Donor−Acceptor Macrocycles Incorporating Tetrathiafulvalene and Pyromellitic Diimide: Syntheses and Crystal Structures

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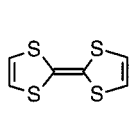
The Mitsunobu reaction is shown to be a versatile method for the incorporation of pyromellitic diimide (PMDI) acceptors into new macrocyclic structures containing tetrathiafulvalene (TTF) donors. In the case of macrocycle **5**, the more efficient bis-pyrroloTTF donor was used instead of TTF. Macrocycle **1** revealed distinct charge-transfer interactions in the *trans*-configuration, but not in the corresponding *cis*-form. Depending on the spatial geometry, *inter*- and *intra*molecular interactions between the TTF-donor and the PMDI-acceptor take place. X-ray crystal structures of macrocycles **1**-*cis*, **1**-*trans*, **2** and **5** are reported.

Introduction

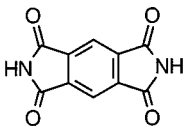
Molecular structures composed of covalently linked electron donor and acceptor moieties have received attention due to interesting optical or electrical properties. Several examples of this type of structure involve derivatives of tetrathiafulvalene (TTF) as the donor moiety.[1] On account of its electrochemical properties, TTF has been a key component in systems showing interesting properties for NLO materials, conducting, super- and semiconducting materials, molecular sensors and other applications in the area of molecular electronics.

Recently Cava et al.[2] reported the synthesis of a donor-acceptor system resembling the Aviram and Ratner proposal[3] that molecular rectification may be obtained in assemblies of molecules with the general structure donor-σ-acceptor in which σ represents a covalent, nonconjugated bridge.[1]

Excited-state, charge separation-, and energy transfer processes have been investigated in model systems for artificial photosynthesis in which the general structure is donor-spacer-acceptor. A number of examples incorporate a pyromellitic diimide (PMDI) moiety as the electron accepting part.[4] PMDI derivatives form alternating stacks with π-donors such as dialkoxynaphthalene.[5] The π-stacking interactions of donors and acceptors, both neutral and charged, have been used to template in the synthesis of supramolecular structures, e.g. catenanes.[6] For example, Sanders et al. have used templating due to the π-association of PMDI derivatives with donor macrocycles in the construction of neutral catenated structures showing *intra*molecular charge-transfer (CT) absorption.[7] It therefore seemed of interest to combine the donor abilities of TTF with the acceptor PMDI in a cyclophane structure.



TTF



PMDI

Covalently linking TTF and PMDI into macrocyclic structures that restrict their conformational mobility could provide us with an insight into the complementarity of the two units, hopefully indicating whether or not charge-transfer interactions are present in such systems. Recently, Moriarty and co-workers have reported the crystal structure of a TTF macrocycle containing a quinone moiety. The configuration of the TTF unit in this cyclophane is *cis* and the two planes containing the TTF and quinone moieties in the crystal are nonoverlapping (orthogonal), suggesting that any charge-transfer interaction present in the crystal is *inter*molecular.[8]

In this paper we present the synthesis of the TTF−PMDI macrocycles **1** and **2**, together with their crystal structures, as well as the synthesis of linear TTF−PMDI derivatives **3** and **4**. All compounds were synthesized using TTF derivatives containing aminoalkyl linkers. We also report the synthesis of macrocycle **5**, which contains a pyrroloTTF donor moiety and was synthesized by Mitsunobu alkylation of PMDI, a procedure also used for derivatives **1** and **2**.[9] Glycol chains were chosen as the linkers between the two moieties, providing flexibility and increased solubility.

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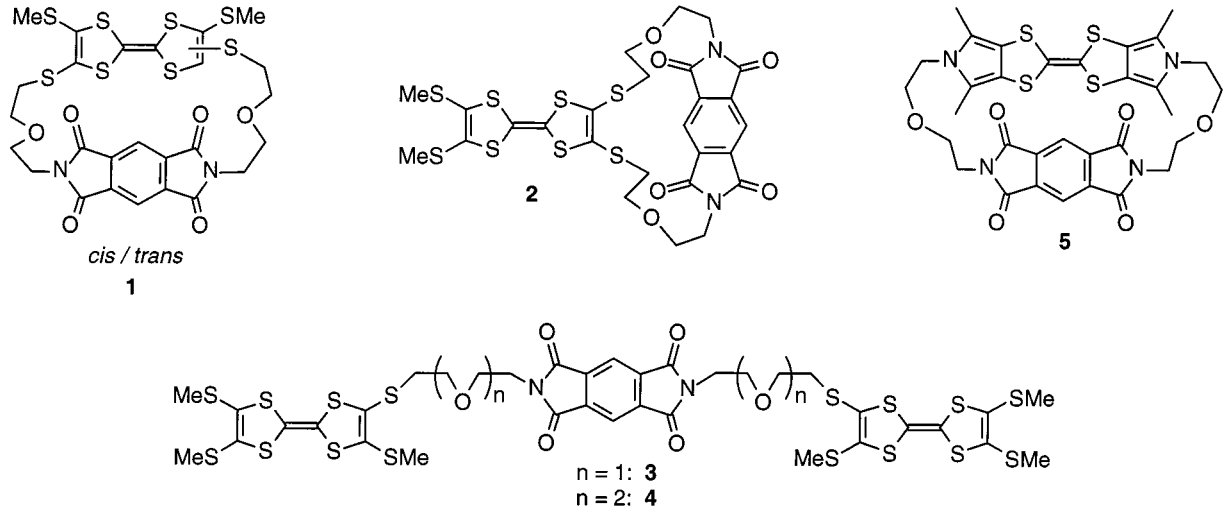
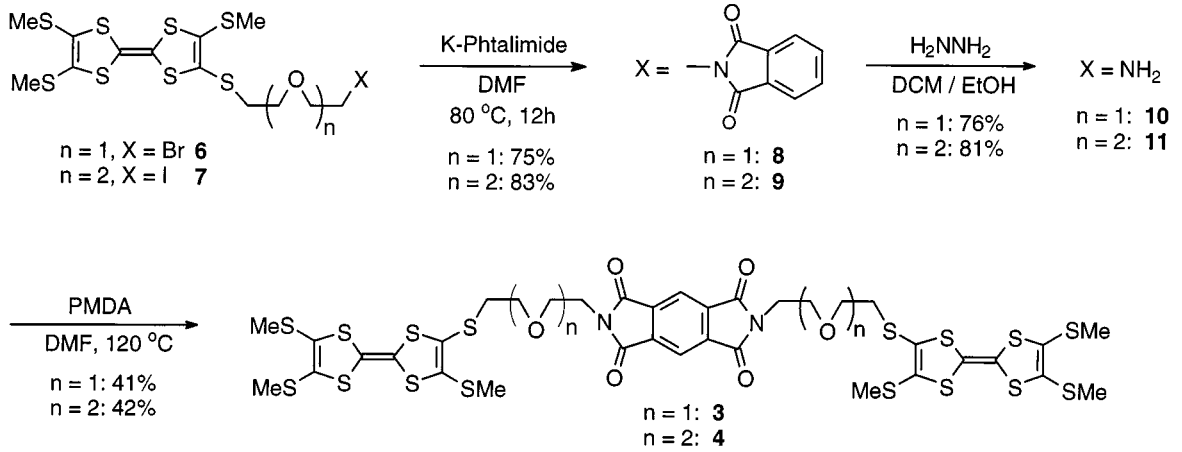


