Tetrathiafulvalenes as Building-blocks in Supramolecular Chemistry

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Recently an overlap has emerged between two important fields of current preparative chemistry. These are the fields of supramolecular chemistry and tetrathiafulvalene chemistry. It is the aim of this review to give an account of recent developments in this overlap-zone along with a brief background.

Figure 1 Oxidation of TTF affords stable cationic species.

1 Conceptual Development of Tetrathiafulvalene Chemistry[1]

The investigation of tetrathiafulvalene (TTF) was initiated almost seventy years ago,[2] but prior to 1970 only sporadic reports of TTF derivatives appeared in the literature, and these concerned mainly non-targeted by-products.[3]

From 1970 investigations were intensified, following the observation by Wudl *et al.*[4] that TTF forms a stable radical cation when treated with chlorine, and in 1973 the first 'organic metal' TTF-TCNQ was discovered.[5] In its neutral state TTF is an orange organic solid. However, it readily loses electrons in the presence of oxidizing agents, to form initially the purple radical cation, and subsequently the yellow dication. Both species are aromatic in the Hückel sense and surprisingly stable.

Soon after the discovery of TTFs' donor-properties, an important experiment was done in which TTF was mixed with an electron acceptor, tetracyanoquinodimethane (TCNQ). The resulting black, crystalline charge-transfer complex showed an electrical conductance which was several orders of magnitude higher than usual for organic solids. It also showed other characteristic features resembling metals, thereby justifying the term 'the first o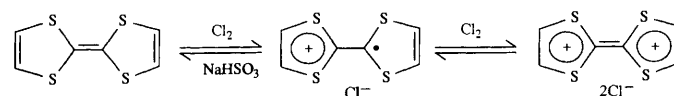rganic metal'. From now on, the physical and chemical investigation of TTF-derivatives became a new and important field which required interdisciplinary efforts worldwide. Many new physical terms have been coined as a result of these efforts. A particularly important result by Bechgaard and Jérome in 1980 was the finding of the first organic superconductor.[6] Tetramethyltetraselenafulvalene hexafluorophosphate ([TMTSF]$_2$PF$_6$) was found to be *superconducting* at 0.9 K at 12 kbar, a property which had not previously been observed in any organic compound.

The search for new organic conductors and superconductors is still active and an impressive number of TTF derivatives have been prepared and investigated. However, the main emphasis of these investigations has been on the solid-state properties of the TTF-salts and only recently have several groups simultaneously initiated a study of TTF as a building-block in supramolecular and macromolecular chemistry.

2 Cation-sensitive Tetrathiafulvalenes

During the past few years considerable attention has been paid to molecular systems containing a redox-active functionality and a host unit capable of cation binding. Such systems can be

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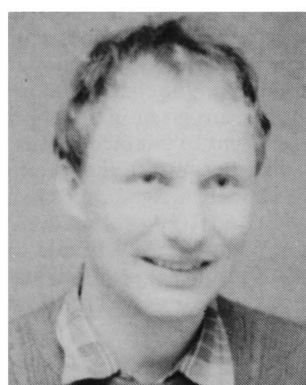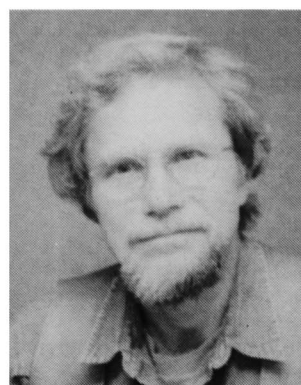
**Tine Jørgensen**   **Thomas Kruse Hansen**   **Jan Becher**

Table 1 Landmarks in TTF chemistry

1926: The first TTF derivative, dibenzo-TTF was synthesized under a general study of five-membered ring systems.[2]

1965: Deprotonation of 1,3-dithiolium salts afforded TTF derivatives for the first time.[3]

1970: First synthesis of parent TTF. TTF forms a stable purple radical cation on reaction with chlorine gas.[4]

1973: First observation of metallic conductivity in an organic solid (TTF)(TCNQ).[5] TCNQ = tetracyanoquinodimethane. Conductivity: 500 $(\Omega\text{-cm})^{-1}$.

1980: Superconductivity observed in a TTF derivative: tetramethyltetraselenafulvalene hexafluorophosphate([TMTSF]$_2$PF$_6$).[6]

1980— TTF was derivatized extensively in the search for organic (super-)conductors.

1985— Macrocylic TTF-based systems investigated with the aim of making molecular devices, sensor, switches, and shuttles.

regarded as chemical sensors as well as redox-switchable ligands.

Several systems incorporating aza-, thia-, and oxamacrocycles and -cryptates have been investigated; the redox-active unit has also been varied a great deal, with ferrocenes and metal complexes frequently used.
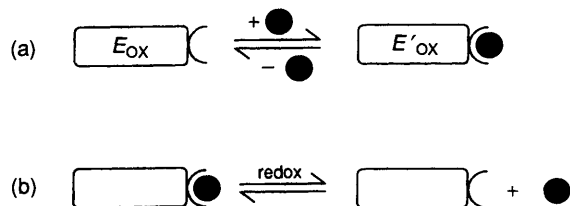
Figure 2 (*a*) Redox-detected sensor molecule; (*b*) redox-controlled ligand system.

In a *sensor system* a 'transducer' built into the molecule responds to complexation in the host with a change in physical properties. Depending on the transducer, this effect can be monitored by measuring shifts in colour, redox-properties, pH, etc.

A *redox controlled/switchable ligand system* is essentially similar, but the roles of the two parts are reversed so that a physical change of the transducer unit is imposed by an external stimulus, *e.g.* electro-chemical or in other systems light, in order to change the binding abilities of the ligand part, and thereby to control uptake and release of guest molecules. In the TTF case, it can be anticipated that oxidation of the redox-active transducer creates a positive charge which inductively decreases the binding ability of the attached host-unit towards cations.

Whichever point of view is chosen, it is evidently important to study a range of different host units, 'transducer units', and linker types/geometries in order to establish their specificity of binding, their sensitivity, and the (electro-)chemical stability of such systems.
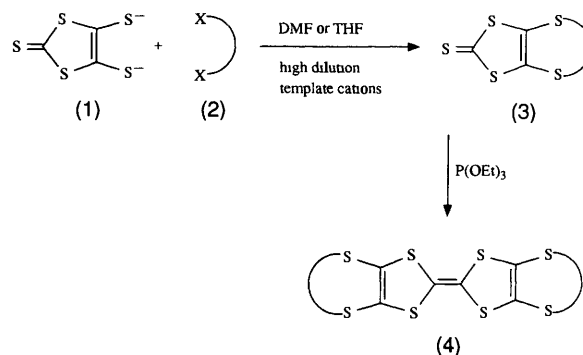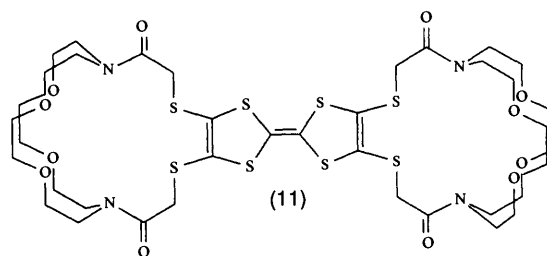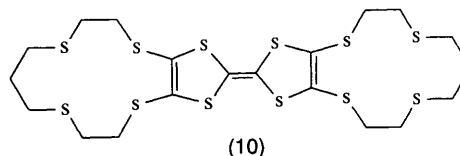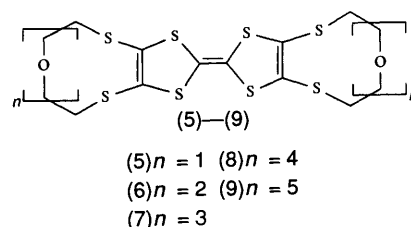
2.1 Planar TTF Derivatives

2.1.1 Synthesis

In 1985 a compound (7) was synthesized by Otsubo and co-workers,[7] in which a small crown ether was annelated to a TTF core. Since then, TTF has been incorporated in a number of different macrocyclic systems,[8] aiming at molecular sensors, switches, wires, and shuttles, in all cases exploiting the inherent electron-donor properties present in the TTF moiety.

