Review Forma, **15**, 233–248, 2000

Tetrathiafulvalene-Based Supramolecular Chemistry; Recent Developments

Mogens Brøndsted NIELSEN, Christian LOMHOLT and Jan BECHER*

Department of Chemistry, University of Southern Denmark, Odense University,
Campusvej 55, DK-5230 Odense M, Denmark
**E-mail: jbe@chem.sdu.dk*

(Received April 19, 2000; Accepted May 19, 2000)

Keywords: Catenanes, Macrocycles, Supramolecular Chemistry, Switches, Tetrathiafulvalene

Abstract. This account highlights recent developments in the field of supramolecular tetrathiafulvalene (TTF) chemistry. Progresses in synthetic TTF chemistry have enabled the preparation of a number of elaborate molecular systems. Some of these systems can act as either sensors or molecular switches. Among these systems interlocked architectures such as rotaxanes and catenanes make a significant contribution.

1. Preamble

The construction of molecular devices which can operate as machines upon external energy transfer has been of high interest recently, as such systems may be able to store and process information at the molecular level (BALZANI *et al.*, 1998 and LEHN *et al.* 1988, 1990). Using non-covalent interactions between aromatic π-donors of the hydroquinone type and π-acceptors based on derivatives of paraquat, Stoddart *et al.* have prepared a number of molecular shuttles and switches controllable by external stimuli (BALLARDINI *et al.*, 1996). An elegant example is provided by a 'self-complexing' compound in which a naphthalene or hydroquinone π-donor and the π-acceptor cyclobis(paraquat-*p*-phenylene) (2) are covalently linked (ASHTON *et al.*, 1997).

2. Introduction to Tetrathiafulvalenes

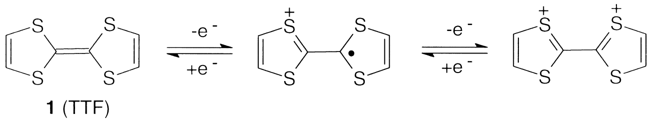
Tetrathiafulvalene (TTF, 1) is a reversible, stable two-electron donor (Scheme 1) and has as such found widespread use in supramolecular chemistry. Since the discovery of high electrical conductivity in a chloride salt of TTF (WUDL *et al.*, 1972) and metallic behaviour in the charge-transfer complex with 7, 7, 8, 8-tetracyano-*p*-quinodimethane (TCNQ) (FERRARIS *et al.*, 1973) a huge number of TTF derivatives have been synthesized (SCHUKAT and FANGHÄNEL, 1995). The developments in synthetic TTF chemistry have allowed the ready preparation of large quantities of derivatised TTF building blocks. It has thus become possible to incorporate TTF into macrocyclic (NIELSEN and BECHER, 1997a) and supramolecular systems (JØRGENSEN *et al.*, 1994a), with the ultimate goal to construct systems capable to act as for example sensors, catalysts or switches at the molecular level.

The discovery of the cyanoethyl protecting group for TTF-thiolates (Scheme 2) was a break-through in synthetic TTF chemistry (SIMONSEN *et al.*, 1996). Stepwise deprotection/alkylation protocols have been developed and used for the synthesis of a number of macrocyclic systems (Fig. 1), very often in high yields on account of the effective alkylation of TTF-thiolates. However, the four attachment sites of TTF usually result in mixtures of two inseparable isomers, a *cis* and a *trans* isomer (Fig. 2). This isomeric problem is avoided when the pyrrolo-annelated TTFs 3 and 4 are used. Efficient syntheses of these strong π-donors have recently been developed (ZONG *et al.*, 1996; JEPPESEN *et al.*, 1999)

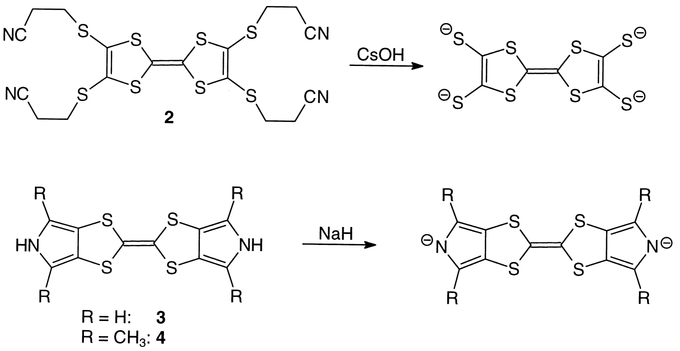
3. Macrocyclic TTFs as Cation Sensors

In previous reviews (JØRGENSEN *et al.*, 1994a; NIELSEN *et al.*, 1997a) we have described the ability of the crown-ether annelated TTFs 9-11 (Fig. 3) to complex alkali metal cations (Li^+, Na^+ and K^+) resulting in an increase of the first oxidation potential. The second potential remained unchanged, which was explained by expulsion of the cation after the first oxidation (Route 1 in Scheme 3). However, more than 250 equiv. of cations were necessary to observe any shifts for these ligands.

The cyclic voltammogram of the thiacrown 12 showed an anodic increase of both oxidation waves upon addition of Ag^+ ions ($\Delta E_{ox}{}^1 = +170$ mV, and $\Delta E_{ox}{}^2 = 70$ mV), whereas the reduction waves remained unchanged. This observation indicates that exchange is slow



Scheme 1. Reversible oxidations of TTF.



Scheme 2. Reactive TTF-nucleophiles.

