hz, 4H, CH_2), 1.75 (quintet, $J = 7.4$ Hz, 4H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 130.60, 130.48, 124.62, 124.49, 110.69, 110.66, 34.96, 31.81, 30.32, 19.20, 5.71; MS-(EI) m/z: 724 (M^+, 44%). Anal. Calcd for $C_{16}H_{22}I_2S_8$ (724.6): C, 26.52; H, 3.06; S, 35.39. Found: C, 26.86; H, 2.71; S, 35.80. CV (MeCN): $E_{1/2} = 0.51$ V, 0.76 V.

2,6(7)-Bis[(5-iodopentyl)thio]-3,7(6)-bis(methylthio)-tetrathiafulvalene (8b). Chromatography (silica gel, CH_2-

Cl_2:hexanes 3:2, $R_f = 0.65$), yield 99%, orange oil: ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.18 (t, $J = 6.9$ Hz, 4H, CH_2I), 2.81 (t, $J = 7.1$ Hz, 4H, SCH_2), 2.42 (s, 6H, SCH_3), 1.84 (quintet, $J = 7.3$ Hz, 4H, CH_2), 1.66 (quintet, $J = 7.2$ Hz, 4H, CH_2), 1.53 (quintet, $J = 6.9$ Hz, 4H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 130.01, 129.93, 125.18, 125.09, 110.56, 35.88, 32.88, 29.26, 28.59, 19.19, 6.41; MS(EI) *m/z*: 752 (M^+, 1). Anal. Calcd for $C_{18}H_{26}I_2S_8$ (752.7): C, 28.72; H, 3.48; S, 34.07. Found: C, 28.95; H, 3.32; S, 34.32. CV (MeCN): $E_{1/2} = 0.51$ V, 0.76 V.

2,6(7)-Bis[[2-(2-iodoethoxy)ethyl]thio]-3,7(6)-bis(methylthio)tetrathiafulvalene (8c). Chromatography (silica gel, CH_2Cl_2/hexanes 4:1, $R_f = 0.6$), yield 86%, dark orange oil: ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.74 (t, $J = 6.7$ Hz, 4H, OCH_2CH_2I), 3.69 (t, $J = 6.5$ Hz, 4H, SCH_2CH_2O), 3.25 (t, $J = 7.0$ Hz, 4H, OCH_2CH_2I), 2.99 (t, $J = 6.6$ Hz, 4H, SCH_2CH_2O), 2.44 (s, 6H, SCH_3); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 131.27, 131.07, 124.14, 123.92, 110.23, 71.73, 69.53, 35.44, 19.17, 2.53; MS(EI) *m/z*: 755 (M^+, 100). Anal. Calcd for $C_{16}H_{22}I_2O_2S_8$ (756.6): C, 25.40; H, 2.93; S, 33.91. Found: C, 25.55; H, 2.98 ; S, 33.84. CV (MeCN): $E_{1/2} = 0.46$ V, 0.71 V.