We have utilized the readily available 1,3-dithiole-2-thione-4,5-dithiolate (1)[9] as a key starting material in the synthesis of planar TTF-based sensor systems which generally consists of a

central TTF moiety, situated between two macrocycles. Reaction between dithiolate (1) and a range of electrophiles (2) generated a series of thiones (3), which were converted into the corresponding TTF systems (4) in a standard coupling reaction with trialkyl phosphites.[10]

In Figure 4, seven TTF derivatives are shown which have been investigated as potential metal ion sensor systems.

Figure 3 General procedure for the preparation of planar macrocyclic TTF derivatives.

(5)—(9)

(5)n = 1 (8)n = 4
(6)n = 2 (9)n = 5
(7)n = 3

(10)

(11)

Figure 4 Planar TTF containing macrocyclic systems.

2.1.2 ¹H-NMR Study of TTF-Crown Ether Derivatives.[10]

Two of the TTF derivatives with crown ethers as the host part, (5) and (8), have been studied by ¹H-NMR. The chemical shift positions of compounds (5) and (8), were measured in the presence of increasing amounts of sodium ions, in order to gain insight into the changes taking place during complexation. The spectra are given in Figure 5. The spectrum of (5) (ring size equivalent to 9-crown-3) was independent of the salt concentration. In contrast, the spectrum of (8)(equivalent to 18-crown-6), showed a significant change in resonance position of the $-\text{SCH}_2\text{CH}_2\text{O}-$ protons even for a relatively low ratio of Na$^+$ ions per molecule. The fact that (5) did not show a shift in the NMR resonance positions lends support to the assumption that the changes observed for (8) were due to complex formation.

2.1.3 Cyclic Voltammetry Study of TTF-Crown Ether Derivatives

A cyclic voltammetry study was undertaken with compounds (5)—(9) which revealed in all cases a two-electron reversible
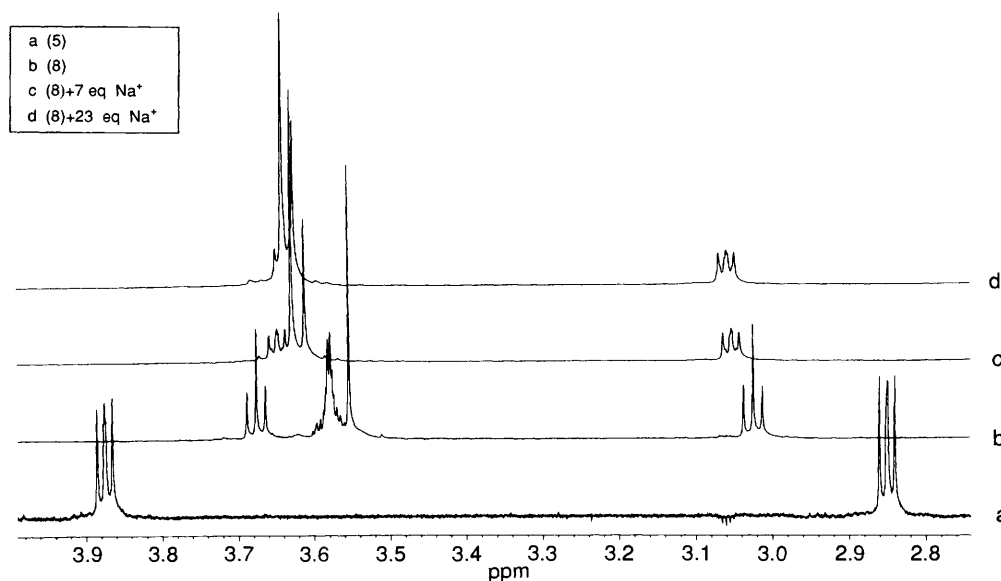
a (5)
b (8)
c (8)+7 eq Na⁺
d (8)+23 eq Na⁺

Figure 5 ¹H-NMR spectra of TTF-crown ether derivatives, with and without Na⁺ ions

oxidation with $E_{\frac{1}{2}(1)} = 0.48$ V and $E_{\frac{1}{2}(2)} = 0.64$ V. Similar experiments were performed with controlled amounts of alkali metal hexafluorophosphates added (in acetonitrile with 0.1 M TBAPF₆ and a standard calomel electrode as reference). The observed shifts in Table 2 are maximum values achieved after addition of an excess of metal salts (approximately 250 equivalents).

Table 2 Shifts in the first oxidation potentials on addition of metal ions

> 250 equiv of	Li⁺ mV	Na⁺ mV	K⁺ mV	Ag⁺ mV
(5)	0	0	0	—
(6)	0	0	0	—
(7)	0	+ 10	0	—
(8)	+ 10	+ 80	+ 10	—
(9)	0	+ 15	+ 60	—
(10)	0	0	0	+ 170
(11)	− 50	− 50	− 60	+ 90

The observed shifts were in all cases towards a more anodic (more positive) potential as expected for a repulsive coulombic interaction. Furthermore only $E_{\frac{1}{2}(1)}$ was shifted whereas $E_{\frac{1}{2}(2)}$ remained unchanged. Compounds (8) and (9) showed the largest shifts, and the selectivity profile appeared to be in good agreement with the general correlation between hole size in crown ethers and radius of alkali metal ions.[11] Thus, (8) seems to have the highest affinity to sodium ions since this ion induces the largest shift, whereas the largest shift for (9) was observed when potassium ions were added. Compared with an all-oxygen crown these sulfur-containing macrocycles had a rather low affinity. The magnitude of the shift was found to be dependent on the concentration of the alkali metal ion up to a certain limit. The cyclic voltammogram of (8) is shown in Figure 6.

An explanation of the fact that only the first oxidation peak is influenced by alkali metal ions could be sought in the following model: oxidation of the TTF unit produces a positive charge in close proximity to the ligand system which can be expected to repel the sodium ions, thereby lowering the binding constant and literally 'pushing' the alkali metal ion out of the ring. It should, however, be emphasized that sodium ion exchange is very fast compared to the timescale of the CV as well as the NMR experiments. When the interaction with sodium ions is
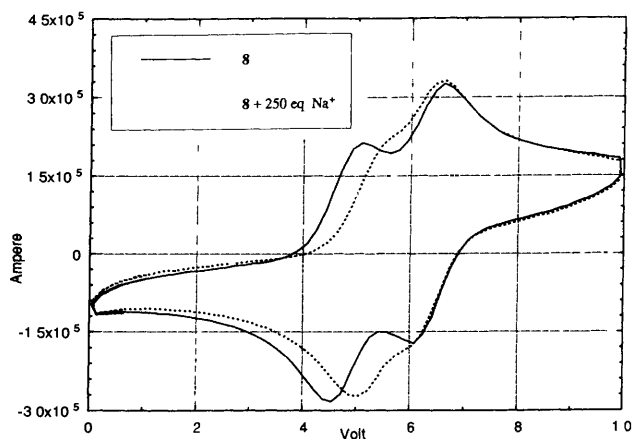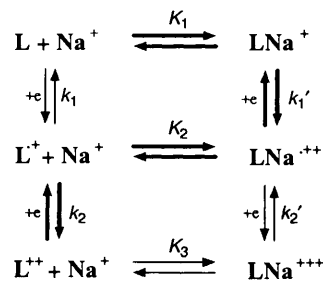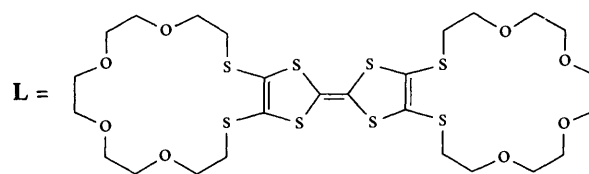