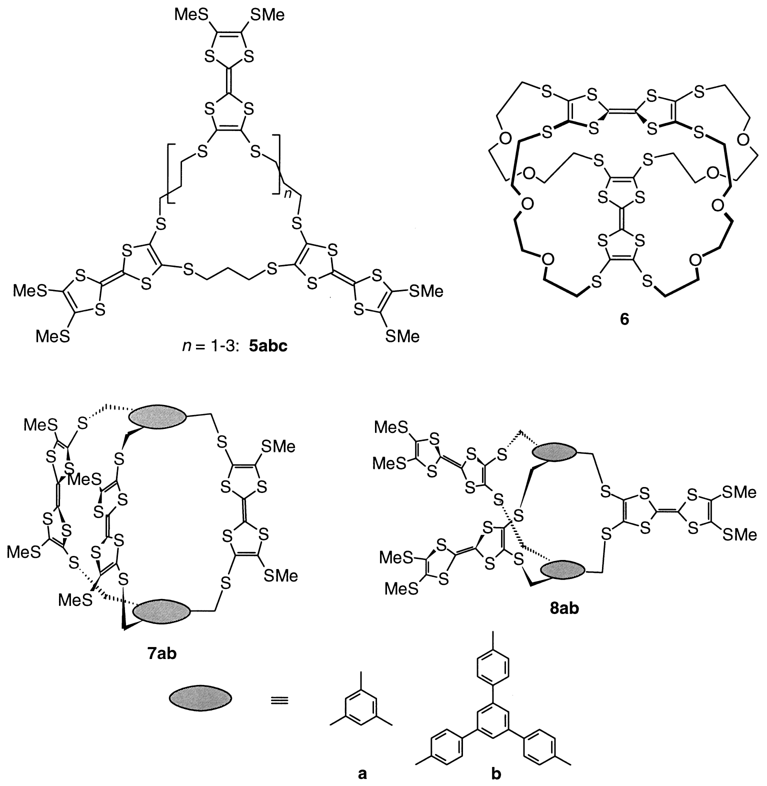


Fig. 1. TTF-macrocycles and cage molecules prepared by step-wise deprotection/alkylation af cyanoethyl-protected TTF-thiolates.[6]

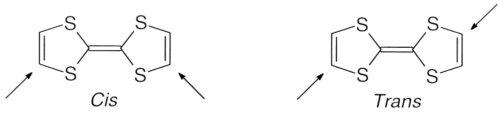
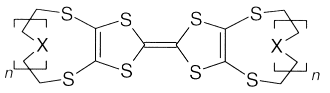
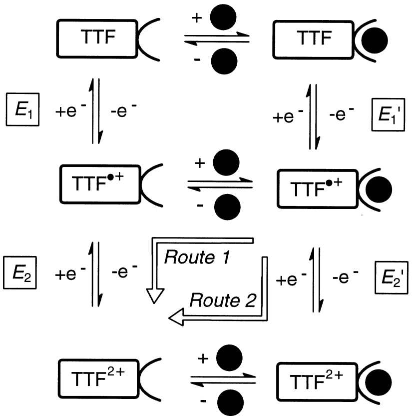


Fig. 2. Definition of *cis* and *trans* isomeri for substituted TTFs.



X = O, *n* = 3-5 **9**, **10**, **11**
X = S, *n* = 2 **12**

Fig. 3. Crown-ether annelated TTFs.

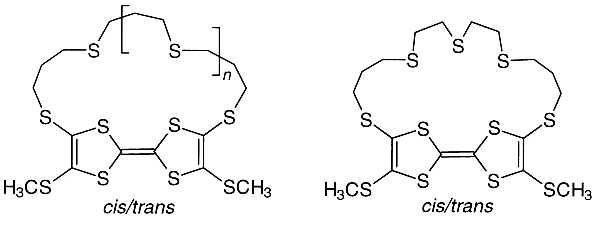


Scheme 3. Schematic illustration of a TTF sensor. After the first oxidation, the guest may be expelled (route 1) or kept hosted (route 2). E_1, E_1', E_2, and E_2' denote the redox potentials for the shown processes.

and route 2 is operating for oxidation of the system.

It was concluded that the relative weak responses result from the weak coupling between the metal cation and the redox active fulvene center. However, an enhanced sensitivity for cations exerted by TTF-thiacrowns cyclized in the 2, 7(6)-positions has recently been reported (DERF *et al.*, 1999). The 2, 7(6)-cyclized thiacrowns presented in Fig. 4 were synthesized and investigated by LSIMS (Liquid Secondary Ionisation Mass Spectrometry), ^{1}H NMR and cyclic voltammetry with respect to their inclusion of Ag^+ ions. According to ^{1}H NMR titration studies only complexation of the terminal SC = $CSCH_3$ fragments in macrocycles 13 and 14 was observed. In contrast, for 15 the complexation preferentially involved the thiacrown cavity, which may be explained by a better orientation of the coordinating S atoms. The X-ray crystal structure of *cis*-13 confirms that the propylene fragments cannot ensure a correct structural environment for complexation. The titration curves of the complex between 15 and Ag^+ show a plateau for 0.6 equiv. of added Ag^+. The ratio between *cis* and *trans* isomers is 60/40 suggesting that only the *cis* isomer binds Ag^+. A stability constant of $K_a = 10^{3.26}$ ($CDCl_3$-CD_3CN 1:1) for the *cis*-15•Ag^+ complex was determined from these data. Adding Ag^+ ions to 13 and 14 did not result in any changes of the cyclic voltammograms, whereas the first oxidation wave of 15 was significantly anodically shifted upon addition of up to 1 equiv. of Ag^+ (Route 1).

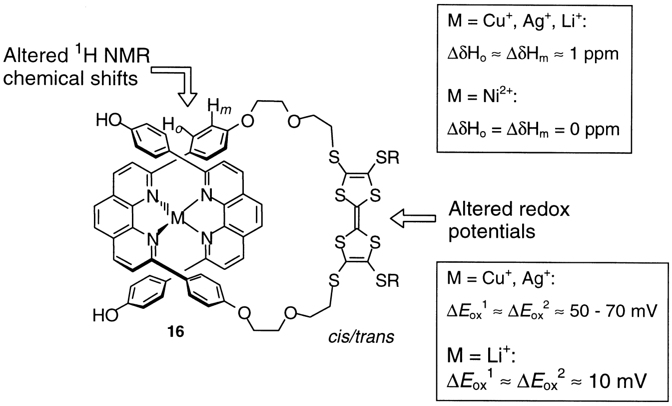
The templating abilities of Cu^+ to coordinate two phenanthroline ligands in a tetrahedral complex has been employed to prepare a TTF-containing Cu(I)-catenate (JØRGENSEN *et al.*, 1994b). Using the same strategy, we have used TTF as a sensor unit for the metal ions Cu^+, Ag^+ and Li^+ in precatenate complexes 16 (Fig. 5) (BANG *et al.*, 2000). The central metal alters the chemical shifts of the macrocyclic protons, in particular H_m and H_o, as well as the redox potentials of the TTF unit. Interestingly, both the first and second TTF redox potentials were significantly increased for the Cu^+ and Ag^+ complexes, signalling that the metal ion is not expelled after the first oxidation (Route 2, Scheme 3).