Macrocycle 9a. Typical Procedure for 9a−c. A solution of TTF bis-iodide **8a** (0.48 g, 0.66 mmol) and bipyridyl (0.105 g, 0.656 mmol) in MeCN was refluxed for 3 d (monitored by TLC). The reaction mixture was cooled and the solvent removed *in vacuo* with the resulting dark precipitate redissolved in water, washed with $CHCl_3$ (3 × 100 mL), and concd. The resulting green solid was chromatographed (silica gel, MeOH:2 M NH_4Cl:$MeNO_2$ 5:4:1), and the product was isolated as a green band ($R_f = 0.6$). The solvent was removed, and the green solid was dissolved in a minimum amount of water and treated with a saturated solution of NH_4PF_6 until the precipitation of green solid starts. The solid was filtered and recrystallized from MeCN/ether yielding 0.29 g (48%) of **9a** as dark green needles: mp 217 °C dec; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.44 (d, $J = 6.8$ Hz, 4H, H2 and H2′), 8.82 (d, $J = 6.8$ Hz, 4H, H3 and H3′), 4.89 (dt, $J = 13.0$ and 5.5 Hz, 2H, CH_aN), 4.69 (br. dt, $J = 13.1$ and 5.0 Hz, 2H, CH_bN), 3.08 (dt, $J = 13.6$ and 5.6 Hz, 2H, CH_aS), 2.70 (dt, $J = 13.4$ and 5.8 Hz, 2H, CH_bS), 2.44 (s, 6H, SCH_3), 2.08 (m, 4H, NCH_2CH_2), 1.57 (m, 2H, CH_aCH_2S), 1.14 (m, 2H, CH_bCH_2S); ^{13}C-NMR (93 MHz, DMSO-d_6) δ 147.41, 146.59, 131.46, 125.69, 119.40, 109.39, 60.51, 32.59, 27.66, 23.16, 18.40; PDMS: *m/z:* 626.5 calcd for $C_{26}H_{30}N_2S_8$: 627.0. Anal. Calcd for $C_{26}H_{30}F_{12}N_2P_2S_8{\cdot}CH_3CN$: C, 35.11; H, 3.47; N, 4.39. Found: C, 34.76; H, 3.41; N, 3.41. CV (MeCN): $E_{1/2} = -0.85$ V, −0.36 V, 0.58 V, 0.82 V.

Macrocycle 9b. Reflux for 5 d. Same workup as for **9a**. Recrystallization from acetone/ether gave *cis*/*trans* **9b** as green crystals: yield 0.145 g (21%); mp 144−145 °C dec; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.42 and 9.39 (2 d, $J = 7.1$ and 6.8 Hz, 4H, *cis* and *trans* H2 and H2′), 8.89 and 8.83 (2 d, $J = 6.8$ and 6.8 Hz, 4H, *trans* and *cis* H3 and H3′), 4.76 (t, $J = 5.5$ Hz, 4H, CH_2N), 2.72 (t, $J = 7.1$ Hz, 2H, CH_aS), 2.42 (s, 6H, SCH_3), 1.98 (m , 4H, NCH_2CH_2), 1.55 and 1.44 (2 m, 4H, *cis* and *trans* CH_2CH_2S), 1.25 and 1.10 (2 m, 4H, *cis* and *trans* CH_2); ^{13}C-NMR (93 MHz, DMSO-d_6) δ 150.81(c), 148.50(t), 148.38(c), 146.12(t), 145.49(c), 131.61(t), 130.93(c), 126.78(t), 126.65(c), 122.67(c), 121.89(t), 112.05(c), 110.71(t), 61.53(c), 61.28(t), 35.53(c+t), 30.77(c), 29.55(c), 29.32(t), 28.44(t), 24.12(c), 23.67(t), 18.80(c), 18.71(t); PDMS: *m/z*: 654.6 calcd for $C_{28}H_{34}N_2S_8$: 655.1. Anal. Calcd for $C_{28}H_{34}F_{12}N_2P_2S_8$: C, 35.59; H, 3.63; N, 2.96. Found: C, 35.73; H, 3.72; N, 3.00. CV (MeCN): $E_{1/2} = -0.85$ V, −0.37 V, 0.54 V, 0.78 V.