Figure 6 Cyclic voltammogram of the TTF-crown ether derivative (8)

excluded, the second oxidation peak will naturally be identical to the neutral species, as the CV indeed show. Scheme 1 summarizes the possible equilibria and suggests a principal route for the process occurring during a CV cycle:

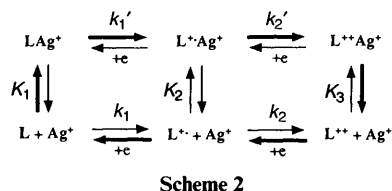The assumption that a complexed metal ion guest is expelled

Scheme 1

upon oxidation – and that it is taken up again after reduction confirms the theory, such systems could serve as redox switchable ligand systems and eventually be useful in transport studies.

2.1.4 Thiacrown Ether TTF Derivatives

When similar experiments were performed with the sulfur crowned macrocyclic system (10),[12] the cyclic voltammograms showed two reversible one-electron oxidation steps at $E_{\frac{1}{2}(1)} = 0.53$ V and $E_{\frac{1}{2}(2)} = 0.89$ V (in dichloromethane, SCE reference). No changes were observed when alkali metal ions were added. However, large anodic shifts of the first oxidation wave ($\Delta E_{pa1} = +170$ mV) were induced by addition of silver perchlorate, and in this case the second wave was affected as well ($\Delta E_{pa2} = 70$ mV). Both oxidation waves (the peak values E_{pa1} and E_{pa2}) were changed, but the reduction waves (E_{pc1} and E_{pc2}) remained unchanged (the peak values are in reversible cases related to the redox potential: $E_{\frac{1}{2}(1)} = (E_{pa1} + E_{pc1})/2$. This indicates a different situation with respect to the kinetics of the system. Probably exchange is slower in this all-sulfur system compared with the previous example, and the route outlined in Scheme 2 can be suggested for this system:

$$\begin{array}{ccccc}
LAg^+ & \underset{+e}{\overset{k_1'}{\rightleftharpoons}} & L^{+\cdot}Ag^+ & \underset{+e}{\overset{k_2'}{\rightleftharpoons}} & L^{++}Ag^+ \\
K_1 \updownarrow & & K_2 \updownarrow & & K_3 \updownarrow \\
L + Ag^+ & \underset{+e}{\overset{k_1}{\rightleftharpoons}} & L^{+\cdot} + Ag^+ & \underset{+e}{\overset{k_2}{\rightleftharpoons}} & L^{++} + Ag^+
\end{array}$$

Scheme 2

2.1.5 A Cyclic Voltammetry Study of a TTF-Cryptand

In system (11), the TTF moiety was combined with two bicyclic systems, affording the cryptand system (11) in good yield (Figure 4). The TTF unit was attached to an 18-crown-6 (O_4N_2) via an amide linker.[13] Compared to the previous systems, we have here a more flexible ligand likely to be capable of stronger binding due to the three-dimensional complexation sites. Larger binding constants may have a favourable effect on the electrochemical response to complexation, and it should be noticed that complexation can take place in more than one geometrical fashion, as proposed in Figure 7.
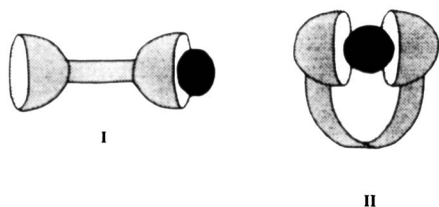

Figure 7 Geometrically different complexation modes. 1:1 binding vs. intramolecular sandwich formation.

In general, the complexed metal ion can be expected to interact with the π-system and cause a change of the ligand system in at least two different ways, both of which are relevant to the interpretation of the redox behaviour of the systems:

(i) The presence of a positive metal in the host will exert an inductive or through-bond effect on the TTF system resulting in an increase of the oxidation potential (E_{ox}).

(ii) The complexation may induce an *allosteric* effect by a change of ligand conformation. A change in geometry could result in an increase in oxidation potential provided a bending of the TTF unit is forced on the system. Conformational changes involving rotation of the outer sulfur atoms are also likely to cause changes in redox behaviour. Furthermore, if the ligand system can get in close contact with the TTF unit, the resulting electron–electron repulsion could raise the energy of the HOMO orbital, and consequently lower the oxidation potential.

When Li^+, Na^+, or K^+ ions are added to (11) both oxidation waves are shifted to lower potentials, while addition of silver ions results in a substantially different voltammogram. It is remarkable that the first oxidation wave is shifted towards a higher potential ($\Delta E_{\frac{1}{2}(1)} = +90$ mV) whereas the second moves to a lower potential ($\Delta E_{\frac{1}{2}(2)} = -70$ mV). A likely explanation is that the first electrochemical oxidation induces a conformational change due to the presence of the extra positive charge from the radical cation formed.

In conclusion, this final example of a planar TTF system showed a selective response to addition of metal cations, following the trend of the previous examples; all these systems can be considered first-generation TTF-based sensor systems.
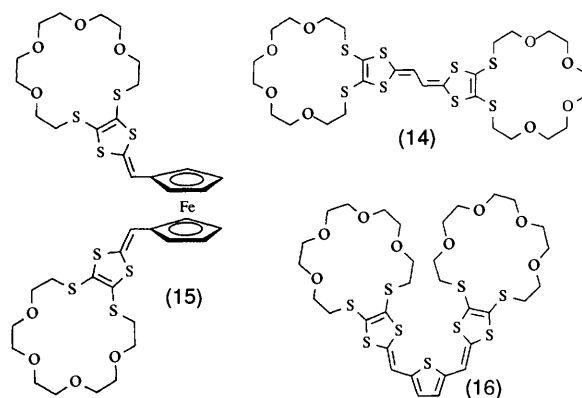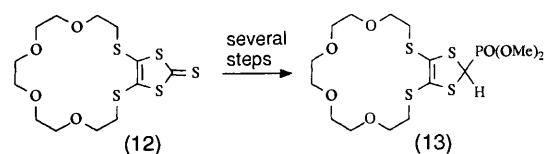
Scheme 3

2.1.6 Modifications in the TTF Unit

Having established that it is possible to influence the oxidation potential of the TTF unit via crown ether-mediated electrostatic sodium ion interactions, we undertook a study in collaboration with Dr. M. R. Bryce (University of Durham), investigating vinylogous TTF systems.[14] Key intermediates in this type of chemistry are Horner–Wittig reagents of type (13) which can be generated from thiones of type (12). When (13) was mixed with a bis-aldehyde or ketone substrate in dry THF and reacted with LDA at room temperature, we obtained 'extended TTF derivatives' of type (14)—(16). Alternatively the carbanion of (13) could be generated at -78 °C and subsequently treated with the aldehyde.

Preliminary electro-chemical data suggest that these extended compounds are less sensitive to alkali ions than their TTF counterparts. Furthermore, semi-empirical methods [on (14) and (16)] indicate that the HOMO orbitals in these cases are mainly localized in the centre of the molecules, quite far away from the crown ether. This seems to be a likely explanation of the low sensitivity which is observed for (14)—(16). It also stresses the value of computational methods for predicting the sensitivity of donor systems.