$n = 1$: **13**
$n = 2$: **14**

15

Fig. 4. TTF-thiacrowns.



16

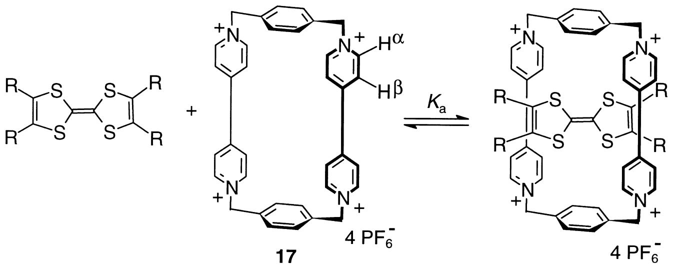
Fig. 5. Precatenate complex.

4. Interlocked Molecules

The developments in supramolecular chemistry in the past twenty years have demonstrated many elegant self-assembled interlocked molecules prepared in high yields such as catenanes and rotaxanes (AMABILINO and STODDART, 1995). Because of the specific redox properties of the TTF group, a special interest has emerged to incorporate TTF into such systems in order to construct molecular systems for example switches, taking advantage of the three possible redox states of TTF and their reversible conversions.

4.1. *Complexation Studies*

The cyclic acceptor cyclobis(paraquat-*p*-phenylene) (17) is able to act as a host for TTF (PHILP *et al.*, 1991). The X-ray crystal structure of the green 1:1 complex formed between TTF and 17 revealed a channel-type structure formed by the cyclic acceptor occupying TTF in its central cavity. In acetonitrile solution a CT absorption band is observed at λ_{max} 855 nm. The association constant of the complex was determined to K_a = 10000 M^{-1} in acetonitrile (ASHTON *et al.*, 1999) and 2600 M^{-1} in acetone (DEVONPORT *et* *al.*, 1997) (Scheme 5, Fig. 6). However, functionalisation of the TTF nucleus results in different donor properties (measured by the first redox potential $E_{1/2}{}^{1}$) and has a profound influence on the inclusion ability (LAU *et al.*, 1999). Thus, the weak donor tetramethylthiotetrathiafulvalene (TMT-TTF, 18) associates in a very weak complex. Association constants of $K_a = 170\ \mathrm{M}^{-1}$ in acetonitrile and $40\ \mathrm{M}^{-1}$ in acetone have been determined from the ratio of complexed and uncomplexed cyclophane proton resonances (slow-exchange on the 250 MHz NMR time-scale, Fig. 7). In contrast, the bis (pyrrolo) TTF 4 forms a strong complex ($K_a = 7900\ \mathrm{M}^{-1}$ in acetone) as a combination of its low redox potential and its extended π-surface. When a tetramercapto-TTF is substituted with polyether linkers (19), the association constant is increased dramatically as compared to TMT-TTF (ASAKAWA *et al.*, 1999), since the formation of hydrogen bonds between the oxygens and the bipyridinium α-H′s (relative to nitrogen) can add to the stability of the complex. Recent calculations show that the ethyleneoxy groups are indeed very important in the complexation process (HOUK *et al.*, 1999).



Scheme 4. Equilibrium for the inclusion of a TTF derivative in the cavity of the cyclic acceptor 17.

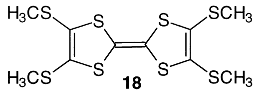
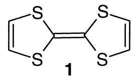
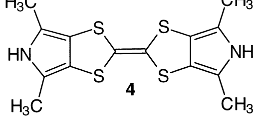
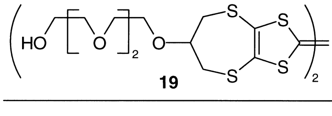
	Solvent	$E_{1/2}^{1}$ (V)	K_a (M^{-1})
 18	MeCN Me_2CO	0.51	170 40
 1	MeCN Me_2CO	0.34	10000 2600
 4	Me_2CO	0.33	7900
 19	MeCN		10000

Fig. 6. Association constants for the inclusion of TTF derivatives in the cyclic acceptor 17 correlated with the first redox potential of the free, uncomplexed TTFs.

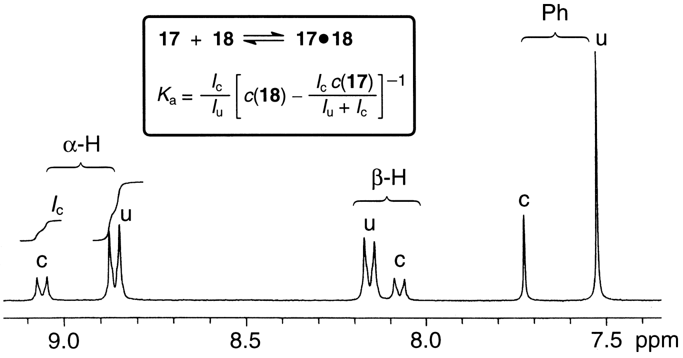
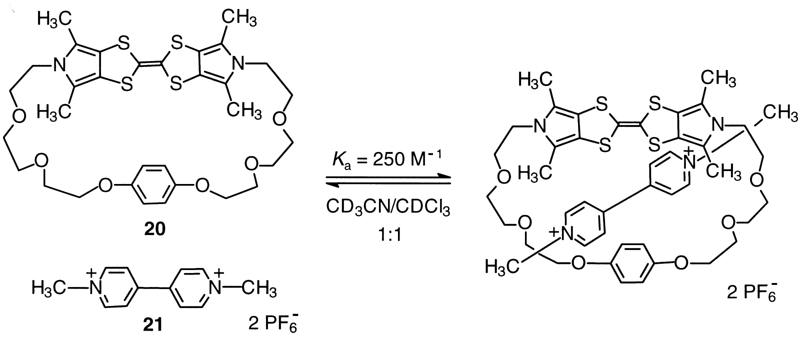


Fig. 7. Selected region of the ^{1}H NMR spectrum of the equilibrium solution between 17, 18 (ca. 1:2) and the complex 17•18 at 303 K. Employing the exact initial concentrations $c(17)$ and $c(18)$ the association constant K_a can be calculated from the integrals I_c and I_u of complexed (c) and uncomplexed (u) cyclophane resonances.