Macrocycle 9c. Reflux for 8 d. Same workup as for **9a**. Recrystallization from acetonitrile/ether gave *cis*/*trans* **9c** green crystals: yield 0.090 g (20%); mp 215−217 °C dec; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.41 and 9.35 (two d, $J = 6.8$ and 6.8 Hz, 4H, *cis* and *trans* H2 and H2′), 8.90 and 8.84 (two d, $J = 6.9$ and 6.8 Hz, 4H, *trans* and *cis* H3 and H3′), 4.90 and 4.84 (two t, $J = 4.2$ Hz, 4H, *trans* and *cis* CH_2N), 4.10 and 3.93 (br, m and t, $J = 4.2$ Hz, 4H, *cis* and *trans* NCH_2CH_2O), 3.75 and 3.47 (t and t, $J = 5.6$ Hz, 4H, *cis* and *trans* SCH_2CH_2O), 3.05 and 2.93 (br m and t, $J = 5.6$ Hz, 4H, *cis* and *trans* SCH_2CH_2O), 2.41 and 2.40 (two s, 6H, *cis* and *trans* SCH_3); ^{13}C-NMR (93 MHz, DMSO-d_6) δ 150.98(c), 148.68(t), 146.90(c), 146.61(t), 146.20(c), 132.50(c+t), 126.05(t), 124.92(c), 121.80(c), 120.16(t), 109.28(t), 108.80(c), 70.99(c), 68.31(c), 68.08(t), 67.36(t), 60.68(c+t), 34.96(c+t), 18.37(c), 18.27(t); PDMS: *m/z*: 658.3 calcd for $C_{26}H_{30}N_2O_2S_8$: 659.0. Anal. Calcd for $C_{26}H_{30}F_{12}N_2O_2P_2S_8{\cdot}{}^1/_2CH_3CN$: C, 33.45; H, 3.27; N, 3.61. Found: C, 33.58; H, 3.27; N, 3.16. CV (MeCN): $E_{1/2} = -0.86$ V, −0.40 V, 0.51 V, 0.76 V.

Bis(2,5-dimethyl-*N*-(5-chloropentyl)pyrrolo[*c*])tetrathiafulvalene 11. To a solution of bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (400 mg, 1.18 mmol) in dry DMF (20 mL) was added under nitrogen excess NaH (142 mg, 5.90 mmol) in portions at rt. The reaction mixture was stirred for 30 min, and 1-bromo-5-chloropentane (657 mg, 3.54 mmol) in dry DMF (5 mL) was added. The reaction mixture was stirred for 1 h and carefully poured into water (30 mL). The precipitate was filtered and washed with water and methanol in sequence. Purification of the crude was accomplished on a short column on silica gel using CH_2Cl_2 as eluent, providing the product as a light yellow solid (582 mg, 90%): mp 230−232 °C dec; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.70 (t, $J = 7.2$ Hz, 4H), 3.52 (t, $J = 6.5$ Hz, 4H), 2.15 (s, 12H), 1.79 (m, 4H), 1.60 (m, 4H), 1.45 (m, 4H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 120.18, 118.05, 114.92, 44.63, 44.36, 32.17, 30.44, 24.09, 12.02; IR (KBr) 3400 (M), 2980 (S), 1510 (m), 1395 (m), 1380 (S), 1320 (S), 640 (m) cm^{-1}; MS (EI) *m/z*: 547 (M^+, 85). Anal. Calcd for $C_{24}H_{32}N_2S_4Cl_2$: C, 52.62; H, 5.89; N, 5.11; S, 23.41. Found: C, 52.34; H, 5.98; N, 5.01; S, 23.26.

Bis(2,5-dimethyl-*N*-(5-iodopentyl)pyrrolo[c])tetrathiafulvalene 12. The reaction mixture of bis(2,5-dimethyl-*N*-(5-chloropentyl)pyrrolo[*c*])tetrathiafulvalene (300 mg, 0.54 mmol) and NaI (820 mg, 5.47 mmol) in acetone (20 mL) was refluxed for 2 d under nitrogen. The reaction was cooled to rt, and acetone was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water, and dried over Na_2SO_4. The solvent was removed, and the crude was purified by a short column on silica gel using CH_2Cl_2 as eluent to afford a light yellow solid (306 mg, 77%): mp 182−183 °C dec; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.69 (br, 4H), 3.18 (t, $J = 6.9$ Hz, 4H), 2.14 (s, 12H), 1.82 (m, 4H), 1.62−1.39 (m, 8H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 118.18 (br), 114.93, 44.46 (br), 32.90, 29.64, 27.68, 12.05, 6.31; MS (*m/e*): 128 (100), 142 (15), 164 (10), 182 (7), 197 (15), 254 (13), 730 (M^+, 11); IR (KBr) 3450 (s), 2950 (s), 1480 (m), 1410 (m), 1380 (m), 1325 (s), 1175 (m) cm^{-1}; HRMS (m/z) calcd for $C_{24}H_{32}N_2S_4I_2$ 730.6881, found 730.6889. CV (MeCN): $E_{1/2}$= 0.29 V, 0.69 V.