2.2 Study of Distorted, Macrocyclic TTF Derivatives

2.2.1 Synthesis

In the previous sections we have in the main discussed the planar TTF derivatives with annelated macrocyclic moieties. A key step in their synthesis is the cyclization process, which in principle can produce an unlimited number of oligomeric products. In Figure 3 only the monomeric (1:1) product is shown and indeed, by the use of high-dilution techniques it was possible to maxi-

mize the yield of this product For the pentaethylene and hexaethylene chains an efficient template effect (sodium ions were present) assured very high yields (>80%) of the monomeric product independently of dilution and solvent (DMF, THF, EtOH) However, with shorter chains (varying in length from diethylene glycol to tetraethylene glycol) it was only possible to obtain 60—65% of the monomeric products, and only if the right mixing-technique and solvent were used In these cases, higher oligomers were unavoidably formed as well (Figure 8) [15]
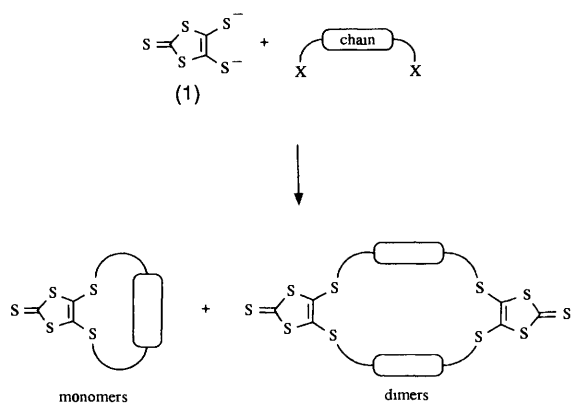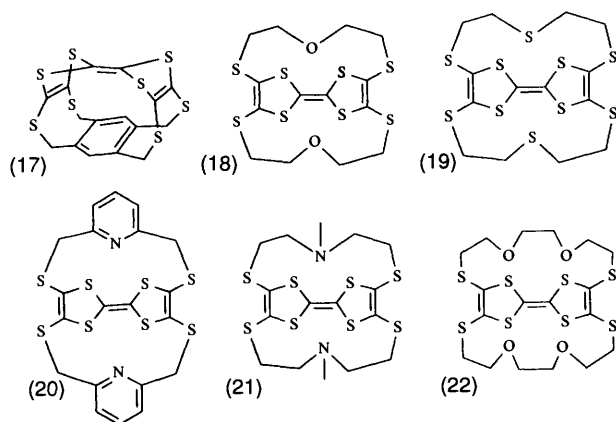

Figure 8 Formation of oligomers in the reaction of bis-nucleophiles with bis-electrophiles

Scheme 4

When the reaction conditions were modified, it was possible to isolate up to 25% of the dimeric (2 2) product In a procedure similar to the original synthesis of (17) by Mullen,[16] the dimeric products underwent an intramolecular coupling on treatment with triethylphosphite to produce novel TTF cage molecules (18)—(22) (Scheme 4), which incorporated oxygen [(18) and (22)], nitrogen [(20) and (21)], or sulfur atoms (19) in the side chains These molecules were constitutional isomers to the planar TTF crown ethers, prepared by intermolecular coupling of the corresponding 1 1 adducts, by now with the side chains running from one end of the TTF unit to the other In general, the TTF unit of these compounds was distorted away from the planarity and the degree of distortion reflected the length and flexibility of the macrocyclic chains

2 2 2 Bis-TTF-macrocycles

It should be noted that phosphite coupling normally proceeds in an intramolecular fashion, giving rise to monomeric cage molecules We have observed intermolecular coupling in a few cases, producing low yields of larger 'belt'-type macrocycles Recently Mullen et al [17] have reported a surprising reaction in which cage molecule (17) was electrolysed at a constant anodic potential,

followed by treatment with DMSO This procedure transformed the monomeric product (17) into a dimeric belt system in moderate yields (44—53%) (Scheme 6)

Applied to other monomeric TTF cages this method might lead to novel systems having the transducer and ligand units arranged in a geometrically different fashion In particular, such bis-TTF systems might be useful for making redox-switched anion-sensors, since they incorporate the possibility of generating positive charges inside a macrocyclic cavity
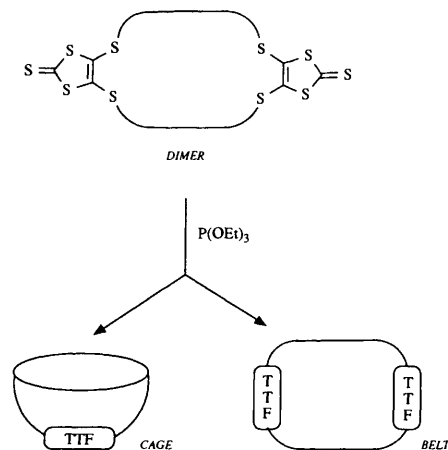
Scheme 5
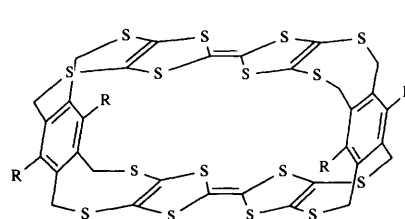
Scheme 6

2 2 3 Cage Molecules as Potential Sensors

In principle, these TTF cage molecules could also bind metal cations to produce redox-active ligands In particular a CPK model of compound (22) looked attractive because the model appeared to be bowl-shaped with the TTF unit constituting the bottom and the glycol chains forming the rim However, judging from PDMS (Plasma Desorption Mass Spectrometry)[18] and extraction experiments[19] this molecule appeared to be a poor ligand toward alkali metal ions In Figure 9 the X-ray structures of (18) and (22) are given They clearly show that the cavity of compound (18) is very small and that the two oxygen atoms point out of the cavity The cavity size in (22) looked far more attractive, but again the four oxygen atoms were pointing out of the cavity Although this might be a solid-state effect, it appeared to be a likely explanation for the poor ligand properties in solution Furthermore, the bent TTF unit probably acted as a stretched 'spring' and made the glycol chains fairly inflexible

2 2 4 Factors affecting the Oxidation Potentials

Since tetrathiafulvalene derivatives are normally planar, this series of compounds offered a unique opportunity for the study of oxidation potentials as a function of the degree of distortion and of the through-space effects of the heteroatoms in the macrocyclic chain, by comparing the X-ray crystal structures with the experimental oxidation potentials and by using semi-empirical methods (in this case MNDO-PM3) This was done in order to achieve a better understanding of the factors influencing various physical properties, which may be helpful in a
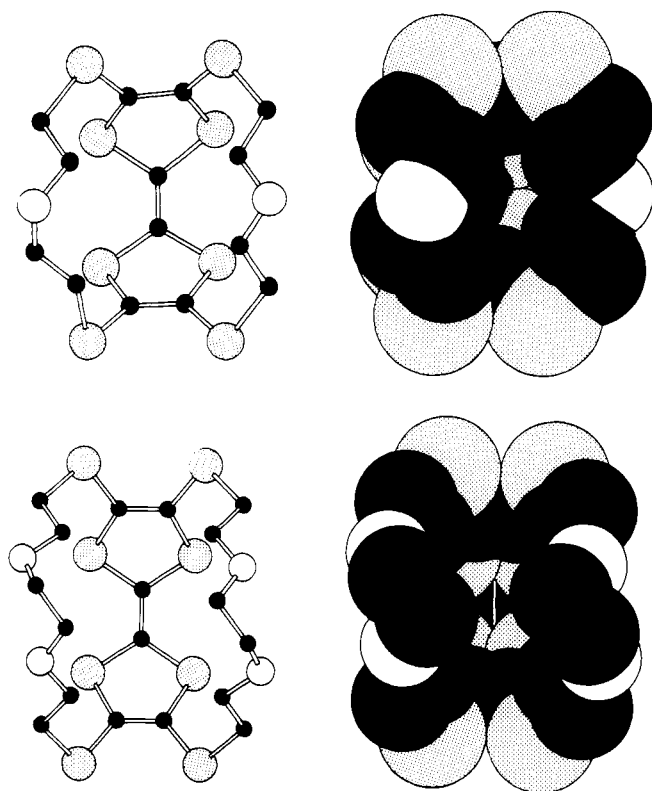
Figure 9 Ball and stick, and CPK view of molecules (18) and (22). Black, carbon; medium shade, sulfur; white, oxygen.