Scheme 5. Inclusion of paraquat in a TTF-macrocycle.

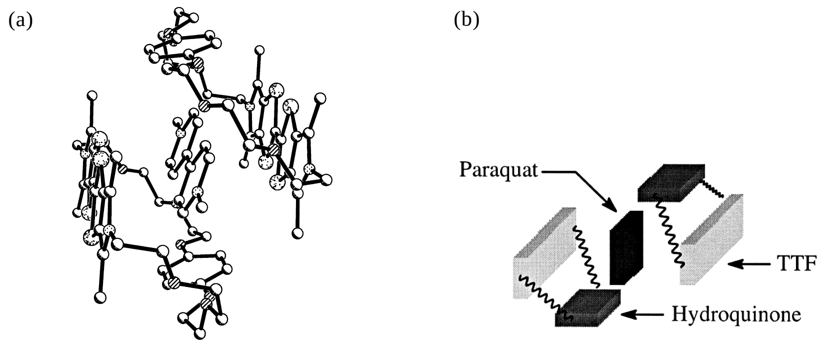


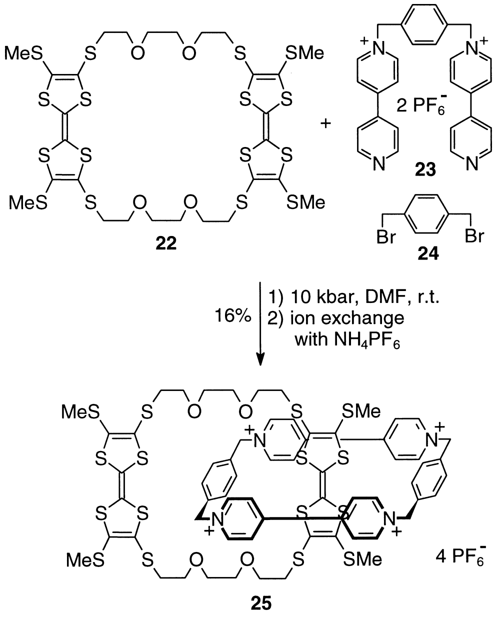
Fig. 8. (a) X-ray crystal structure (centrosymmetric) of the 2:1 complex between 20 and 21. The solvent molecules and counter ions are omitted for clarity. (b) Schematic drawing of the solid state $(20)_2$•21 complex.

Macrocycles containing two electron donors can act as host molecules for electron acceptors, such as paraquat (21). Such complex formation was studied for the macrocycle 20 in the solid and in the solution state (Scheme 5), by X-ray crystal structure analysis and ^{1}H NMR spectroscopy (LAU *et al.*, 1999). In solution ($CDCl_3$-CD_3CN 1:1) a complex with 1:1 stoichiometry was identified from a Job plot with an association constant of 250 M^{-1}. However, in the solid state a complex consisting of two molecules of 20 per one molecule of 21 was observed (Fig. 8). Each macrocycle adopts a conformation with an angle between the hydroquinone and the tetrathiafulvalene moiety of 70.1°. Two macrocycles dimerise to form a box-like structure encapsulating one completely planar paraquat molecule. The distance between the two tetrathiafulvalene moieties is 7.08 Å, which is optimal for CT and/or π–π interactions to stabilize inclusion of paraquat, although paraquat in this case is tilted 15.9° away from co-planarity with the TTFs.

4.2. Donor-acceptor catenanes based on TTF

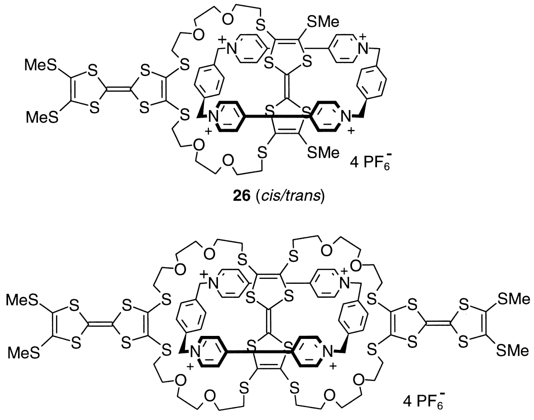
A number of catenanes between polyether-bridged tetramercapto-TTFs and the cyclic acceptor have been reported. Treating the macrocycle 22 with the dication 23 and the dibromide 24 under ultra-high pressure resulted in formation of the catenane 25 (Scheme 6) (NIELSEN *et al.*, 1997b).

Two similar catenanes (26 and 27) are shown in Fig. 9 (LI and BECHER, 1996; NIELSEN *et al.*, 1997b). The catenanes 25 and 26 were both obtained as a mixture of *cis/trans* isomers starting from a *cis/trans* isomeric mixture of the free macrocycle. However, only the *cis* configuration of the central TTF in 27 was obtained from the *cis/trans* mixture of the



Scheme 6. Catenane formation.

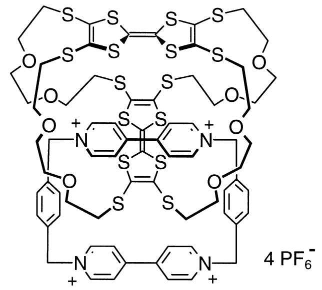
macrocycle. In order to shed light on the factors responsible for this isomeric selectivity during the catenation process (Scheme 7), we designed a quadruple-bridged *criss-cross* overlapped cyclophane (6) (NIELSEN *et al.*, 1998a). Only the arrangement in which both TTFs are in the *cis* configuration seemed able to generate a catenane according to a CPK model. Indeed, only the *cis*, *cis* catenane 28 was isolated as evidensed by ^{1}H NMR spectroscopy (Fig. 10).