Synthesis

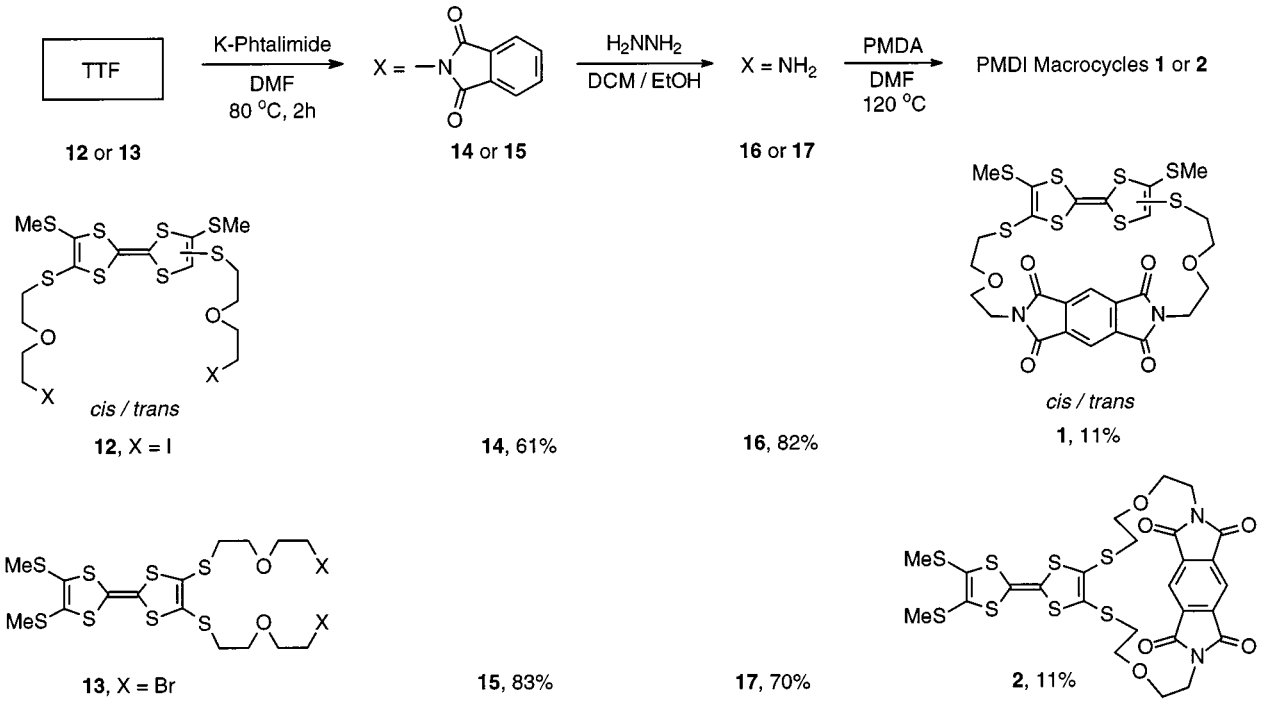
In order to synthesize donor/acceptor macrocycles containing TTF and PMDI moieties a simple ring closing strategy was chosen. A TTF-bisthiolate was reacted with a PMDI unit linked with a terminal leaving group, using the TTF-tetrathiolate (TTFTT) protection/deprotection protocol.[10] However, this method resulted in complete decomposition of the PMDI unit in the presence of the strong thiolate nucleophile. A different route to the macrocycles was therefore needed. The usual method for obtaining PMDI derivatives is the reaction of primary amines with pyromellitic dianhydride (PMDA).[11] It should therefore be possible to cyclize a TTF derivative, containing linkers with terminal amino groups, with pyromellitic dianhydride. This strategy was applied to the preparation of the linear derivatives **3** and **4** (Scheme 1).

TTF-amines **10** and **11** were prepared using the classic Gabriel transformation adapted from the reported literature procedure.[12] All TTF starting materials, **6**, **7**, **12**, **13**, **22**, and **23**, were prepared by the standard deprotection/alkylation method using a cyanoethyl-protected TTF. Thus iodo compounds **7** and **12** were obtained directly by alkylating with large excesses of bis(2-iodoethoxy)ethane or 2-(2-iodoethoxy)ethyl iodide, respectively, while the bromo compounds were obtained by alkylating with 2-(2-iodoethoxy)-ethanol with subsequent bromination using CBr_4/PPh_3 in CH_2Cl_2 solution. Reaction of **6** and **7** in DMF solution with potassium phthalimide gave the the phthalimide derivatives **8** and **9** in fair yields as viscous orange oils. Addition of H_2NNH_2 to a CH_2Cl_2/EtOH (1:1) solution of the phthalimide derivatives gave **10** and **11** as orange oils after column chromatography. Reacting the TTF-amines with PMDA in dry DMF at 120 °C overnight followed by chromatographic workup gave the linear TTF−PMDI derivatives **3** and **4** in moderate yields as greenish-brown glasses.

CPK models indicated that the short glycol linker should be long enough to reach across the TTF moiety, both in 2,7(6)- and in 2,3-substituted derivatives. Both the phthalimide- and the amine-forming reactions gave acceptable yields of the rather unstable TTF-amines. The macrocyclizations were performed by simple mixing of the intermediates. Thus, PMDA and TTF-amine **16** or **17** were dissolved in dry DMF under an atmosphere of dry N_2, and



Scheme 1. Synthesis of the linear TTF−PMDI derivatives **3** and **4**



Scheme 2. Synthesis of TTF–PMDI macrocycles **1** and **2** by TTF-amine formation

the reaction mixture was heated at 120 °C for 3 d. Chromatographic workup gave the desired macrocycles **1** and **2** in 11% yield only, probably reflecting instability of the TTF-amines (Scheme 2).

Cyclophane **2** crystallized as thin green needles whereas **1** crystallized (from toluene or $CHCl_3$/MeOH) in two different forms, orange and green needles, which could be separated mechanically.

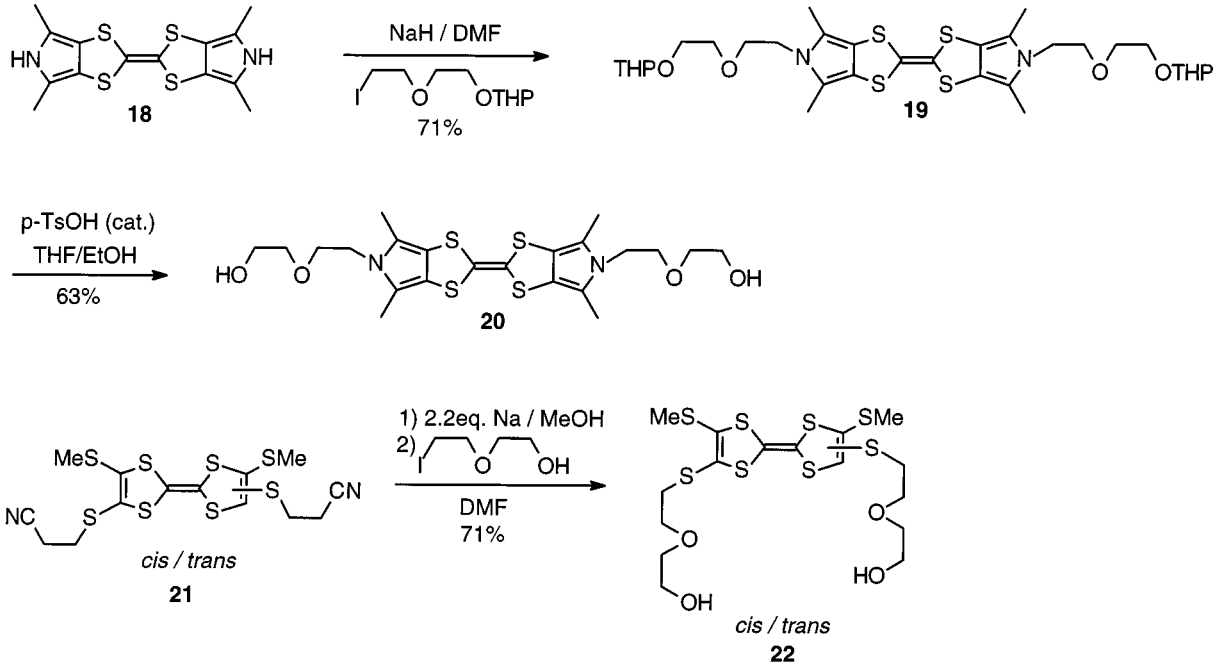
It is evident that the synthetic strategy described above is not versatile for macrocyclic TTF–PMDI compounds on account of the number of steps involved and the low yield in the final step. *N*-Alkylation of PMDI using Mitsunobu conditions has recently been reported.[13] Due to the low solubility of PMDI in THF, slow addition of a mixture of PPh_3, TTF-alcohol and PMDI to a stirred solution of Di-Ethyl AzoDicarboxylate (DEAD), in a large volume of solvent, was used. Thus cyclophanes **1** and **2** were obtained in a single step from TTF derivatives **22** and **23** in 39–52% yields. The low solubility of PMDI ensures that only a fraction is in solution, thus favouring *intra*molecular reaction. The synthesis of **5** was likewise performed using Mitsunobu alkylation. It should be noted that attempts to *N*-alkylate the pyrroloTTF with a PMDI derivative containing a terminal leaving group, failed due to the instability of the PMDI unit in the presence of nucleophiles. Therefore, the synthesis of the pyrroloTTF precursor was achieved by *N*-alkylation of pyrroloTTF **18**[14] with THP-protected 2-(2-iodoethoxy)ethanol and NaH, followed by subsequent removal of the THP group (Scheme 3). The final Mitsunobu ring closing step is shown in Scheme 4.