rational design of new compounds. The X-ray structures of compounds (17)—(21) revealed that the bending of the TTF unit was roughly similar. In contrast to ordinary TTFs which are red-orange, these molecules were almost colourless. To a first approximation, oxidation of the less bent (22) (0.41 V/SCE) would be expected to be easier than oxidation of the very bent derivatives (17)—(21) because bending should cause a less efficient delocalization of the radical cation generated by oxidation. Indeed, (17), (18), and (21) show oxidation potentials around 1.0 V. Because of its insolubility, (19) was not studied. However, (20) has an oxidation potential of only 0.27 V and is consequently more easily oxidized than (22) although it is significantly more bent. This fact was imposssible to explain using a model that assumed a simple correlation between oxidation potentials and bending. Previously it had been reported[20] that the oxidation potentials of the planar TTF derivatives correlated quite well with the ionization potentials calculated by the MNDO program. This turned out to be true for the bent derivatives as well. The calculated ionization

potentials correlated well with the experimental oxidation potentials of (17)—(22). Further insight was sought by calculating the ionization potentials of tetramethylthio-TTF with increasing degrees of bending. This showed the expected increase in oxidation potentials with increased bending. Then, by calculating the ionization potential while keeping the tetrathio-TTF core fixed in the bent conformation, and from this value subtracting the ionization potentials of the fully optimized structures with the appropriate side chains added, we were left with a new value, which could be called 'the side-chain influence'. It appeared that the glycol chains in (18) and (22) added (+ 0.18 eV; + 0.24 eV) to the ionization potentials whereas the bis-methylpyridine in (20) reduced the ionization potential (− 0.23 eV). The sulfur–nitrogen distance in compound (20) was very short (3.8 A) and the effect could be thought of as an electron–electron repulsion raising the HOMO energy. Furthermore, calculations on the face-to-face complex of TTF with benzene showed that the HOMO energy was raised as the distance between the two π-systems decreased, and the effect began to become significant when the distance fell below 4 Å. In compound (17) the distance is 4.1 Å. The trends in oxidation potentials could then be rationalized in terms of three fundamental effects. The *first* of these can be thought of as an inductive or through-bond effect, the *second* as a HOMO localization due to bending, and the *third* as a through-space effect in which electron–electron repulsion raises the HOMO energy.

The above analysis suggests that TTF compounds with lower oxidation potentials may be made by forcing an aromatic system or the lone pairs of a heteroatom close (< 4 Å) to the TTF π-system and at the same time preventing bending of the TTF moiety. In the present cage compounds the repulsion between the π-system is relieved by bending the TTF part of the molecule, and the observed oxidation potentials are a consequence of the energetic balancing of these two effects. If, however, the 'chain' could be made sufficiently rigid and longer than the TTF molecule itself, it might be possible to achieve very low oxidation potentials. One such possibility could be to use anthracene or tetracene with sufficiently short connecting chains as linkers.

2.3 Sensor Systems based on Electroactive Units other than TTF

2.3.1 Introduction

TTF is of course not the first system to have been used as the electroactive unit in sensor systems. A large variety of electro-responsive units have been used, which can be divided into those containing reducible and those containing oxidizable centres. Both categories have been built into organic- and organometallic receptor/host assemblies, to provide specific binding sites for cations, anions, or neutral organic guest species. Since P. D. Beer has published[21] an excellent review on redox-active systems prior to 1989, we will only give a brief account of recent examples here in order to place the TTF-based systems in a proper context.
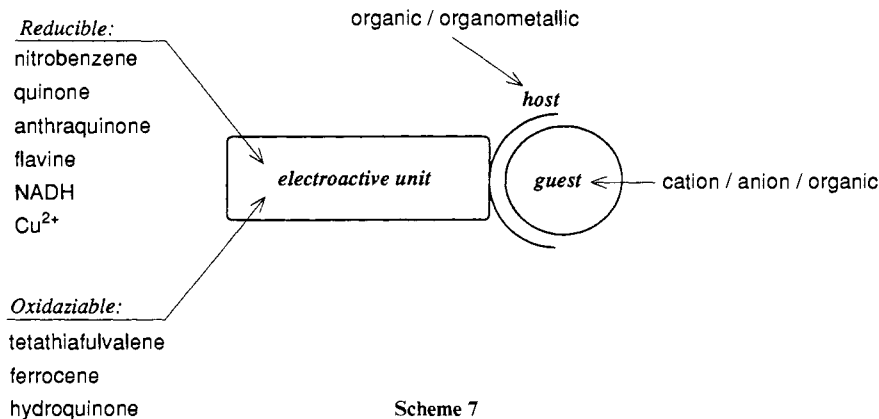
Scheme 7

2 3 2 Sensor Systems with Reducible Electroactive Units

Among the reducible electroactive units, nitrobenzene- and quinone-based systems have been used extensively During reduction such systems become negatively charged As a consequence, sensor models possessing reducible electroactive sites often show enhanced cation-binding after reduction With the presence of a positively charged cation in the host compartment, a system will usually exhibit an anodic shift of the reduction potentials The magnitude of the anodic shifts is often strongly dependent on the charge/radius ratio of the alkali metal ions The shifts generally decrease in the order $Li^+ > Na^+ > K^+$, reflecting the fact that ion pairing between metal cations and the respective reduced anion radical redox centre is stronger for smaller cations which posses a higher polarizing power
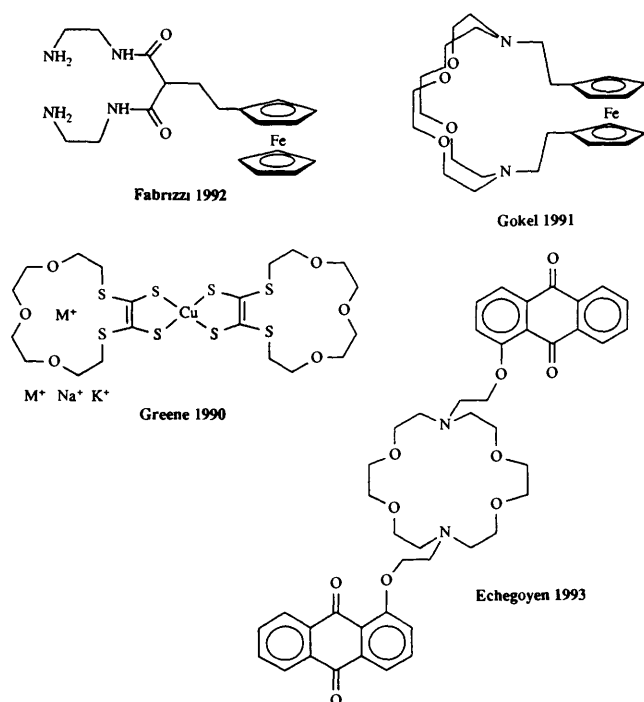