26 (*cis/trans*)

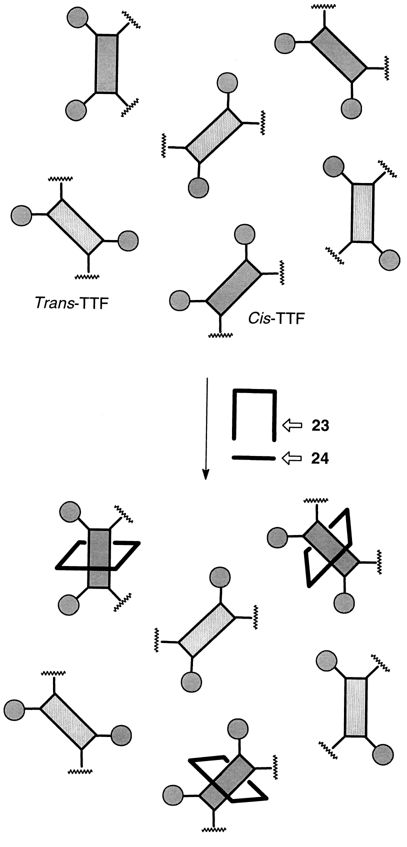
27 (*cis*)

Fig. 9. Catenane 26 was isolated as a mixture of *cis/trans* isomers, whereas only the *cis* catenane of 27 was obtained from catenation of an isomeric mixture of the corresponding macrocycle.



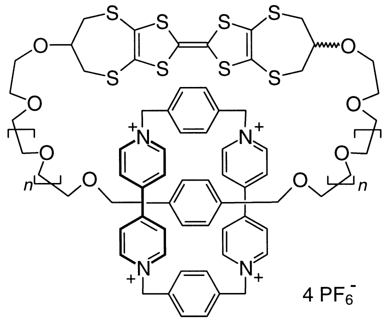
28 (*cis, cis*)

Fig. 10. Only the *cis, cis* catenane 28 is sterically allowed.



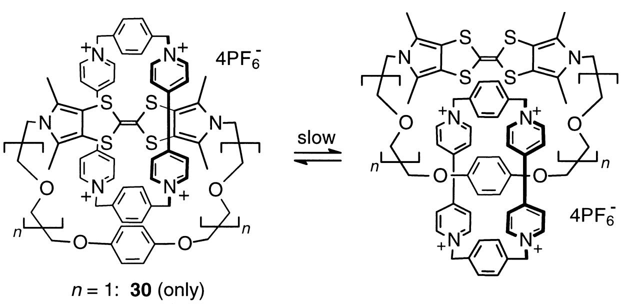
Scheme 7. Schematic illustration of the selection of a single isomer in the encirclement of TTF.

Based on the complexation studies we hoped to be able to predict which donor unit to be catenated, when two different donor entities are present in the same macrocycle. However, such a prediction turned out to be rather complicated. Thus, Stoddart and coworkers (ASAKAWA *et al.*, 1999) isolated the catenanes 29ab in which the benzyl unit is encircled both in solution and in the solid state, even though benzyl is a poorer donor than TTF (Fig. 11). We observed a preference for the hydroquinone donor relative to the strong bis(pyrrolo)TTF donor in the catenanes 31 and 32 (LAU *et al.*, 1999) whereas the bis (pyrrozlo) TTF exclusively was encircled in catenane 30 (Scheme 8). These findings reflect the complicated and subtle balance between all the individual noncovalent forces acting in cooperation. A major factor is the ability of the polyether oxygens to form hydrogen bonds to the bipyridinium hydrogen atoms positioned in the α-position with respect to the nitrogen atoms. Occupation of the extended bis(pyrrolo)TTF moiety by 17 makes these interactions more difficult as compared to a situation where 27 occupies the smaller hydroquinone moiety.



n = 1, 2: **29ab**

Fig. 11. The cyclic acceptor encircles the benzyl unit and not the TTF in these two catenanes.



n = 1: **30** (only)
n = 2: **31a** (minor)
n = 3: **32a** (minor)

n = 2: **31b** (major)
n = 3: **32b** (major)

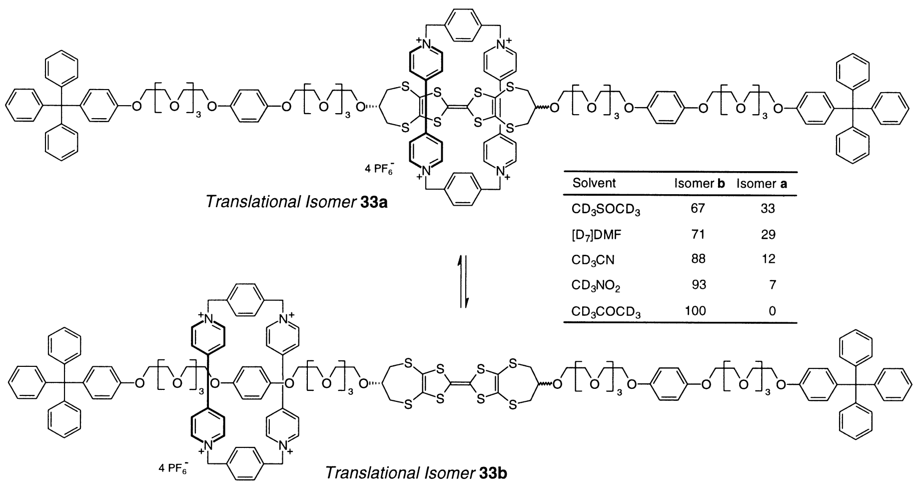
Scheme 8. Translational isomeri a in catenane containing both a bis(pyrrolo)TTF and a hydroquinone donor.

5. Molecular Switches

Catenanes and rotaxanes are good candidates for the preparation of molecular switches, since the population of different translational isomers may be determined by external stimuli (BALZANI *et al.*, 1998). Stoddart and coworkers (ANELLI *et al.*, 1997) prepared the two-station prototype shuttle 33ab containing one TTF and two hydroquinone donor stations (Scheme 9). Depending on which donor is encircled by the cyclophane, two possible translational isomers exist. The ratio between the two translational isomers was observed to be very solvent dependent, with a preference however for the hydroquinones (33b). Electrochemical studies (cyclic voltammetry in acetonitrile) revealed an anodic increase of the first oxidation wave by +35 mV relative to the free dumbbell, whilst the second wave showed a shift of +5 mV. This observation is explained by a hampering of the shuttling movement of the cyclophane along the dumbbell by oxidation of the TTF nucleus. Hence, the first oxidation of TTF results in an increased energy barrier to the passage of the cyclophane along the thread causing the cyclophane to be effectively tethered at a hydroquinone site. Accordingly, the second oxidation of TTF is pertubed to a lesser extent than the first.