Macrocycle 13. The reaction mixture of bis(2,5-dimethyl-*N*-(5-iodopentyl)pyrrolo[*c*])tetrathiafulvalene **12** (240 mg, 0.328 mmol) and bipyridyl (51 mg, 0.328 mmol) in dry MeCN (15 mL) was refluxed under nitrogen for 3 d. The dark colored reaction mixture was cooled to rt and concd under reduced pressure. The purification of the crude by chromatography on silica gel using a mixture solution (MeOH:2 M NH_4Cl:$MeNO_2$ = 5:2:1) as a eluent afforded a dark-blue band (R_f = 0.3). The combined blue fractions were concd under reduced pressure and diluted with water (20 mL). The aqueous solution was treated with concd NH_4PF_6 in water until precipitation was initiated. Filtration afforded a dark-blue solid, which was recrystallized from diethyl ether/MeCN to give dark-blue crystals (76 mg, 25%): mp > 250 °C; ^{1}H NMR (360 MHz, DMSO-d_6) δ 8.95 (d, $J = 6.7$ Hz, 4H), 8.50 (d, $J = 6.7$ Hz, 4H), 4.61 (t, $J = 7.0$ Hz, 4H), 3.89 [t (br), 4H], 2.19 (s, 12)1.72 (m, 4H), 1.50 (m, 4H), 1.18 (m, 4H); ^{13}C NMR (93 MHz, DMSO-d_6) δ 148.65, 145.42, 126.15, 119.33, 117.11, 113.45, 60.00, 43.91, 29.13, 27.18, 21.70, 11.92. Anal. Calcd for $C_{34}H_{40}N_4F_{12}S_4P_2$: C, 44.25; H, 4.37; N, 6.07; S, 13.90. Found: C, 44.09; H, 4.48; N, 6.35; S, 13.56. CV (MeCN): $E_{1/2} = -0.84$ V, −0.36 V, 0.45 V, 0.76 V.

2-[(4-Chlorobutyl)thio]-3,6,7-tris(methylthio)tetrathiafulvalene (15). Compound **14** (0.47 g, 1.1 mmol) was dissolved in dry DMF (40 mL), and the solution was degassed with N_2 for 15 min. A solution of $CsOH{\cdot}H_2O$ (0.20 g, 1.2 mmol) in dry MeOH (3 mL) was added, and the reaction mixture was stirred for 30 min. A solution of 1-bromo-4-chlorobutane (0.21 g, 1.2 mmol) in DMF (2 mL) was then added, and the mixture was stirred for 12 h. The solvent was removed *in vacuo*, and the resulting orange oil was chromatographed (silica gel, CH_2Cl_2/hexanes 3:2, $R_f = 0.65$) yielding 1.48 g (94%) of **15** as a orange oil: ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.55 (t, $J = 6.5$ Hz, 2H, CH_2Cl), 2.83 (t, $J = 7.0$ Hz, 2H, CH_2S), 2.42 (s, 9H, SCH_3), 1.90 (m, quintet), $J = 7.1$ Hz, 2H, CH_2), 1.79 (m, quintet), $J =$

7.2 Hz, 2H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 130.51, 127.48, 127.39, 124.69, 110.81, 110.71, 44.30, 35.41, 31.04, 26.82, 19.16; MS(EI) *m/z*: 464 (M^+, 100). Anal. Calcd for $C_{13}H_{17}ClS_8$ (465.2) C, 33.56; H, 3.68; S, 55.14. Found: C, 33.64; H, 3.71; S, 55.29. CV (CH_2Cl_2): $E_{1/2} = 0.53$ V, 0.87 V.