Electrochemistry and UV/Vis Absorption

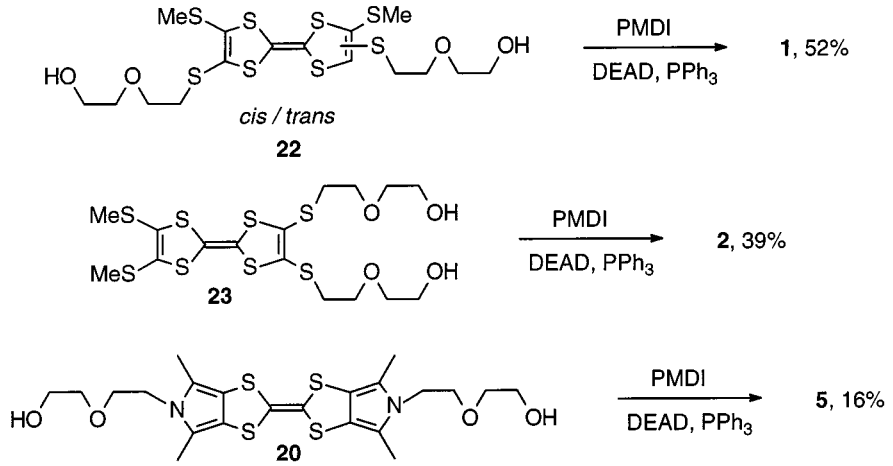
Charge-transfer interactions are often recognized as characteristic absorptions in the visible or the near-infrared area, absorptions different from those of the respective donor and acceptor moieties. Charge-transfer also affects the potentials of the redox active components in the compounds. However, weak CT interactions are generally not expected to affect the redox potentials given by cyclic voltammetry on account of the relatively insensitive nature of this technique.[15]

For the linear compounds **3** and **4** only small shoulders to the TTF absorption are seen in the UV/Vis spectrum at about 590 nm. Cyclic voltammetry studies showed that the potentials of the TTF units are virtually unchanged and thus that charge-transfer interactions are negligible, if present at all (Table 1).

The cyclic structure **2** also revealed a small shoulder due to the TTF-absorption and furthermore the redox potentials were not increased significantly. This is in accordance with the observed crystal structure, where the PMDI moiety is too short to reach entirely across the TTF core. In contrast to this, an equilibrium mixture of macrocycle **1** shows a distinct charge-transfer absorption at 590 nm (ε = 110 $M^{-1}cm^{-1}$, Figure 1). This value is comparable to values reported by Sanders et al.[7] It is important to note that only the *trans* isomer gives rise to *intra*molecular charge-transfer interactions. The ^{1}H-NMR signal from the PMDI protons is present as two singlets separated by about 0.06 ppm. It was possible, by mechanical separation, to isolate a batch of the almost pure *cis* isomer, which by NMR was seen to contain approximately 10% of the *trans* isomer.



Scheme 3. Synthesis of TTF and pyrroloTTF derivatives with terminal hydroxy functionalities



Scheme 4. Ring closure reactions toward macrocycles **1**, **2** and **5** under Mitsunobu conditions

Table 1. Electrochemical data. Potentials were measured against Ag/AgCl in DCM with Bu_4NPF_6 (0.1 M) as a supporting electrolyte

Compound	**1** *c*/*t*	**22**	**2**	**23**	**5**	**20**	**3**	**4**	**7**
$E^1_{1/2}$/V	0.54	0.52	0.51	0.53	0.30	0.30	0.51	0.51	0.53
$E^2_{1/2}$/V	0.89	0.80	0.86	0.80	0.82	0.80	0.85	0.84	0.84

This solution showed a broad shoulder to the TTF absorption in the UV/Vis region. The solution was allowed to stand for 48 h in the light, during which time isomerisation took place. The UV/Vis absorbance was measured once again, revealing this time a distinct charge-transfer band at 590 nm ($\varepsilon = 110\ M^{-1}\ cm^{-1}$). NMR of this solution revealed a *cis*/*trans* ratio of approximately 1:1. This indicates that the major contribution to the CT absorption arises from the *trans* isomer as a result of *intra*molecular interaction.

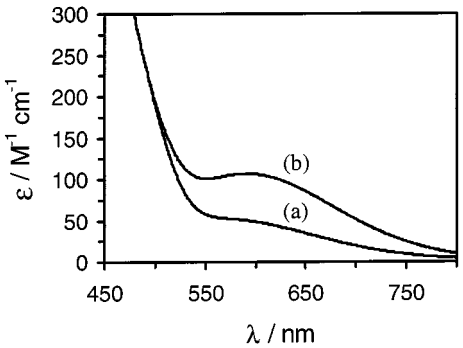


Figure 1. UV/Vis absorption spectrum of **1**: (a) 9:1 *cis*/*trans* mixture and (b) 1:1 *cis*/*trans* mixture, both in DCM

The potentials of the TTF unit showed significant increases by about 20mV for the first potential and 90mV for the second. In contrast, the macrocycle **5**, with the stronger

pyrroloTTF donor, showed no marked CT interaction in the UV/Vis spectra.

X-ray Crystal Structures

The crystal and molecular structures of **1**-*cis*, **1**-*trans*, **2** and **5** were determined by X-ray diffraction. The molecular structures of **1**-*cis* and **1**-*trans* are depicted in Figure 2 and 3. In both structures the plane of the central TTF part (defined by S1, S2, S3, S4, C1 and C2) is almost parallel to the plane of the PMDI moiety, but there are pronounced differences in other parts. Compound **1**-*cis* has an extended conformation where the glycol linkers are stretched out, a situation that leads to an interplanar distance of about 6.9 Å. This conformation provides room for a toluene guest molecule in the middle of the macrocycle. The guest molecule is fairly parallel to the planes mentioned above. In **1**-*trans* the macrocycle has a compressed conformation where the two planes are separated by a distance of about 3.45 Å, leaving no room for a solvent molecule. In **1**-*cis* the two methyl groups point away from the TTF plane on the exterior of the macrocycle. In **1**-*trans* these methyl groups also point away from the TTF plane, but in this case towards the interior of the macrocycle. In both structures the TTF moieties are somewhat concave, having the four outer C atoms on the same side of the central plane. In **1**-*cis* the TTF is more bent, with C3, C4, C5 and C6 at distances of 0.30−0.45 Å from the plane defined by the fulvene part, whereas in **1**-*trans* C3, C4, C24, C25 have deviations of only 0.02−0.17 Å from this plane. The proximity of TTF and PMDI in **1**-*trans* favours an *intra*molecular4 charge-transfer. In **1**-*cis* *intra*molecular charge-transfer is not possible for geometric reasons, and *inter*molecular charge-transfer is hardly possible either because the stacking sequence in the crystal packing is PMDI−TTF...TTF−PMDI..., i.e. donors and acceptors are not directly in contact. In **1**-*trans*, on the other hand, some *inter*molecular charge-transfer may be present as well, since the stacking is TTF−PMDI...TTF−PMDI...etc. The interplanar distances between molecules are about as short as the distance within molecules, but some transverse translation makes the overlap smaller. In neither of these two structures do short *inter*molecular contacts such as hydrogen bonds seem to be present.[16]

The structure of **2** is presented in Figure 4. There are two independent but very similar molecules. Again the TTF plane and the PMDI plane are close to parallel, and the interplanar distance is about 3.5 Å. However, in this struc-