Taking advantage of TTF's reversible redox chemistry, the catenane 34a was observed to act as a molecular switch (Scheme 10) (ASAKAWA *et al.*, 1998). Thus, upon oxidation of the TTF unit (either chemically or electrochemically) the cyclic acceptor was moved from the TTF unit to the 1, 5-dioxynaphthalene donor unit, affording the isomer 34b. Subsequent reduction regenerates the original isomer 34a.

The ability of the dication TTF^{2+} to act as an electron acceptor has been exploited in the construction of the three-pole switch presented in Scheme 12 (ASHTON *et al.*, 1999). When the three components, TTF, the cyclic acceptor 17, and the macrocycle 1, 5-dinaphtho[38]crown-10 (35), are mixed together, the first redox potential of the TTF is increased by 70 mV according to cyclic voltammetry in acetonitrile. This observation



Solvent	Isomer **b**	Isomer **a**
CD_3SOCD_3	67	33
[D_7]DMF	71	29
CD_3CN	88	12
CD_3NO_2	93	7
CD_3COCD_3	100	0

Scheme 9. Translational isomeri in a rotaxane containing TTF and hydroquinone donor stations.

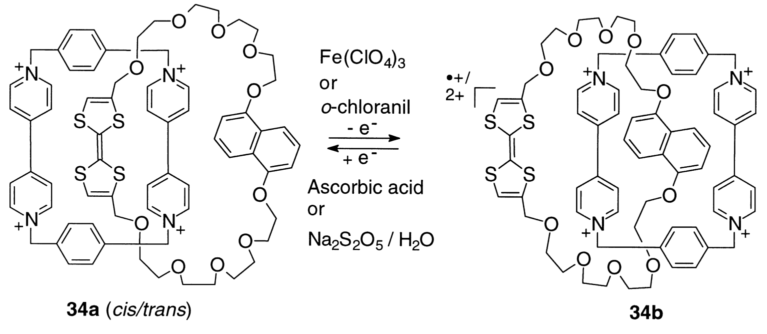
indicates that the TTF is complexed inside the cyclic acceptor making the oxidation more difficult. However, the second oxidation now occurs easier, by 14 mV, relative to a solution of TTF alone. This result indicates that the radical cation has left the cyclic acceptor, but enters the naphthocrown host when oxidised to the dication. These processes are reversible and the system can be characterised as a three-pole switch. The association constant for the 35•TTF^{2+} complex was determined by absorption and emission spectral titrations in acetonitrile to $K_a = 4.1 \times 10^3$ M^{-1} (298 K), confirming the strong association between the naphtocrown and the TTF dication.

A thermally controlled TTF-based molecular switch was obtained by tethering the cyclic acceptor and the TTF unit together (Scheme 12), affording the ‘self-complexing’ compound 35a—we describe this intramolecular interaction as an anchimeric complexation (NIELSEN *et al.*, 1998b). A solution of the open “uncomplexed” form 36b (obtained by fractional crystallisation) was according to UV-Vis observed to slowly equilibrate during about 19 h to a mixture of 36a (CT band at λ_{max} 785 nm) and 36b (Fig. 12). However, when this equilibrium solution was refluxed, almost total “decomplexation” occured as evidensed by disappearance of the CT absorption band, but upon storage of the solution for one day at room temperature the equilibrium was reestablished-with a small decrease, however, in the equilibrium CT absorption.

Together with Prof. Stoddart and his group, we are currently trying to develop a “chemical muscle” based upon a related molecular donor-acceptor system. Such a rotaxane system is designed to change size in the lateral directions upon when adressed electrochemically (oxidation/reduction).

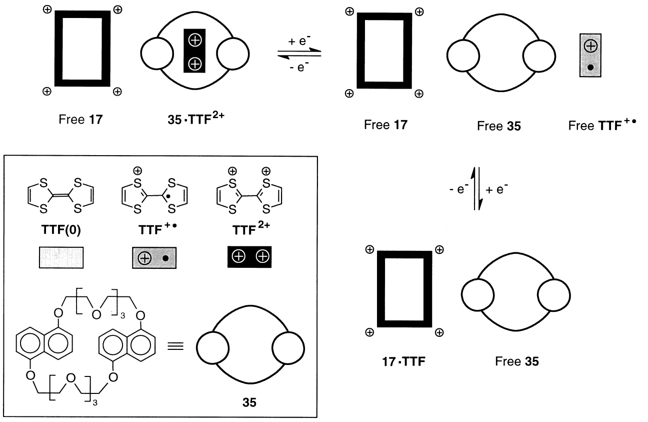
6. Donor-Acceptor Macrocycles

Intramolecular CT interactions were investigated for a number of donor-acceptor macrocycles, containing both a TTF and a bipyridinium unit (Fig. 13). Thus, the macrocycles 37a–c show broad CT absorption bands with λ_{max} in the region 620–670 nm (SIMONSEN *et al.*, 1997). The conformational flexibility in the R group of 37b and 37c results in a smaller intensity of the CT-band compared to that of 37a. According to both ^{1}H NMR and X-ray

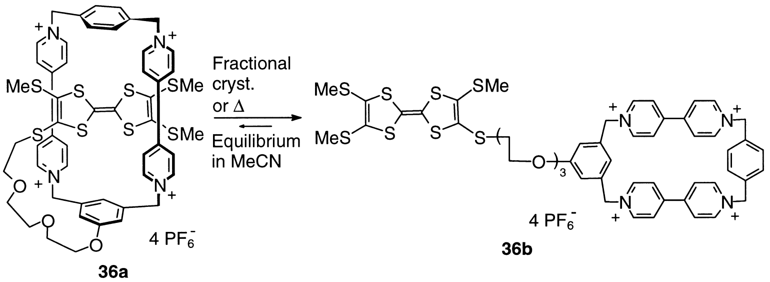


34a (*cis/trans*) **34b**

Scheme 10. Chemically and electrochemically triggered redox-switching of a catenane.