Fabrizzi 1992

Gokel 1991

M^+ Na^+ K^+

Greene 1990

Echegoyen 1993

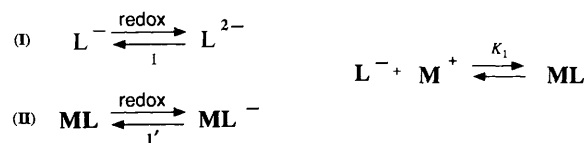**Figure 10** Four sensor model systems containing different redox active units

The anthraquinone-based sensor system made by Echegoyen *et al* [22] in 1993 (Figure 10), had potential as a redox-switched shuttle for cations and electrons across membranes When the system was studied by cyclic voltammetry it showed two quasi-reversible redox pairs, indicating that the two anthraquinone units acted independently and uncoupled First, two radical anions were formed, and then two dianions were generated After addition of 0 5—2 equivalents of sodium tetraphenyl borate, two additional redox couples were observed simultaneously at a more anodic potential, corresponding to an easier reduction of the complex All four redox couples were resolved, although this system was not expected to show a high binding affinity for sodium ions In most other electrochemical investigations with simple quinones, only potential shifts (rather than a splitting into two couples) are observed as a function of the concentration of metal ion Distinct waves are normally only observed when the initial binding constant K_1 of the neutral ligand system is large In such a case, the differences of the formal redox potentials for the free ligand (E_f^{free}) and the complex ($E_f^{complex}$) can be used to calculate quantitative values of the electrochemical binding enhancement of metal cations, according to the following equation [23]

$$E_f^{complex} - E_f^{free} = \frac{-RT}{nF}\left\{\ln\frac{(K_1)}{(K_2)}\right\} \tag{1}$$

(K_1 = binding constant for unreduced ligand, K_2 = binding constant for reduced ligand)

It was possible to use equation 1 on the anthraquinone system to calculate the following binding enhancement values (for sodium ions) after reduction, $1\ 4 \times 10^3$ (K_2/K_1) and $7\ 5 \times 10^2$ (K_3/K_2), K_3 = the binding constant for doubly reduced ligand These enhancement values were calculated on the basis of the corresponding $E_{\frac{1}{2}}$ values for each of the waves and the enhancement was relatively large compared with structurally related systems This made the new system a promising redox-switchable ligand system since the enhancement value is of obvious importance in transport studies where cycling between reduction and oxidation should promote release and uptake of ions

Another reducible redox unit was incorporated in Green's sensor system [24] from 1990 This system resembled compound (7), having two 15-crown-S_2-O_3 macrocycles as ligand part of the molecule Instead of TTF, a Cu^{III} tetrathiolate unit (in such compounds, a formal oxidation state III for copper is not unusual) was incorporated as the redox-active centre with either Na^+ or K^+ as counter ions Independently of the counterion a reversible reduction at $-\ 0\ 70$ V, and an irreversible oxidation at $+\ 0\ 24$ V were observed A relatively large shift in the reduction potentials was induced when an additional amount of alkali metal salt was added to the system Replacing tetrabutylammonium tetrafluoroborate by sodium tetrafluoroborate as supporting electrolyte induced an anodic shift of 175 mV, whereas smaller shifts were induced by using lithium or potassium salts The magnitude of the shifts of $E_{\frac{1}{2}}$ and the order ($Na^+ > Li^+ > K^+$) indicated that a simple ion-pairing model alone could not explain the shifts, and thus cation binding by the host was assumed to play a significant role in the processes In contrast to the previous anthraquinone example, this system behaved in an electrochemically similar fashion compared to the TTF-based systems Instead of the appearance of a new resolved redox couple, a shift in the position of the redox wave was induced by addition of alkali metal ions This reflected that the electrochemical steps 1 and 1' were averaged together

(I) $L^- \underset{1}{\overset{redox}{\rightleftharpoons}} L^{2-}$

(II) $ML \underset{1'}{\overset{redox}{\rightleftharpoons}} ML^-$

$L^- + M^+ \overset{K_1}{\rightleftharpoons} ML$

Scheme 8

When K_1 is small, and the binding between the ligand system and the metal ion in question is weak, only one wave is observed In such cases, it was necessary to add a large excess of sodium cations in order to achieve the maximum shift The rather large shift value may be explained by the proximity of the cations bound in the host to the redox-active centre and the fact that dithiolene complexes are strongly delocalized allowing complexed cations to interact strongly with the redox-active centre

2 3 3 Sensor Systems with Oxidizable Electroactive Units

The two remaining examples in Figure 10, both contain a ferrocene unit as the redox-active centre In the system reported by Gokel and co-workers [25] in 1991, ferrocene was linked to a 18-crown-N_2-O_4 macrocycle forming a cryptand structure, which proved to be an efficient sodium and potassium ion responsive assembly With only 0 25 equivalents $NaClO_4$ added to the ligand system, a second, well-resolved redox couple appeared in the CV at a more positive potential (+ 188 mV) As the Na^+ concentration was increased further, the peak currents of the new redox couple also increased at the expense of the original couple, which disappeared completely in the presence of 1 0 equivalents of Na^+ cation The cathodic shift was indicative of a destabilization of the oxidized form of the complex compared to the reduced form This should allow the system to serve as a redox-switchable ligand because the oxidized form had a lower affinity for Na^+ compared with the reduced form However, it still possesed some affinity for Na^+, as evidenced by the com-

plete reversibility of the redox couple corresponding to the complex The binding ratio was calculated for Na$^+$, K$^+$, and Ca^{2+}, using equation 1 Addition of lithium salts did not induce any new redox couples For sodium ions it was found that $K_1/K_2 = 1\ 5 \times 10^3$, for potassium ions $K_1/K_2 = 1\ 2 \times 10^2$, and for calcium ions $K_1/K_2 = 4\ 3 \times 10^4$ The cyclic voltammograms after addition of 0 0, 0 5, and 1 0 equivalents of Na$^+$ are reproduced in Figure 11
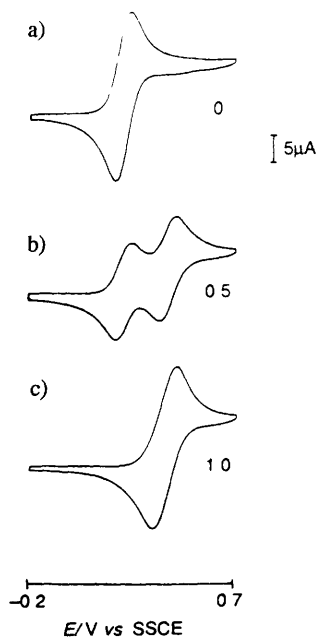

Figure 11 Cyclic voltammograms of Gokel's ferrocene cryptand system, after addition of (a) 0 equivalents, (b) 0 5 equivalents, and (c) 1 0 equivalent of NaClO$_4$

The second ferrocene-based system shown in Figure 10 was made by Fabbrizzi *et al* [26] in 1992 Their amido-linked podand system showed a surprising cathodic shift in the redox potentials, when complexed with Ni^{2+} All cyclic voltammograms were made in aqueous solutions at pH 10 5, with NaClO$_4$ present as electrolyte Before complexation, oxidation took place at $E_{\frac{1}{2}} = +0\ 402$ V (*vs* NHE) This peak was shifted -42 mV to $E_{\frac{1}{2}} = +0\ 360$ V upon addition of Ni^{2+} Thus, the close presence of a positively charged centre (Ni^{2+}) made it easier to form the positively charged ferrocenium subunit Electrostatic effects were invoked in order to explain this behaviour along with the fact that the system lost two protons during complexation When the complex was formed, the amide nitrogens would carry a formal negative charge, leading to stabilization of the positively charged oxidized species The negative charge, formally placed on the nitrogens, would not be completely offset by the Ni^{2+}, consequently oxidation would occur at a lower potential