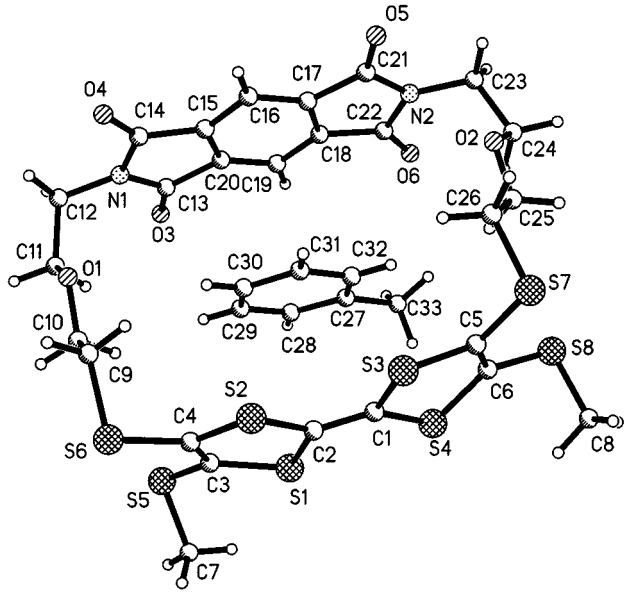


Figure 2. Crystal structure of **1**-*cis*

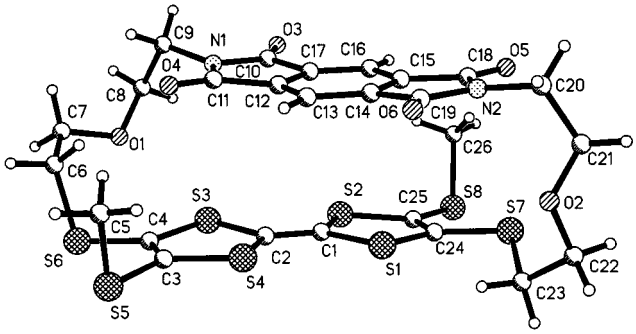


Figure 3. Crystal structure of **1**-*trans*

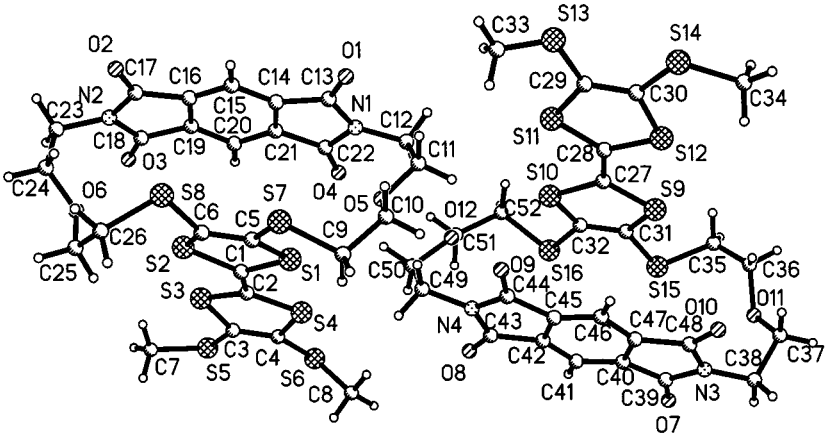


Figure 4. Crystal structure of **2**

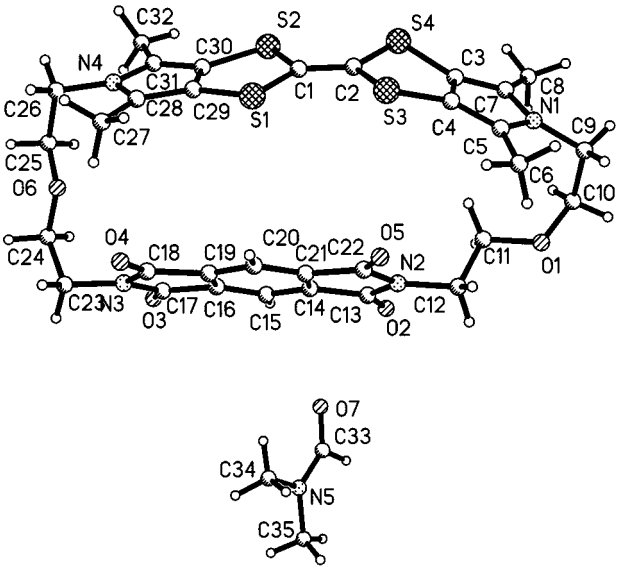


Figure 5. Crystal structure of **5**

ture the two parts only overlap between the centre ring of PMDI and one end of TTF, thus allowing little *intra*molecular charge-transfer. In the crystal packing there appear to be conditions suitable for some *inter*molecular charge-transfer, since pairs of rather parallel PMDI and TTF parts, separated by about 3.5 Å, connect neighbouring molecules. This is corroborated by a rather small deviation from planarity of TTF units and by the dark color of the crystals.

Figure 5 shows the molecular structure of **5**. In this case the central TTF part of the pyrroloTTF moiety and the PMDI moiety make an interplanar angle of 43° although their long axes are parallel. This structure does not exclude *intra*molecular charge-transfer, although it may only be marginal. However, the crystal packing favours some *inter*-molecular charge-transfer by allowing donor-acceptor contacts similar to those observed in **1**-*trans* and **2**, again in good accordance with the dark colour of the crystals. The TTF-group in **5** is rather bent with C3 and C4 about 0.6 Å out of the average central plane. In this structure one DMF guest molecule is incorporated per macrocycle molecule. However, no H-bond interactions are observed in the latter two structures.

Conclusions and Outlook

We have demonstrated the Mitsunobu reaction to be a versatile method of incorporating PMDI moieties into macrocyclic structures containing TTF-donors. Macrocycle **1** showed distinct charge-transfer interactions in the *trans* configuration but not in the *cis* form. Depending on the spatial geometry, weak *inter*- and *intra*molecular interactions between TTF and the electron deficient PMDI unit take place. This interaction may be utilized for the design of more elaborate systems such as catenanes through a synthesis based on molecular recognition between donors and acceptors.

Experimental Section

General: DMF was dried by standing over 4A molecular sieves for at least 3 d and used without distillation. Acetone was dried by standing over $CaSO_4$ (Drierite) for 2 d prior to use, MeOH was distilled over magnesium turnings and stored over 4A molecular sieves. Toluene was dried and stored over sodium wire and was used without distillation. THF was distilled from sodium/benzophenone. All other solvents and chemicals were used without further purification. − Melting points were measured on a Büchi melting point apparatus and are uncorrected. − Analytical TLC was performed on Merck DC-Alufolien Kiselgel 60 F_{254} on 0.2 mm aluminum sheets or on Polygram Alox N/UV_{254} Alumina on 0.2 mm plastic sheets. − Column chromatography was performed using Merck Kieselgel 60 (0.040−0.063 mm, 230−400 mesh). Deactivation of silica was accomplished by stirring with 5% Et_3N in DCM for 10 min after which time it was filtered off, washed with DCM and dried. − ^{1}H NMR spectra were recorded on a Varian Gemini 300 MHz or a Bruker AC250 250 MHz apparatus and used TMS as the internal standard. − ^{13}C-NMR spectra were recorded using nondeuturated solvent residue as an internal standard. Chemical shift values are measured in ppm. The following abbreviations are used in quoting NMR-data: s = singlet, bs = broad singlet, d = doublet, t = triplet, dt = doublet of triplets, dd = doublet of doublets, arom. = aromatic. − Plasma Desorption Mass Spectra (PDMS) were recorded on a Bio-Ion 20R time-of-flight instrument. − Electron Impact (EI) mass spectra were recorded on a Varian MAT 311A triple quadropole instrument and Fast Atom Bombardment (FAB) mass spectra were recorded on a Kratos MS 50 TC instrument. − IR absorption spectra were recorded on a Perkin−Elmer 1720 Infrared Fourier Transform Spectrometer. − UV/Vis absorption spectra were recorded on a Shimadzu UV160A or a UV3100 instrument. − Cyclic Voltammetry (CV) was performed using an ECO Chemie, PGSTAT10 potentiostat, with a Pt disc working electrode, a Pt wire as counter electrode and Ag/AgCl as reference electrode. The voltammograms were recorded in DCM with Bu_4NPF_6 (0.1 M) as supporting electrolyte with a scan rate of 100mV/s. − Elemental analyses were carried out by the Microanalytical Laboratory, University of Copenhagen or Atlantic Microlab, Inc., Norcross Georgia, USA.

Compounds 1 and 2. − Procedures for Ring Closure. − Method A, Imide Formation: The procedure is analogous to that for the linear compounds **3** and **4** with equimolar amounts of reactants.

Method B: Mitsunobu reaction. TTF-dialcohol **22** (248 mg, 0.46 mmol) or **23** (248 mg, 0.46 mmol), PMDI (100 mg, 0.46 mmol) and PPh_3 (366 mg, 1.40 mmol) were dissolved in either dry dioxane or dry THF (200 mL) and the resulting solution was added to a solution of DEAD (252 mg, 1.45 mmol) in the same solvent over 3 h. The reaction mixture was then allowed to stand overnight after which time the solvent was removed in vacuo. Column chromatography (silica, DCM/EtOAc, 19:1) gave the products as green powders.

Tetrathiafulvalene 1, *cis/trans*: Yield: 0.17 g (0.24 mmol, 52%), m.p. >240 °C. Recrystallization from toluene or $CHCl_3$/MeOH gave a mixture of orange and green crystals. ^{1}H NMR ($CDCl_3$): δ = 2.39, 2.40 (2 × s, 6 H, SC**H**$_3$), 2.85 (2 × t, 4 H, *J* = 7.2 Hz, SC**H**$_2$), 3.51

(t, 4 H, *J* = 7.2 Hz, C**H**$_2$O), 3.71 (t, 4 H, *J* = 4.9 Hz, C**H**$_2$O), 3.97 (t, 4 H, *J* = 4.9 Hz, NC**H**$_2$), 8.27, 8.33 (2 × s, 2 H, Arom. **H**, c/t mixture). − ^{13}C NMR ($CDCl_3$): δ = 18.95, 19.04 (S**C**H$_3$), 35.34, 35.91, 38.34, 38.73 (S**C**H$_2$, N**C**H$_2$), 67.37, 67.69, 69.78, 71.20 (**C**H$_2$O), 110.88, 111.52 (Fulvene **C**=**C**), 118.42, 118.62 (Arom. **C**−**H**), 123.35, 123.92 (TTF cyclic **C**=**C**), 131.64, 132.89 (TTF cyclic **C**=**C**), 137.26, 137.29 (Arom. **C**−**C**=O), 166.24, 166.35 (**C**=O). − MS (EI); *m*/*z* (%): 716 (M, 100), 256 (10), 223 (10), 173 (14), 91 (13). − Calcd. for $C_{26}H_{24}N_2O_6S_8$ (716.97): C 43.56, H 3.37, N 3.91, S 35.77. Found: C 43.60, H 3.44, N 3.81, S 35.61.