2-[(4-Iodobutyl)thio]-3,6,7-tris(methylthio)tetrathiafulvalene (16). This was prepared as **8a** using **15** (0.39 g, 0.84 mmol) and NaI (3 g, 20.0 mmol) in acetone (50 mL), followed by chromatography (silica gel, CH_2Cl_2:hexanes 2:3, $R_f = 0.65$) to give **16** as an orange oil: yield 0.43 g (92%); ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.20 (t, $J = 6.8$ Hz, 2H, CH_2I), 2.85 (t, $J = 7.0$ Hz, 2H, CH_2S), 2.43 (s, 3H, SCH_3), 2.42 (s, 6H, SCH_3), 1.90 (quintet, $J = 7.4$ Hz, 2H, CH_2), 1.79 (quintet, $J = 7.3$ Hz, 2H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 130.61, 127.52, 127.41, 124.65, 110.95, 110.74, 35.01, 31.87, 30.36, 19.19, 5.63; MS-(EI) *m/z*: 556 (M^+, 2). Anal. Calcd for $C_{13}H_{17}IS_8$ (556.7): C, 28.05; H, 3.07; S, 46.08. Found: C, 28.29; H, 3.09; S, 46.24. CV (CH_2Cl_2): $E_{1/2} = 0.52$ V, 0.86 V. CV (MeCN): $E_{1/2} = 0.50$ V, 0.75 V.

Compound 18. To a solution of **16** (0.26 g, 0.47 mmol) in refluxing MeCN (30 mL) was added **17**[21] (1.5 equiv, 0.20 g, 0.67 mmol) in hot MeCN (40 mL) under nitrogen. The reaction mixture was refluxed for 5 d and cooled (after 2 d an orange/red solid start to precipitate). The precipitate was filtered, washed with cold MeCN (2 × 20 mL), and dried to red/brown solid. The crude product was subjected to column chromatography (silica gel, MeOH:2 M NH_4Cl:$MeNO_2$ 5:2:1) whereupon one green band appeared ($R_f = 0.4$). The green fractions were collected, and the solvent was removed under reduced pressure. The resulting solid was redissolved in a minimum amount of water and a solution of NH_4PF_6 was added, when orange crystals precipitated, yielding 0.190 g (46%): mp 186 °C dec; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.36 (d, $J = 6.5$ Hz, 2H, H2), 9.27 (d, $J = 6.4$ Hz, 2H, H2′), 8.77 (d, $J = 6.5$ Hz, 2H, H3), 8.73 (d, $J = 6.5$ Hz, 2H, H3′), 4.71 (t, $J = 7.0$ Hz, 2H, CH_2N), 4.42 (s, 3H, NCH_3), 2.91 (t, $J = 7.0$ Hz, 2H, CH_2S), 2.44 (s, 3H, SCH_3), 2.43 (s, 3H, SCH_3), 2.42 (s, 3H, SCH_3), 2.10 (m, quintet), 2H, NCH_2CH_2), 1.62 (m, quintet), 2H, SCH_2CH_2); ^{13}C-NMR (93 MHz, DMSO-d_6) δ 148.53, 148.05, 146.59, 145.77, 130.54, 126.58, 126.48, 126.07, 125.98, 122.69, 109.72, 109.67, 60.24, 48.00, 34.59, 29.42, 25.58, 18.50 (2C), 18.47; PDMS: *m/z*: 600.9 calcd for $C_{24}H_{28}N_2S_8$: 601.0. Anal. Calcd for $C_{24}H_{28}F_{12}N_2P_2S_8$: C, 32.36; H, 3.17; N, 3.14. Found: C, 32.41; H, 3.18; N, 3.09. CV (MeCN): $E_{1/2} = -0.83$ V, -0.39 V, 0.52 V, 0.77 V.