Scheme 11. A three-pole supramolecular switch.



Scheme 12. 'Self-complexing' macrocycle.

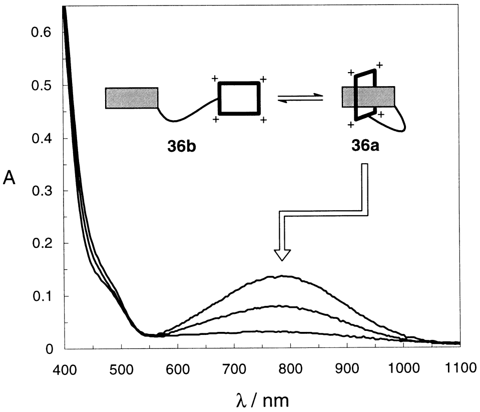
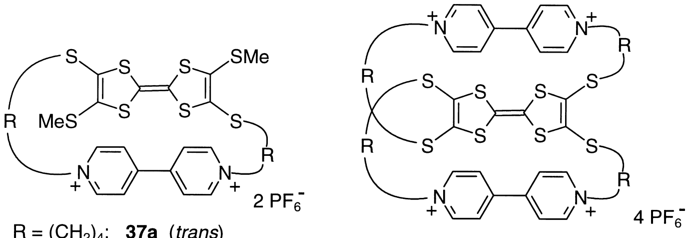


Fig. 12. The time variation of the maximum absorbance (λ_{max} ~ 785 nm) of initially 'decomplexed' 36b (2.6×10^{-4} M in acetonitrile).



R = $(CH_2)_4$: **37a** (*trans*)
R = $(CH_2)_5$: **37b** (*cis/trans*)
R = $CH_2CH_2OCH_2CH_2$: **37c** (*cis/trans*)

38 (*trans*)

Fig. 13. Donor-acceptor mono- and bicycles.

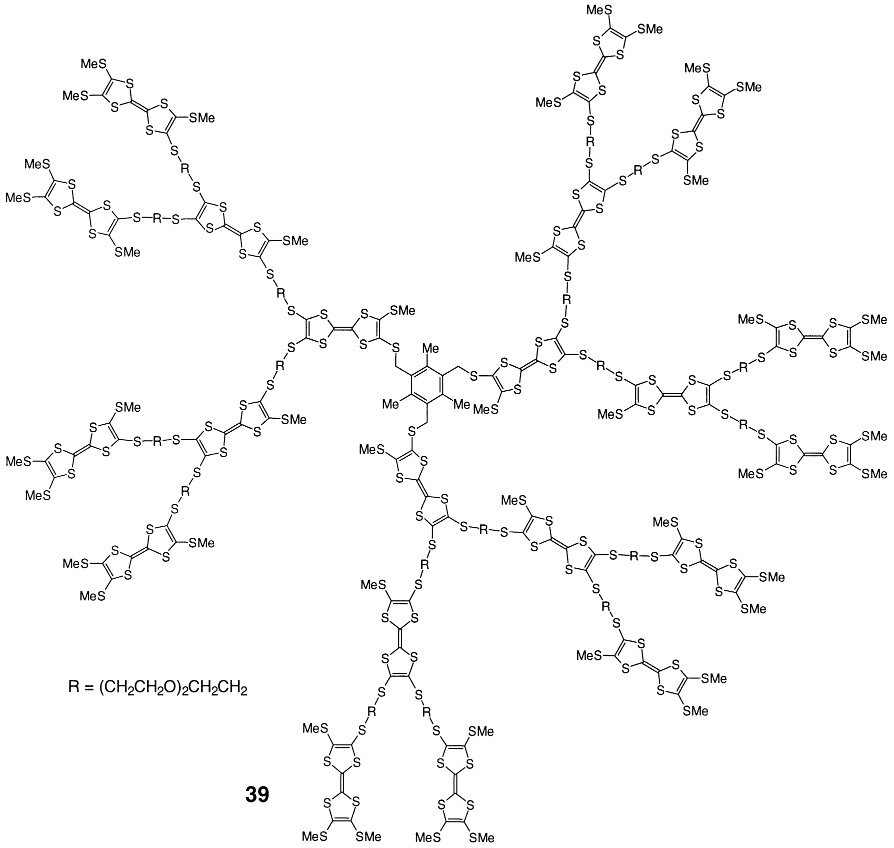
crystal structure analysis, only the *trans* configuration 37a was isolated upon reacting a TTF-diiodide (*cis/trans* mixture) with bipyridine. In contrast, *cis/trans* mixtures were obtained of the less constrained 37b and 37c. Also, the bicycle 38 (*trans*) containing two bipyridinium units has been prepared (SIMONSEN *et al.*, 1998). Conformational restrictions unable the TTF to interact with both acceptors at the same time, resulting in a similar CT-absorption as obtained for 37a. However, the two bipyridinium units present in 38 induce very large anodic shifts in both TTF oxidation potentials (70–90 mV). These shifts can be ascribed to a combination of CT interactions and electrostatic repulsion between the four pyridinium cationic centers and the oxidized TTF system.

7. Dendritic Macromolecules Incorporating TTFs

M. R. Bryce and coworkers have reported a number of interesting dendritic macromolecules (also termed “starburst polymers” or “cascade molecules”) based on TTF (BRYCE *et al.*, 1996). Such molecules comprise a polyfunctional core surrounded by covalently linked layers of monomers, with a branch occuring at each monomer unit. One such dendrimer (39) containing a total of 21 TTF units is shown in Fig. 14 (CHRISTENSEN *et al.*, 1998). The close spatial contact between TTFs in the dendrimer resulted in intramolecular π-dimerisations of the generated radical cations upon electrochemical oxidation. As a result of the many redox active units present, a great challenge exists in employing macromolecules of this kind as catalysts or in molecular recognition processes.

8. Conclusions

The electron donating abilities of TTF have been exploited in a number of supramolecular host-guest systems in order for these to act as either sensors or molecular switches. The developments in both synthetic TTF chemistry and supramolecular chemistry have made possible the construction of many elaborate systems, with applications in both the chemical, physical and biological world. Much synthetic TTF-work has been focusing on the TTF-tetrathiolate on account of its ready preparation and strong nucleophilicity. The recent access to pyrrolo-annelated TTFs possessing strong π-donor properties offers great opportunities in the design and construction of future supramolecular systems.