Tetrathiafulvalene 2: Yield 0.13 g (0.18 mmol, 39%), m.p. >240 °C. Recrystallization from toluene or $CHCl_3$/MeOH gave green needles. ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 6 H, SC**H**$_3$), 2.87 (t, 4 H, *J* = 5.2 Hz, SC**H**$_2$), 3.61 (t, 4 H, *J* = 5.2 Hz, C**H**$_2$O), 3.81 (t, 4 H, *J* = 5.2 Hz, C**H**$_2$O), 4.00 (t, 4 H, *J* = 5.2 Hz, NC**H**$_2$), 8.28 (s, 2 H, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 19.08 (S**C**H$_2$), 36.01, 38.07 (S**C**H$_2$, N**C**H$_2$), 66.54, 69.81 (**C**H$_2$O), 109.38, 109.81 (Fulvene **C**=**C**), 118.40 (Arom. **C**−H), 122.10, 127.55 (TTF cyclic **C**=**C**), 137.52 (Arom. **C**−**C**=O), 166.88 (**C**=O). − MS (EI); *m*/*z*: 716 (M, 100), 313 (53), 256 (49), 238 (56), 173 (66), 118 (64), 91 (78), 76 (57). − Calcd. for $C_{26}H_{24}N_2O_6S_8$ (716.97): C 43.56, H 3.37, N 3.91. Found: C 43.36, H 3.30, N 3.79

Compounds 3 and 4. − General Procedure for Imide Formation

2,6-Bis{2,3,6-tris(methylthio)tetrathiafulvalen-7-yl-[2-(2-(2-thioethoxy)ethoxy)ethyl]}pyrrolo[3,4-*f*]isoindole-1,3,5,7-tetraone (4): TTF **11** (0.56 g, 1.10 mmol) and PMDA (0.12 g, 0.55 mmol) were dissolved in dry DMF (10 mL) containing 4 Å molecular sieves. The reaction mixture was kept under an atmosphere of nitrogen at 120 °C overnight. It was then filtered using celite, which was then rinsed with $CHCl_3$. The solvent was removed from the filtrate in vacuo. Column chromatography (silica, DCM/EtOAc, 19:1) gave the product **4** (0.28 g, 0.23 mmol, 42%) as a greenish/brown glass.

^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 18 H, SC**H**$_3$), 2.93 (t, 4 H, *J* = 6.6 Hz, SC**H**$_2$), 3.62 (m, 12 H, C**H**$_2$O), 3.79 (t, 4 H, *J* = 5.6 Hz, C**H**$_2$O), 3.96 (t, 4 H, *J* = 5.6 Hz, NC**H**$_2$), 8.27 (s, 2 H, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 18.95, 19.05 (S**C**H$_3$), 35.39, 37.86 (S**C**H$_2$, N**C**H$_2$), 67.72, 69.93, 69.99, 70.46 (**C**H$_2$O), 110.67, 110.80 (Fulvene **C**=**C**), 118.26 (Arom. **C**−**H**), 124.36, 130.84 (TTF cyclic **C**=**C**), 127.37, 127.64 (TTF cyclic **C**=**C**), 137.28 (Arom. **C**−**C**=O), 166.24 (C=O). MS(PDMS); *m*/*z*: 1193.9 (M). − Calcd. for $C_{40}H_{44}N_2O_8S_{16}$ (1193.76): C 40.25, H 3.71, N 2.35, S 42.97. Found: C 40.06, H 3.68, N 2.38, S 42.90.

2,6-Bis{2,3,6-tris(methylthio)tetrathiafulvalene-7-yl-[2-(2-thioethoxy)ethyl]}pyrrolo[3,4-*f*]isoindole-1,3,5,7-tetraone (3): The product is a greenish/brown glass. Yield: 41%. ^{1}H NMR ($CDCl_3$): δ = 2.39, 2.42 (2 × s, 18 H, SC**H**$_3$), 2.91 (t, 4 H, *J* = 6.2 Hz, SC**H**$_2$), 3.64 (t, 4 H, *J* = 6.2 Hz, C**H**$_2$O), 3.76 (t, 4 H, *J* = 5.5 Hz, C**H**$_2$O), 3.96 (t, 4 H, *J* = 5.5 Hz, NC**H**$_2$), 8.27 (s, 2 H, Arom. C−H). − ^{13}C NMR ($CDCl_3$): δ = 18.89, 19.02, 19.04 (S**C**H$_3$), 35.46, 37.95 (S**C**H$_2$, N**C**H$_2$), 67.42, 69.19 (**C**H$_2$O), 110.50, 110.94 (Fulvene **C**=**C**), 118.29 (Arom. **C**−**H**), 123.72, 131.22 (TTF cyclic **C**=**C**), 127.35, 127.55 (TTF cyclic **C**=**C**), 137.27 (Arom. **C**−**C**), 166.29 (**C**=O). MS(PDMS); *m*/*z*: 1105.4 (M). − Calcd. for $C_{36}H_{36}N_2O_6S_{16}$ (1105.65): C 39.11, H 3.28, N 2.53, S 46.39. Found: C 39.31, H 3.39, N 2.53, S 46.48.

Tetrathiafulvalene 5: PyrroloTTF **20** (238 mg, 0.48 mmol), PMDI (100 mg, 0.46 mmol) and PPh_3 (241 mg, 0.92 mmol) were dissolved in dry THF (150 mL) and kept under argon. DEAD (160 mg, 0.92 mmol) was added by syringe and the reaction mixture was stirred overnight. Concentration in vacuo and column chromatography (silica, deactivated with 5% Et_3N in DCM, DCM/EtOAc, 19:1) afforded **5** as a dark solid. Yield: 27.8 mg (0.04 mmol, 17%). − ^{1}H NMR ([D$_7$]DMF): δ = 2.19 (s, 12 H, pyrrole−C**H**$_3$), 3.40 (t, 4 H, *J* = 5.5 Hz, C**H**$_2$O), 3.62 (t, 4 H, *J* = 4.6 Hz, C**H**$_2$O), 3.79 (t, 4 H, *J* = 5.7 Hz, PMDI−NC**H**$_2$), 4.02 (t, 4 H, *J* = 4.6 Hz, Pyrrole−NC**H**$_2$), 8.19 (s, 2 H, PMDI-Arom. C−H). − ^{13}C NMR (DMF-d$_7$): δ = 11.64 (pyrrole−CH$_3$), 38.42, 38.72 (PMDI−N**C**H$_2$), 44.88 (pyrrole−N**C**H$_2$), 68.45, 70.18 (**C**H$_2$O), 107.27, 113.81, 117.38 (pyrrole−C and TTF core), 119.63 (PMDI Arom. **C**−**H**), 137.24 (PMDI Arom. **C**−**C**), 165.97 (**C**=O). − MS (EI); *m*/*z* (%): 696 (M + 2, 23), 694 (M, 100), 347 (13), 226 (4), 182 (6).

Compound 14. − General Procedure for Phthalimide Formation

2,7(6)-Bis(methylthio)-3,6(7)-bis[2-(2-phthalimidoethoxy)ethylthio]-tetrathiafulvalene (14): TTF-halogen compound **12**, X = I, (8.25 g, 10.90 mmol) and potassium phthalimide (4 equiv., 8.08 g, 43.6 mmol) was dissolved in DMF (200 mL) and stirred at 80 °C overnight under an atmosphere of dry N_2. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue was redissolved in DCM and washed with water, dried ($MgSO_4$) and subjected to column chromatography (silica, DCM/EtOAc, 49:1). The product (5.28 g, 6.64 mmol, 61%) was obtained as a thick red oil that solidified on standing. ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 6 H, SC**H**$_3$), 2.93 (t, 4 H, *J* = 6.5 Hz, SC**H**$_2$), 3.65 (t, 4 H, *J* = 6.3 Hz, OC**H**$_2$CH$_2$S), 3.73 (t, 4 H, *J* = 5.6 Hz, C**H**$_2$O), 3.90 (t, 4 H, *J* = 5.7 Hz, NC**H**$_2$), 7.14 (dd, 4 H, *J* = 3.2 Hz, 5.7 Hz, Arom. **H**), 8.85 (dd, 4 H, *J* = 2.9 Hz, 5.5 Hz, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 18.92 (S**C**H$_3$), 35.35, 37.20 (S**C**H$_2$, N**C**H$_2$), 67.75, 69.18 (**C**H$_2$O), 110.64, 110.68 (Fulvene **C**=**C**), 123.29, 133.98 (Arom. **C**−**H**), 123.96, 124.29, 130.96, 131.25 (TTF cyclic **C**=**C**), 132.15 (Arom. **C**−**C**), 168.34 (**C**=O). − MS (EI); *m*/*z* (%): 794 (M, 100), 576 (12), 441 (15), 174 (79), 130 (30). − Calcd. for $C_{32}H_{30}N_2O_6S_8$ (795.08): C 48.34, H 3.80, N 3.52, S 32.26. Found: C 48.30, H 3.84, N 3.58, S 32.10.