2,3-Bis[(4-chlorobutyl)thio]-6,7-bis(methylthio)tetrathiafulvalene (20). Compound **19** (0.46 g, 1.0 mmol) was dissolved in DMF (30 mL), and the solution was degassed with nitrogen for 30 min. A solution of $CsOH·H_2O$ (0.35 g, 2.1 mmol) in MeOH (5 mL) was added, and the reaction mixture was stirred for an additional 30 min, when a solution of 1-bromo-4-chlorobutane (0.34 g, 2.0 mmol) in DMF (2 mL) was added. The reaction mixture was stirred for 2 h and concd *in vacuo* to an orange oil. Chromatography (silica gel, CH_2Cl_2:hexanes 2:3, $R_f = 0.6$) gave **20** as an orange oil: yield 0.42 g (78%); ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.56 (t, $J = 6.4$ Hz, 4H, CH_2Cl), 2.86 (t, $J = 7.0$ Hz, 4H, CH_2S), 2.43 (s, 6H, SCH_3), 1.90 (quintet, $J = 7.5$ Hz, 4H, CH_2), 1.80 (quintet, $J = 7.2$ Hz, 4H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 127.81, 127.50, 110.88, 110.51, 44.28, 35.50, 31.14, 26.95, 19.17; MS(EI) *m/z*: 542 (M^+, 100). Anal. Calcd for $C_{16}H_{22}Cl_2S_8$ (541.7): C, 35.47; H, 4.09; S, 47.34. Found: C, 36.05; H, 4.24; S, 48.18. CV (CH_2Cl_2): $E_{1/2} = 0.54$ V, 0.87 V.

2,3-Bis[(4-iodobutyl)thio]-6,7-bis(methylthio)tetrathiafulvalene (21). This was prepared similarly to **8a** using **20** (0.37 g, 0.7 mmol) and NaI (2 g, 13.3 mmol) in acetone (50 mL). Chromatography (silica gel, CH_2Cl_2:hexanes 2:3, $R_f = 0.65$) gave **21** as an orange oil, yield 0.40 g (82%); ^{1}H-NMR (360 MHz, $CDCl_3$) δ 3.20 (t, $J = 6.8$ Hz, 4H, CH_2I), 2.85 (t, $J = 7.0$ Hz, 4H, CH_2S), 2.43 (s, 6H, SCH_3), 1.97 (quintet, $J = 7.4$ Hz, 4H, CH_2), 1.78 (quintet, $J = 6.7$ Hz, 2H, CH_2); ^{13}C-NMR (93 MHz, $CDCl_3$) δ 127.78, 127.45, 111.07, 110.47, 35.07, 31.93, 30.44, 19.19, 5.62; MS(EI) *m/z*: 724 (M^+, 26). Anal. Calcd for $C_{16}H_{22}I_2S_8$ (724.6): C, 26.52; H, 3.06; S, 35.39. Found: C, 26.61; H, 3.02; S, 35.47. CV (CH_2Cl_2): $E_{1/2} = 0.53$ V, 0.86 V. CV (MeCN): $E_{1/2} = 0.50$ V, 0.76 V.

Compounds 22 and 23. To a solution of **21** (0.29 g, 0.4 mmol) in refluxing MeCN (40 mL) was added a solution of **17** (0.25 g, 0.84 mmol) in hot MeCN (40 mL) under nitrogen. The reaction mixture was refluxed for 3 d and then cooled (after 2 d a solid start to precipitate). The precipitate was filtered, washed with cold MeCN (2 × 20 mL), and dried to give a red/brown solid. From the filtrate was recovered 0.10 g of the starting TTF. The crude product was dissolved in water (2 mL) and subjected to column chromatography (silica gel, MeOH:2 M NH_4Cl:$MeNO_2$ 5:2:1) whereupon two bands appeared, one yellow/green band ($R_f = 0.6$) and one green band ($R_f = 0.3$). The fractions were collected, and the solvent was removed by reduced pressure. The resulting solids were redissolved in a minimum amount of water, and a solution of NH_4PF_6 was added until precipitation of the products started.