R = $(CH_2CH_2O)_2CH_2CH_2$

39

Fig. 14. Tetrathiafulvalene $[TTF]_{21}$-glycol dendrimer.

REFERENCES

Amabilino, D. B. and Stoddart, J. F. (1995) *Chem. Rev.*, **95**, 2725.

Anelli, P. -L., Asakawa, M., Ashton, P. R. Bissell, R. A., Clavier, G., Górski, R., Kaifer, A. E., Langford, S. J., Mattersteig, G., Menzer, S., Philp, D., Slawin, A. M. Z., Spencer, N., Stoddart, J. F., Tolley, M. S. and Williams, D. J. (1997) *Chem. Eur. J.*, **3**, 1113.

Asakawa, Ashton, P. R., Balzani, V., Credi, A., Hamers, C., Mattersteig, G., Montalti, M., Shipway, A. N., Spencer, N., Stoddart, J. F., Tolley, M. S., Venturi, M., White, A. J. P. and Williams, D. J. (1998) *Angew. Chem. Int. Ed. Engl.*, **37**, 333.

Asakawa, M., Ashton, P. R., Balzani, V., Boyd, S. E., Credi, A., Mattersteig, G., Menzer, S., Montalti, M., Raymo, F. M., Ruffilli, Stoddart, J. F., Venturi, M. and Williams, D. J. (1999) *Eur. J. Org. Chem.*, 985.

Ashton, P. R., Ballardini, R., Balzani, V., Boyd, S. E., Credi, A., Gandolfi, M. T., Gómez-López, M., Iqbal, S., Philp, D., Preece, J. A., Prodi, L., Ricketts, H. G., Stoddart, J. F., Tolley, M. S., Venturi, M., White, A. J. P., Williams, D. J., (1997) *Chem. Eur.*, **J. 3**, 152.

Ashton, P. R., Balzani, V., Becher, J., Credi, A., Fyfe, M. C. T., Mattersteig, G., Menzer, S., Nielsen, M. B., Raymo, F. M., Stoddart, J. F., Venturi, M. and Williams, D. J. (1999) *J. Am. Chem. Soc.*, **121**, 3951.

Ballardini, R., Balzani, V. Credi, A., Gandolfi, M. T., Langford, J., Menzer, S., Prodi, L., Stoddart, J. F., Venturi, M., Williams, D. J., Angew. Chem. Int. Ed. Engl., (1996) 35, 978 and refs. cited herein.

Balzani, V., Gómez-Lopéz M. and Stoddart, J. F. (1998) *Acc. Chem. Res*., **31**, 405.

Bang, K. S., Nielsen, M. B., Zubarev, R. and Becher, J. (2000) *Chem. Commun*., 215.

Bryce, M. R. and Dewonport, W. (1996) *Adv. Dendritic Macromol*., **3**, 115.

Christensen, C. A., Goldenberg, L. M., Bryce, M. R. and Becher, J. (1998) *Chem. Commun*., 509.

Derf, F. LE, Mazari, M., Mercier, N., Levillain, E., Richomme, P., Becher, Garín, J., Orduna, J., Gorgues, A. and Sallé, M. (1999) *Chem. Commun*., 1417.

Devonport, W., Blower, M. A., Bryce, M. R. and Goldenberg, L. M. (1997) *J. Org. Chem*., **62**, 885.

Ferraris, J., Cowan, D. O., Walatka, V. V. and Perlstein, J. H. (1973) *J. Am. Chem. Soc*., **95**, 948.

Houk, K. N., Menzer, S., Newton, S. P., Raymo, F. M., Stoddart, J. F. and Williams, D. J. (1999) *J. Am. Chem. Soc*., **121**, 1479.

Jeppesen, J. O., Takimiya, K., Jensen, F. and Becher, J. (1999) *Org. Lett*., **1**, 1291.

Jørgensen, T., Hansen, T. K. and Becher, J. (1994a) *Chem. Soc. Rev*., **23**, 41.

Jørgensen, T., Becher, J., Chambron, J.-C. and Sauvage, J.-P. (1994b) *Tetrahedron Lett*., **35**, 4339.

Lau, J., Nielsen, M. B., Thorup, N., Cava, M. P. and Becher, J. (1999) *Eur. J. Org. Chem*., 2807.

Li, Z.-T. and Becher, J. (1996) *J. Chem. Soc., Chem. Commun*., 639.

Liu, H., LIU, S. and Eshegoyen, L. (1999) *Chem. Commun*., 1493.

Moore, A. J., Goldenberg, K., Bryce, M. R., Petty, M. C., Monkman, A. P. and Port, S. N. (1998) *Adv. Mater*., **10**, 395.

Nielsen, M. B. and Becher, J. (1997a) *Liebigs Ann./Recueil*, 2177.

Nielsen, M. B., Li, Z.-T. and Becher, J. (1997b) *J. Mater. Chem*., **7**, 1175.

Nielsen, M. B., Thorup, N. and Becher, J. (1998a) *J. Chem. Soc*., Perkin Trans., **1**, 1305.

Nielsen, M. B., Nielsen, S. B. and Becher, J. (1998b) *J. Becher, Chem. Commun*., 475.

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

Schukat, G. and Fanghänel, E. (1995) *Sulfur Rep*., **18**, 1.

Simonsen, K. B., Svenstrup, N., Lau, J., Simonsen, O., Mørk, P., Kristensen, G. J. and Becher, J. (1996) *Synthesis*, **3**, 407.

Simonsen, K. B., Zong, K., Rogers, R. D., Cava, M. P. and Becher, J. (1997) *J. Org. Chem*., **62**, 679.

Simonsen, K.B., Thorup, N., Cava, M. P. and Becher, J. (1998) *Chem. Commun*., 901.

Wudl. F, Wobschall, D. and Hufnagel, E. J. (1972) *J. Am. Chem. Soc*., **94**, 671.

Zong, K., Chen, W., Cava, M. P. and Rogers, R. D. (1996) *J. Org. Chem*., **61**, 8117.