2,3-Bis(methylthio)-6,7-bis[2-(2-phthalimidoethoxy)ethylthio]-tetrathiafulvalene (15): The product was recrystallized from toluene/hexanes to give brown crystals, m.p. 134−135 °C. Yield: 83%. ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 6 H, SC**H**$_3$), 2.91 (t, 4 H, *J* = 6.5 Hz, SC**H**$_2$), 3.63 (t, 4 H, *J* = 6.6 Hz, C**H**$_2$O), 3.72 (t, 4 H, *J* = 5.6 Hz, C**H**$_2$O), 3.89 (t, 4 H, *J* = 5.5 Hz, NC**H**$_2$), 7.70 (dd, 4 H, *J* = 3.1 Hz, 5.3 Hz, Arom. **H**), 7.84 (dd, 4 H, *J* = 3.1 Hz, 5.5 Hz, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 19.02 (S**C**H$_3$), 35.24, 37.17 (S**C**H$_2$, N**C**H$_2$), 67.69, 69.20 (**C**H$_2$O), 110.64, 110.82 (Fulvene **C**=**C**), 123.28, 133.96 (Arom. **C**−**H**), 127.42, 127.77 (TTF cyclic **C**=**C**), 132.12 (Arom. **C**−**C**), 168.29 (**C**=O). − MS (EI); *m*/*z* (%): 794 (M, 6), 359 (3), 174 (100), 76 (35). − Calcd. for $C_{32}H_{30}N_2O_6S_8$ (795.08): C 48.34, H 3.80 N 3.52, S 32.26. Found: C 48.40, H 3.80, N 3.52, S 32.40.

2,3,6-Tris(methylthio)-7-[2-(2-phthalimidoethoxy)ethylthio]-tetrathiafulvalene (8): Chromatography [silica, DCM/petroleum ether (bp. 60−80 °C), 9:1] gave an orange oil that solidified on standing, m.p. 91−92 °C. Yield: 75%. ^{1}H NMR ($CDCl_3$): δ = 2.40, 2.43 (2 × s, 9 H, SC**H**$_3$), 2.93 (t, 2 H, *J* = 6.5 Hz, SC**H**$_2$), 3.66 (t, 2 H, *J* = 6.6 Hz, C**H**$_2$O), 3.74 (t, 2 H, *J* = 5.6 Hz, NC**H**$_2$), 3.91 (t, 2 H, *J* = 5.4 Hz, NC**H**$_2$), 7.72 (m, 2 H, Arom. **H**), 7.86 (m, 2 H, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 18.94, 19.06 (S**C**H$_3$), 35.32, 37.21 (S**C**H$_2$, N**C**H$_2$), 67.76, 69.22 (**C**H$_2$O), 110.85 (Fulvene **C**=**C**), 123.30, 133.98 (Arom. **C**−**H**), 124.17, 131.13 (TTF cyclic **C**=**C**), 127.31, 127.65 (TTF cyclic **C**=**C**), 132.16 (Arom. **C**−**C**), 168.34 (**C**=O). − MS (EI); *m*/*z* (%): 591 (M, 100), 373 (16), 238 (36), 174 (34), 147 (30), 104 (37), 44 (49).

2,3,6-Tris(methylthio)-7-{2-[2-(2-phthalimidoethoxy)ethoxy]-ethylthio}tetrathiafulvalene (9): Chromatographic workup [silica, DCM/petroleum ether (bp. 60−80 °C), 9:1] gave the product as an orange oil. Yield: 83%. ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 9 H, SC**H**$_3$), 2.92 (t, 2 H, *J* = 6.7 Hz, SC**H**$_2$), 3.59−3.65 (m, 6 H, C**H**$_2$O), 3.75 (t, 2 H, *J* = 5.6 Hz, C**H**$_2$O), 3.90 (t, 2 H, *J* = 5.5 Hz, NC**H**$_2$), 7.71 (dd, 2 H, *J* = 3.1 Hz, 5.5 Hz, Arom. **H**), 7.85 (dd, 2 H, *J* = 3.1 Hz, 5.5 Hz, Arom. **H**). − ^{13}C NMR ($CDCl_3$): δ = 19.05 (S**C**H$_3$), 35.26, 37.12 (S**C**H$_2$, N**C**H$_2$), 67.91, 69.93, 70.42 (O**C**H$_2$), 110.80, 110.87 (Fulvene **C**=**C**), 123.26, 133.98 (Arom. **C**), 124.62, 130.74 (TTF cyclic **C**=**C**), 127.39, 127.65 (TTF cyclic **C**=**C**), 132.18 (Arom. **C**−**C**=O), 168.34 (**C**=O). − MS (EI); *m*/*z* (%): 635 (M, 100), 388 (17), 373 (19), 238 (36), 174 (48). − Calcd. for $C_{23}H_{25}NO_4S_8$ (635.93): C 43.44, H 3.96, N 2.20. Found: C 43.44, H 4.05, N 2.22.

Compound 16. General Procedure for Amine Liberation

3,6(7)-Bis[2-(2-aminoethoxy)ethylthio]-2,7(6)-bis(methylthio)tetrathiafulvalene (16):

TTF−Phthalimide **14** (1.67 g, 2.10 mmol) was dissolved in a mixture of DCM/EtOH (1:1) and $H_2NNH_2XH_2O$ (0.82 mL, 80% aq. sol., 21 mmol) was added under N_2. The reaction mixture was refluxed for 5 h, cooled to room temperature and the precipitated phthalhydrazide was filtered off. The solvent was evaporated and the residue was subjected to column chromatography (deactivated silica, first DCM/MeOH, 9:1, then further addition of 3% Et_3N) to give the product (0.92 g, 1.72 mmol, 82%) as an orange oil. ^{1}H NMR ($CDCl_3$): δ = 1.65 (s, 4 H, N**H**$_2$), 2.44 (s, 6 H, SC**H**$_3$), 2.87 (t, 4 H, *J* = 5.1 Hz, SC**H**$_2$), 3.01 (t, 4 H, *J* = 6.5 Hz, NC**H**$_2$), 3.53 (t, 4 H, *J* = 5.1 Hz, C**H**$_2$O), 3.67 (t. 4 H, *J* = 6.5 Hz, C**H**$_2$O). − ^{13}C NMR ($CDCl_3$): δ = 18.99 (S**C**H$_3$), 35.47 (S**C**H$_2$), 41.44 (**C**H$_2$N), 69.58, 72.53 (**C**H$_2$O), 110.77 (Fulvene **C**=**C**), 124.42, 130.88 (Cyclic **C**=**C**). − MS (EI); *m*/*z* (%): 535 (M, 8), 311 (3), 225 (3), 120 (13).

6,7-Bis[2-(2-aminoethoxy)ethylthio]-2,3-bis(methylthio)tetrathiafulvalene (17): Orange oil. Yield: 70%. ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 4 H, N**H**$_2$), 2.40 (s, 6 H, SC**H**$_3$), 2.84 (t, 4 H, *J* = 5.2 Hz, SC**H**$_2$), 3.00 (t, 4 H, *J* = 6.5 Hz, NC**H**$_2$), 3.48 (t, 4 H, *J* = 5.2 Hz, C**H**$_2$O), 3.63 (t, 4 H, *J* = 6.5 Hz, C**H**$_2$O). − ^{13}C NMR ($CDCl_3$): δ = 19.03 (S**C**H$_3$), 35.56 (S**C**H$_2$), 41.69 (N**C**H$_2$), 69.54, 73.18 (**C**H$_2$O), 110.41, 111.06 (Fulvene **C**=**C**), 127.50, 127.94 (TTF cyclic **C**=**C**). − MS (EI); *m*/*z* (%): 534 (M, 100), 359 (14), 238 (25), 118 (15), 88 (20). − Calcd. for $C_{16}H_{26}N_2O_2S_8$ (534.87): C 35.93, H 4.90, N 5.24, S 47.95. Found: C 36.09, H 4.92, N 5.18, S 47.78.

7-[2-(2-Aminoethoxy)ethylthio]-2,3,6-tris(methylthio)tetrathiafulvalene (10): Orange oil. Yield 76%. ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 2 H, N**H**$_2$), 2.43, 2.44 (2 × s, 9 H, SC**H**$_3$), 2.88 (t, 2 H, *J* = 5.2 Hz, SC**H**$_2$), 3.01 (t, 2 H, *J* = 6.5 Hz, NC**H**$_2$), 3.51 (t, 2 H, *J* = 5.2 Hz, C**H**$_2$O), 3.66 (t, 2 H, *J* = 6.5 Hz, C**H**$_2$O). − ^{13}C NMR ($CDCl_3$): δ = 19.02 (S**C**H$_3$), 35.49 (S**C**H$_2$), 41.63 (N**C**H$_2$), 69.53, 72.99 (**C**H$_2$O), 110.70, 110.97 (Fulvene **C**=**C**), 124.39, 130.87 (TTF cyclic **C**=**C**), 127.43, 127.54 (TTF cyclic **C**=**C**). − MS (EI); *m*/*z* (%): 461 (M, 100), 373 (11), 238 (28). − Calcd. for $C_{13}H_{19}NOS_8$ (461.78): C 33.81, H 4.15, N 3.03. Found: C 33.88, H 4.00, N 2.98.