22: first fraction, was a dark yellow solid, yield 80 mg (19%); mp 180 °C dec; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.40 (d, $J = 6.4$ Hz, 2H, H2), 9.30 (d, $J = 6.5$ Hz, 2H, H2′), 8.81 (d, $J = 6.5$ Hz, 2H, H3), 8.76 (d, $J = 6.5$ Hz, 2H, H3′), 4.73 (t, $J = 7.0$ Hz, 2H, CH_2N), 4.44 (s, 3H, NCH_3), 3.28 (t, $J = 6.9$ Hz, 2H, CH_2I), 2.94 (t, $J = 6.9$ Hz, 2H, CH_2S), 2.88 (t, $J = 7.0$ Hz, 2H, CH_2S), 2.42 (s, 3H, SCH_3),2.41 (s, 3H, SCH_3), 2.08 (m, quintet), 2H, CH_2), 1.86 (m, quintet), 2H, CH_2), 1.63 (m, 4H, 2 × CH_2); PDMS: *m/z*: 769.1 calcd for $C_{27}H_{33}IN_2S_8$: 769.0. Anal. Calcd for $C_{27}H_{33}F_{12}IN_2P_2S_8·{}^1/_2CH_3NO_2$: C, 30.03; H, 3.23; N, 3.75. Found: C, 29.83; H, 3.38 ; N, 3.45. CV (MeCN) $E_{1/2} = -0.83$ V, -0.39 V, 0.53 V, 0.78 V.

23: second fraction, was a dark red/brown solid, yield 15 mg (3%); ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.36 (d, $J = 6.9$ Hz, 4H, H2), 9.27 (d, $J = 6.6$ Hz, 4H, H2′), 8.78 (d, $J = 6.6$ Hz, 4H, H3), 8.73 (d, $J = 6.7$ Hz, 4H, H3′), 4.70 (t, $J = 7.0$ Hz, 4H, CH_2N),4.43 (s, 6H, NCH_3), 2.93 (t, $J = 7.2$ Hz, 4H, CH_2S), 2.41 (s, 6H, SCH_3), 2.08 (m, quintet), 4H, CH_2), 1.63 (m, quintet), 4H, CH_2). CV (MeCN) $E_{1/2} = -0.84$ V, -0.39 V, 0.53 V, 0.78 V.

Compound 24. To a solution of **8a** (0.36 g, 0.5 mmol) in refluxing MeCN (40 mL) was added a solution of **17** (0.40 g, 1.3 mmol) in hot MeCN (40 mL) under nitrogen. The reaction mixture was refluxed for 6 d and then cooled (after 2 d a solid started to precipitate). The solvent was evaporated *in vacuo*, and the crude product was dissolved in MeCN (2 mL) and chromatographed (silica gel, MeOH:2 M NH_4Cl:$MeNO_2$ 5:2:1). The green band ($R_f = 0.3$), was collected and the solvent was removed by reduced pressure. The resulting solid was redissolved in a minimum amount of eluent, and a solution of NH_4PF_6 was added until the precipitation of the product started: yield 240 mg (35%) of **24** as a dark red/brown solid; ^{1}H-NMR (360 MHz, DMSO-d_6) δ 9.36 (d, $J = 6.8$ Hz, 4H, H2), 9.28 (d, $J = 6.7$ Hz, 4H, H2′), 8.79 (d, $J = 6.7$ Hz, 4H, H3), 8.74 (d, $J = 6.7$ Hz, 4H, H3′), 4.71 (t, $J = 7.2$ Hz, 4H, CH_2N), 4.43 (s, 6H, NCH_3), 2.92 (t, $J = 6.8$ Hz, 4H, CH_2S), 2.44 (s, 6H, SCH_3), 2.09 (m, 4H, CH_2CH_2N), 1.62 (m, 4H, CH_2CH_2S); ^{13}C-NMR (93 MHz, DMSO-d_6) δ 148.73, 148.23, 146.65, 145.82, 131.08, 130.31, 126.62, 126.11, 123.03, 122.37, 109.80, 109.45, 60.33, 48.11, 34.69, 29.54, 25.69, 18.56. Anal. Calcd for $C_{38}H_{44}F_{24}N_4P_4S_8$: C, 32.76; H, 3.18; N, 4.02. Found: C, 32.66; H, 3.29; N, 3.90. CV (MeCN) $E_{1/2} = -0.85$, -0.38, 0.53, 0.78 V.

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