3 A Molecular Shuttle with a TTF-station

3.1 Introduction

As described in the previous sections the fundamental redox properties of TTF have been exploited in several sensor applications A quite different type of system will be introduced here in which TTF's ability to form charge-transfer complexes is as important to the principle as TTF's unusual redox properties This new kind of device, coined the 'molecular shuttle' by Stoddart *et al* ,[27] works according to a principle by which two 'stations' are connected in a chain structure and encircled by a 'shuttle' A prerequisite for obtaining reasonable yields is that the shuttle and the station should be attracted to each other

In the case where the electron-donating TTF serves as the

station, the shuttle should be electron accepting This charge-transfer interaction has been demonstrated beautifully in the case[28] where the acceptor (shuttle) is a cyclobis(paraquat-*p*-phenylene) tetracationic macrocycle and TTF is the donor (station) Mixing of the components afforded a crystalline charge-transfer complex whose structure was determined It turned out to have an interesting channel-type structure (Figure 12) where the tetracationic shuttle formed the channel and TTF occupied the central cavity The next step will involve the TTF being incorporated into a chain This type of chemistry was initially perfected with donors other than TTF, but here only the TTF-containing version will be mentioned
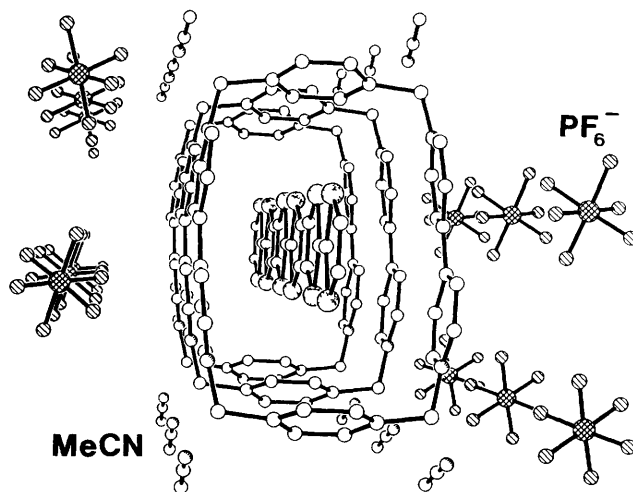

Figure 12 Crystal structure of the charge-transfer complex between TTF and the tetracationic macrocycle

3.2 The Rotaxane-based Shuttle containing a TTF Station

The 'shuttle' made by Stoddart and co-workers[27] was essentially a complicated *rotaxane* [The word rotaxane is derived from the Latin words *rota* meaning wheel and *axis* for axle] One rotaxane they made incorporated a cyclobis(paraquat-*p*-phenylene) macrocyclic unit as the shuttle, which moved on an axis containing one TTF station and two hydroquinol stations

Since the shuttle was a good electron acceptor, it was able to 'thread' the chain, and was held in place by either one of the electron-donating stations (TTF or hydroquinol) by charge-transfer interactions Since TTF is a better electron donor ($E_{\frac{1}{2}} = +0\ 5$ V) then the hydroquinol units ($E_{\frac{1}{2}} = +1\ 1$ V) it is likely that the acceptor macrocycle will form a complex predominantly with the TTF unit The rotaxane, shown in Figure 13, was then formed by blocking the two ends of the chain with 4-trityl-phenylether units which served as 'stoppers' Alternatively the shuttle could be assembled at the last step, using a chain with the stoppers already in place The synthesis itself was an impressive example of 'self-assembly' where non-covalent forces were used to hold components together during assembly, with relatively high yields as a result An NMR investigation of the fully assembled rotaxane showed that selective oxidation of TTF forced the shuttle away from TTF to one of the hydroquinol units This was the result of the oxidized form of TTF (*i e* a radical cation or a dication) being a less efficient donor than neutral TTF Furthermore, the positive charge on TTF$^+$ repelled the tetracationic acceptor macrocycle by coulombic forces Future applications can be envisaged, following major developmental work, in molecular data storage

4 Molecular Switches

4.1 Introduction

The design, synthesis, and manipulation of *molecular devices* is the challenging subject of the field *molecular electronics* Over a
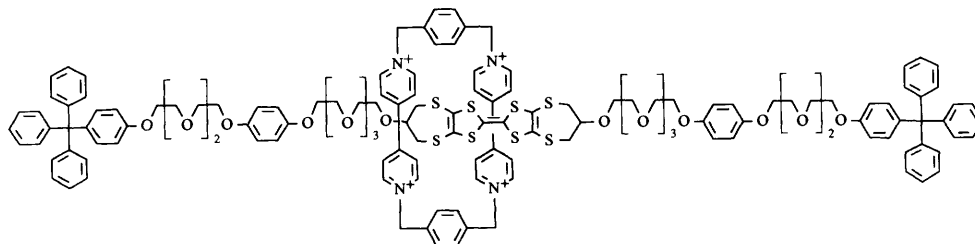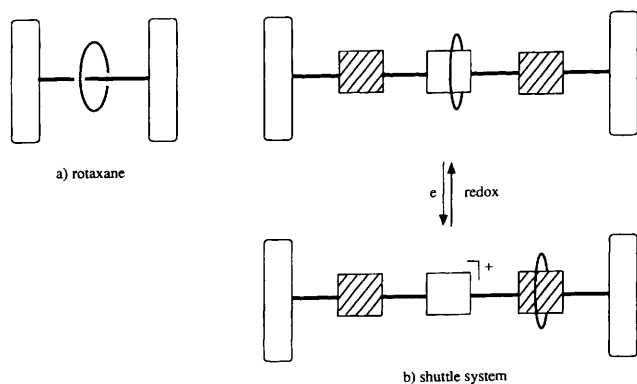
Figure 13 The TTF-containing 'shuttle system'

a) rotaxane
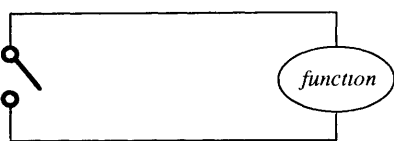
b) shuttle system

Scheme 9

Figure 14 A switch controls a function

period of 60 years, the scale of components has decreased from a typical device size of about 10^{-1} m down to 10^{-6} m However, before further miniaturizing of components based upon semiconductors is possible, problems of over-voltage and heat exchange will have to be overcome

A *switch* is an essential component in electronics, which in principle can be almost any device (or ultimately a molecule), able to interchange between two different states The *on/off*-component can be addressed by electric current, radiation, heat, light *etc*