7-{2-[2-(2-Aminoethoxy)ethoxy]ethylthio}-2,3,6-tris(methylthio)-tetrathiafulvalene (11): Orange oil. Yield 81%. ^{1}H NMR ($CDCl_3$): δ = 1.70 (s, 2 H, N**H**$_2$), 2.43 (s, 9 H, SC**H**$_3$), 2.87 (t, 2 H, *J* = 5.2 Hz, SC**H**$_2$), 3.01 (t, 2 H, *J* = 6.6 Hz, NC**H**$_2$), 3.52 (t, 2 H, *J* = 5.2 Hz, C**H**$_2$O), 3.65 (m, 6 H, C**H**$_2$O). − ^{13}C NMR ($CDCl_3$): δ = 18.94, 19.01 (S**C**H$_3$), 35.26 (S**C**H$_2$), 41.62 (N**C**H$_2$), 69.95, 70.18, 70.40, 73.39 (**C**H$_2$O), 110.74, 110.90 (Fulvene **C**=**C**), 124.44, 130.84 (TTF cyclic **C**=**C**), 127.40, 127.56 (TTF cyclic **C**=**C**). − MS (EI); *m*/*z* (%): 505 (M, 100), 373 (15), 238 (37), 223 (19), 118 (23), 91 (26). − Calcd. for $C_{15}H_{23}NO_2S_8$ (505.83): C 35.62, H 4.58, N 2.77, S 50.70. Found: C 35.88, H 4.62, N 2.78, S 50.50.

Tetrathiafulvalene 19: PyrroloTTF **18** (800 mg, 2.36 mmol) was dissolved in dry, degassed DMF (100 mL). The solution was cooled in an ice bath and NaH (566 mg, 60% dispersion in mineral oil, 14.2 mmol) was added over 5 min. The mixture was stirred for 10 min and THP-protected 2-(2-iodoethoxy)ethanol (2.83 g, 9.44 mmol) was added. The ice bath was removed and stirring was continued at room temperature for 3 h. The mixture was cooled once more. MeOH (5 mL) was carefully added to destroy excess NaH and the solution concentrated to approximately 25 mL and poured onto brine/ice (100 mL). The mixture was transferred to a separating funnel and extracted with DCM (2 × 100 mL). The combined organic phases were washed with water (3 × 100 mL), dried ($NaSO_4$) and the solvent evaporated. Purification by column chromatography (silica, deactivated with 5% Et_3N in DCM, DCM/cyclohexane, 9:1) afforded the product as a pale yellow solid, m.p. 140−142 °C. Yield: 1.15 g (1.69 mmol, 71%).

^{1}H NMR ($CDCl_3$): δ = 1.50−1.80 (m, 12 H, C**H**$_2$), 2.15 (s, 12 H, pyrrole−C**H**$_3$), 3.45−3.60 (m, 12 H, C**H**$_2$O), 3.77−3.89 (m, 8 H, NC**H**$_2$, OC**H**$_2$), 4.56 (t, 2 H, *J* = 3.34 Hz, pyran−C**H**). − ^{13}C NMR ($CDCl_3$): δ = 11.89 (pyrrole−CH_3), 19.32, 25.27, 30.43 (**C**H$_2$), 44.34 (N**C**H$_2$), 62.13, 66.62, 70.72, 70.60 (**C**H$_2$O), 99.03 (O**C**HO), 114.94, 118.61 (two of three signals from the TTF). − MS (EI); *m*/*z* (%): 682 (M, 100), 598 (33), 387 (9), 247 (29).

Tetrathiafulvalene 20: PyrroloTTF **19** (955 mg, 1.40 mmol) was dissolved in THF/EtOH (125 mL, 1:1) and *p*-TsOH was added. The mixture was stirred under N_2 for 24 h at room temp. and then for a further 4 h at 40 °C. The reaction mixture was concentrated to approximately 50 mL and poured into water. The precipitate was extracted into DCM (100 mL) and the organic phase is washed with water, dried ($MgSO_4$) and the solvent evaporated in vacuo. Purification by column chromatography (silica, deactivated with 5% Et_3N in DCM, DCM/MeOH, 9:1) afforded the product as a yellow solid. Yield: 456 mg (0.89 mmol, 63%).

^{1}H NMR ([D$_6$]DMSO): δ = 2.12 (s, 12 H, pyrrole−C**H**$_3$), 3.38 (t, 4 H, *J* = 4.74 Hz, C**H**$_2$O), 3.45 (bs, 4 H, C**H**$_2$O), 3.54 (t, 4 H, *J* = 5.4 Hz, C**H**$_2$O), 4.57 (bs, 2 H, O**H**). − ^{13}C NMR ([D$_6$]DMSO): δ = 11.65 (pyrrole−CH_3), 44.05 (N**C**H$_2$), 60.11 (**C**H$_2$OH), 69.82, 72.34 (**C**H$_2$O), 112.93, 118.43, 118.97 (pyrrole−C and TTF core). − MS (EI); *m*/*z* (%): 514 (M, 100), 426 (28), 393 (18), 257 (11), 247 (15). − Calcd. for $C_{22}H_{30}N_2O_4S_4$ (514.73): C 51.34, H 5.87, N 5.44. Found: C 51.53, H 5.99, N 5.41.

2,7(6)-Bis[2-(2-hydroxyethoxy)ethylthio]-3,6(7)-bis(methylthio)-tetrathiafulvalene (22). − General Procedure for TTF Alkylation: 2,7(6)-Bis(methylthio)-3,6(7)-bis(2-cyanoethylthio)TTF **21** (1 g, 2.14 mmol) was dissolved in dry, degassed DMF (50 mL) and stirred under argon. To this mixture was added a solution of Na (108.4 mg, 4.71 mmol) in dry, degassed MeOH (5 mL) and the resulting dark solution was stirred for 30 min. 2-(2-Iodoethoxy)-ethanol (4.62 g, 21.4 mmol) was added and the reaction mixture was stirred for a further 5 h before the solvent was removed in vacuo. The residue was taken up in DCM (50 mL) and washed with H_2O (50 mL), dried ($MgSO_4$) and the solvent evaporated. The crude product was subjected to column chromatography (silica, DCM/MeOH, 19:1) to yield the product as a thick orange oil, which may solidify on prolonged standing. Yield: 0.82 g (1.53 mmol, 71%). − ^{1}H NMR ($CDCl_3$): δ = 1.82 (s, 2 H, O**H**), 2.42 (s, 6 H, SC**H**$_3$), 2.99 (t, 4 H, *J* = 6.4 Hz, SC**H**$_2$), 3.57 (t, 4 H, *J* = 4.5 Hz, C**H**$_2$O), 3.68 (m, 8 H, C**H**$_2$O). − ^{13}C NMR ($CDCl_3$):

Table 2. Crystal data and refinement parameters for **1**-*cis* and **1**-*trans*

	1-*cis*	**1**-*trans*
chemical formula	$C_{26}H_{24}N_2O_6S_8$, C_7H_8	$C_{26}H_{24}N_2O_6S_8$
formula weight	809.09	716.95
crystal color	orange	green
crystal habit	plate	plate
crystal size [mm]	0.28 × 0.13 × 0.05	0.33 × 0.23 × 0.06
crystal system	monoclinic	monoclinic
space group	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)
unit cell *a* [Å]	27.239(3)	18.5904(19)
unit cell *b* [Å]	7.6824(8)	7.9370(8)
unit cell *c* [Å]	35.302(4)	21.586(2)
unit cell α [°]	90	90
unit cell β [°]	99.495(10)	110.782(10)
unit cell γ [°]	90	90
unit cell volume [Å^3]	7287.0(13)	2977.8(5)
Z	8	4
Calcd. density [g cm^{-3}]	1.475	1.599
Temperature [K]	120(2)	120(2)
F(000)	3360	1480
Radiation [Å]	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)
Absorpt. coeff. [cm^{-1}]	0.537	0.645
Transmission range	0.9737 to 0.8642	0.9623 to 0.8153
φ-range for data coll. [°]	1.17 to 23.25	1.25 to 26.38
No. of measured reflections	28019	30043
No. of unique reflections	5235	6084
Completeness of unique refl.	100.0%	99.9%
R_{int}	0.1007	0.0238
Data/restraints/parameters	5235/24/441	6084/0 /381
No. of refl. with $I > 2\sigma(I)$	3411	5320
R [F, $I > 2\sigma(I)$]	0.0835	0.0303
R_w (F^2, all)	0.2349	0.0781
Goodness-of-fit (*S*)	1.032	1.049
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	1.666, −0.800	1.364, −0.378