4.2 A TTF-controlled Molecular Switch

Lehn and Goulle have recently reported an example[29] of a molecular device capable of switching a fluorescent state on and
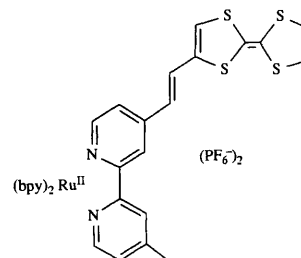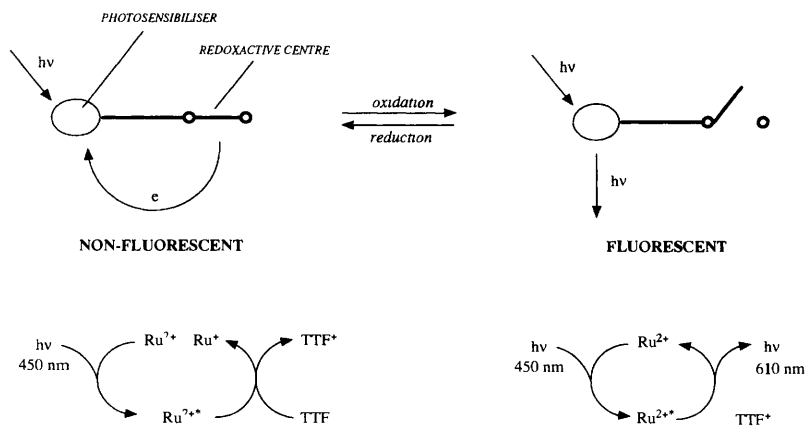
Figure 16 The processes controlling the switch

Figure 15 The TTF-containing switch

off The system incorporated a TTF unit and a photosensitive unit The on/off function followed the oxidation state of the TTF moiety A $Ru^{II}(bpy)_3^{2+}$ system was chosen as the photosensitive unit, and it was attached to the TTF centre by a small vinyl linker (Figure 15) Ruthenium II complexes of bipyridine, are known to be fluorescent, when exited at $\lambda = 450$ nm, giving rise to an emission with $\lambda = 610$ nm When the TTF present in the switch is neutral, the fluorescence is quenched by electron transfer from TTF to Ru^{2+*} [$E(TTF^+/TTF) = 0\ 43$ V, $E(Ru^{2+*}/Ru^+) = 0\ 84$ V]

When the TTF unit was oxidized to form the radical cation, by applying a potential 100 mV higher than the first oxidation step of TTF, the fluorescence was moderately restored However, the intensity was only 30% compared to a control sample containing $Ru^{II}(bpy)_3^{2+}$ It was not possible to return to the nonfluorescent state, probably because of decomposition of the compound Similar results were obtained, when ferrocene, quinone, and hydroquinol were used as the redox active units Nevertheless, this result is encouraging in the developing field of molecular devices

5 Supramolecular TTF-containing Wires made by Self Assembly

The problem of addressing molecular electronic components is of great importance An obvious solution is to connect devices *via* 'electrical' wires of similar dimensions Recently a step towards TTF-based molecular wires was made by Jørgensen *et al* [30] By combining the TTF unit with lipophilic chains capped with large hydrophilic endgroups, (similar to the gelforming arborol aggregates reported by Newkome[31]), Jørgensen *et al* aimed at self-assembled structures where the conductivity was obtained by π–π interactions between partly oxidized TTF
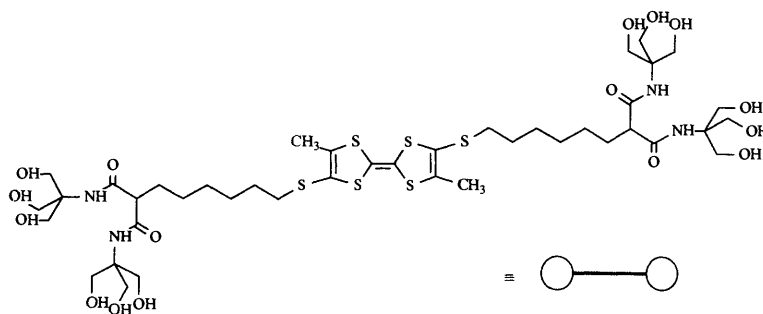

NON-FLUORESCENT

FLUORESCENT

Figure 17 The molecular unit for 'wire-formation'.

molecules. In comparison with ordinary macroscopic wires, the hydrophilic groups would resemble the insulation, and the TTF-stack serve as the conducting copper core.

A gel was indeed formed when the prepared compound (Figure 17) was dissolved in 25% EtOH in hot water. After cooling to room temperature an opaque, orange-yellow gel was formed, which could be oxidized to a green form by addition of aliquots of iodine in EtOH. Phase contrast light microscopy of the gel revealed textures of string-like structure with a length of several microns. These were also visible when crossed polarizing filters were used, showing that the aggregates were ordered structures over distances of several microns. Transmission electron microscopy on gels stained with phosphotungstic acid showed narrow string- or band-like structures, with diameters ranging from 300—1000 Å. Single strings of the aggregates should have a diameter of around 50 Å, therefore the structures were interpreted to be superstructures consisting of several strings. UV–(Vis)–NIR spectroscopy of the oxidized gel revealed a CT-band typical for stacked TTF molecules.

Since the gross morphology is in accordance with a wire-type structure, this is another encouraging result *en route* to commercial applications even though this currently may seem a remote goal. The field of molecular nanostructures is still young, but it seems that an increased ability to control the self-assembly of such superstructures has already been achieved.
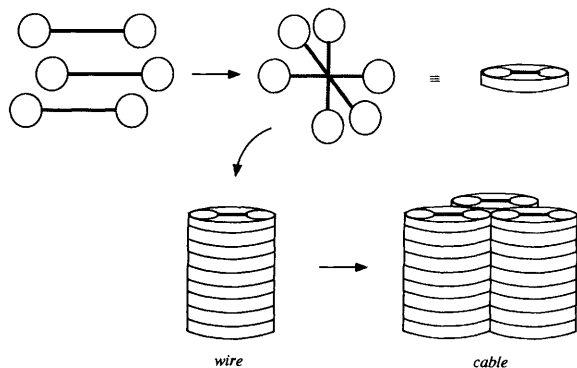

Figure 18 Self-assembly of the TTF derivative forms wires and cables.

6 A Bis-TTF-podand forms C$_{60}$-complexes

The recently reported charge-transfer complex between a TTF derivative and C$_{60}$ will be mentioned here as a final example of the versatility of TTF as a building block in supramolecular chemistry. Sugawara and co-workers[32] synthesized a bis-BEDT-TTF derivative (Figure 20) that formed an intriguing tweezer-like structure when complexed with C$_{60}$.
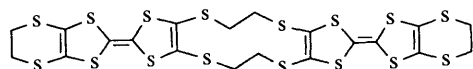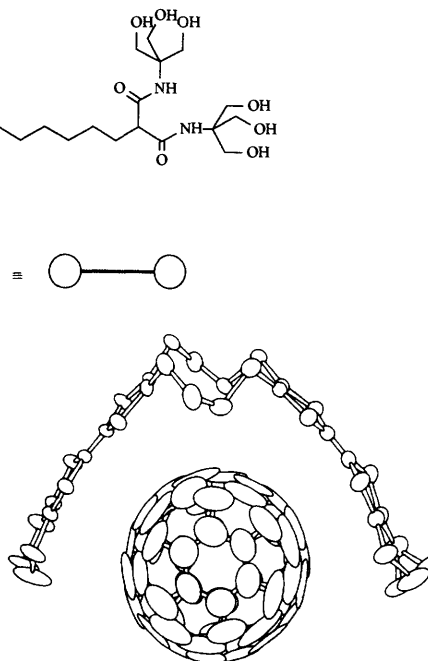

Figure 19 Twin-donor TTF derivative.

Figure 20 ORTEP drawing[32] of C$_{60}$ surrounded by the twin donor viewed along the threefold axis of C$_{60}$.

As a result of the flexible ethylene bridges used to connect the two donor moieties, the inter-planar angle was variable. In neutral crystals the two TTF's were almost parallel, taking a U-shaped conformation, while the angle was 90° in ClO$_4^-$ salts, and the cavity of the podand-like host was increased even more when C$_{60}$ was complexed.

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