Table 3. Crystal data and refinement parameters for **2** and **5**

	2	**5**
chemical formula	$C_{26}H_{24}N_2O_6S_8$	$C_{32}H_{30}N_4O_6S_4$, C_3H_7NO
formula weight	716.95	767.94
crystal color	green	black
crystal habit	prism	octahedron
crystal size [mm]	0.30 × 0.16 × 0.10	0.95 × 0.88 × 0.86
crystal system	monoclinic	orthorhombic
space group	*Pc* (no. 7)	$Pna2_1$ (no. 33)
unit cell *a* [Å]	13.5280(14)	11.730(2)
unit cell *b* [Å]	14.4430(14)	19.386(4)
unit cell *c* [Å]	15.1210(15)	15.910(3)
unit cell α [°]	90	90
unit cell β [°]	98.140(10)	90
unit cell γ [°]	90	90
unit cell volume [Å^3]	2924.6(5)	3617.9(12)
Z	4	4
calcd. density [g cm^{-3}]	1.628	1.410
temperature [K]	120(2)	120(2)
F(000)	1480	1608
radiation [Å]	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)
absorpt. coeff. [cm^{-1}]	0.657	0.318
transmission range	0.9372 to 0.8273	0.7714 to 0.7519
φ-range for data coll. [°]	1.41 to 26.37	1.66 to 26.37
no. of measured reflections	30075	37189
no. of unique reflections	11724	7384
completeness of unique refl.	99.9%	99.9%
R_{int}	0.0644	0.0128
data/restraints/parameters	11724/2/758	7384/1/467
no. of refl. with $I > 2\sigma(I)$	8992	7209
R [F, $I > 2\sigma(I)$]	0.0517	0.0217
R_w (F^2, all)	0.1035	0.0590
goodness-of-fit (*S*)	1.031	1.065
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.435, −0.475	0.209, −0.146

δ = 19.17 (S**C**H_3), 35.63 (S**C**H_2), 61.76, 69.69, 72.21 (**C**H_2O), 110.83, 110.92 (Fulvene **C=C**), 123.97, 124.12, 131.14, 131.32 (TTF cyclic **C=C**). − MS (ES); *m*/*z*: 537.04 [M + H]$^+$, 269.04 [M + 2H]$^{2+}$. − Calcd. for $C_{16}H_{24}O_4S_8$ (536.84): C 35.80, H 4.51. Found: C 35.77, H 4.53.

Crystal Structure Determinations: Suitable single crystals were mounted in a thin protecting layer of oil on glass fibers and transferred to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer. The crystal of **5** would normally be considered too large, but it turned out to produce good data. A Siemens SMART CCD diffractometer was used and data collected at 120 K. An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames; each set with a different angle for the crystal and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data and conversion into intensities corrected for Lorenz, polarization and absorption effects were performed using the programs *SMART*,[17] *SAINT*[17] and *SADABS*.[18] Structure solution, refinement of the structures, structure analysis and production of crystallographic illustrations was carried out using the programs *SHELXS97*,[19] *SHELXL97*,[20] *PLATON*[21] and *SHELXTL*.[22] In all of the structures H atoms were included in calculated positions. The refinements of **1**-*cis* and **2** were complicated by some conformational disorder of linkers and terminal −SCH_3 groups. This disorder was modeled by having some atoms in split positions with isotropic displacement parameters. A summary of crystal data, X-ray data collection parameters and structure refinement results is given in Table 2 and 3. The final atomic coordinates and other crystallographic data have been deposited.[23]

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[1] M. R. Bryce, *Advanced Materials* **1999**, *11*, 11−23; for a recent review on TTF-chemistry see; J. Garín, *Adv. Het. Chem.* **1995**, *62*, 249−304.
[2] S. Scheib, M. P. Cava, *J. Org. Chem.* **1998**, *63*, 1198−1204; see also, R. M. Metzger, *Mater. Sci. Eng.*, **1995**, *C3*, 277−285.
[3] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277−283.
[4] J. A. Cowan, J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2435−2437; J. A. Cowan, J. K. M. Sanders, G. S. Beddard, R. J. Harrison, *J. Chem. Soc., Chem. Commun.* **1987**, 55−58; A. Osuka, H. Yamada, K. Maruyama, N. Mataga, T. Asahi, M. Ohkouchi, T. Okada, I. Yamazaki, Y. Nishimura, *J. Am. Chem. Soc.* **1993**, *115*, 9439−9452; H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada, Y. Sakata, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2626−2629.
[5] D. G. Hamilton, D. E. Lynch, K. A. Byriel, C. H. L. Kennard, *Aust. J. Chem.* **1997**, *50*, 439−445.
[6] Z.-T. Li, P. C. Stein, J. Becher, D. Jensen, P. Mørk, N. Svenstrup, *Chem. Eur J.* **1996**, *2*, 624−633; For a review on rotaxanes, catenanes and other supramolecular structures and methods of synthesis of these, see: D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725−2828 and references cited herein.
[7] D. G. Hamilton, J. K. M. Sanders, J. E. Davies, W. Clegg, S. J. Teat, *Chem. Commun.* **1997**, 897−898; D. G. Hamilton, N. Feeder, L. Prodi, S. J. Teat, W. Clegg, J. K. M. Sanders, *J. Am. Chem. Soc.* **1998**, *120*, 1096−1097; D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur J.* **1998**, *4*, 608−620.
[8] R. M. Moriarty, A. Tao, R. Gilardi, Z. Song, S. M. Tuladhar, *Chem. Commun.* **1998**, 157−158.
[9] TTF is known to isomerize easily in the presence of traces of acid or by influence of light and therefore the TTF derivatives used in the synthesis of **1** exist as a mixture of *cis* and *trans* isomers, which is also the case for the macrocycle. Y. N. Kreitsberga, E. É. Liepin′sh, I. B. Mazheika, O. Y. Neilands, *Zh. Org. Khim.*, **1986**, *22*, 416−420; A. Suoizi, A. Robert, *J. Org. Chem.* **1987**, *52*, 1610−1611; K. Boubekeur, C. Lenoir, P. Batail, R. Carlier, A. Tallec, M.-P. Le Paillard, D. Lorcy, A. Robert, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1379−1381.
[10] For a review on TTF-thiolate chemistry, see: K. B. Simonsen, J. Becher, *Synlett* **1997**, 1211−1220.
[11] B. Petit, E. Maréchal, *Bull. Soc. Chim. Fr.* **1974**, 1591−1596; L. G. Schroff, R. L. J. Zsom, A. J. A. van der Weerdt, P. I. Schrier, J. P. Geerts, N. M. M. Nibbering, J. W. Verhoeven, Th. J. de Boer, *Recueil, Royal Netherlands Chem. Soc.* **1976**, *95*, 89−93; C. A. Hunter, J. K. M. Sanders, G. S. Beddard, S. Evans, *J. Chem. Soc., Chem. Commun.* **1989**, 1765−1767.
[12] L. Binet, J.-M. Fabre, *Synthesis* **1997**, *26*, 1179−1184.
[13] D. G. Hamilton, N. Feeder, S. J. Teat, J. K. M. Sanders, *New J. Chem.* **1998**, 1019−1021.
[14] K. Zong, W. Chen, M. P. Cava, R. D. Rogers, *J. Org. Chem.* **1996**, *61*, 8117−8124.
[15] E. Tsiperman, T. Regev, J. Y. Becker, J. Bernstein, A. Ellern, V. Khodorkovsky, A. Shames, L. Shapiro, *Chem. Commun.* **1999**, 1125−1126.
[16] Dark blue crystals were also found when crystallizing from chloroform/methanol. Crystal structure analysis showed a molecular structure almost identical with **1**-*cis*, but the packing was different, with possible intermolecular charge-transfer, a fact that may account for the dark color. The included solvent was MeOH plus some unidentified species, but the structure could not be refined to publication standard.
[17] *SMART and SAINT. Area Detector Control and Integration Software. Version 4.05*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA **1995**.
[18] G. M. Sheldrick, *SADABS. Program for Empirical Correction of Area Detector Data*. University of Göttingen, Germany **1996**.
[19] G. M. Sheldrick, *Acta Crystallogr. A46* (**1990**) 467.
[20] G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany **1997**.
[21] A. L. Spek, *Acta Crystallogr. A46* (**1990**) C-34.
[22] G. M. Sheldrick, *SHELXTL. Structure Determination Programs.Version 5.10*. Siemens Analytical X-ray Instruments Inc.,Madison, Wisconsin, USA, **1997**.
[23] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44−1223/336033; E-mail: deposit@ccdc.cam.ac.uk] on quoting the depository numbers CCDC-128487, CCDC-128488, CCDC-128489, and CCDC-128490.

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