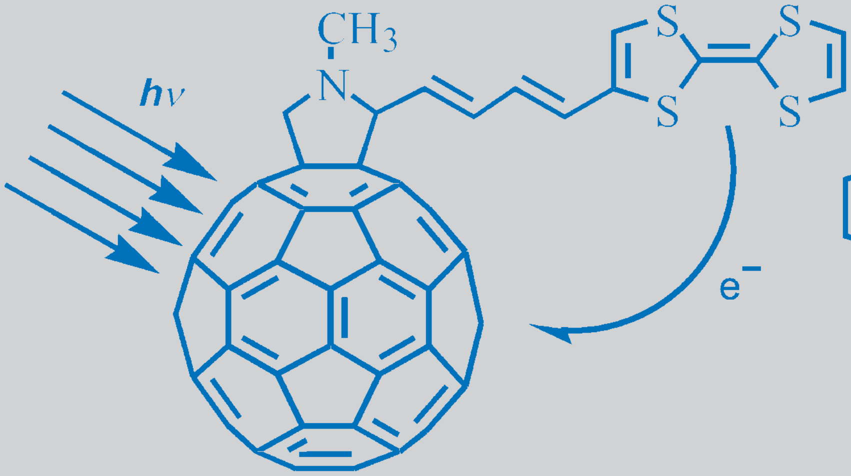
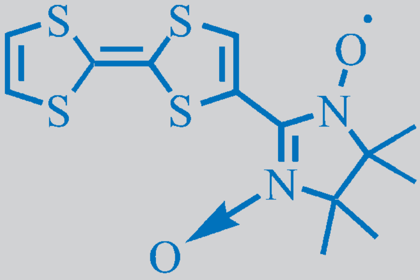
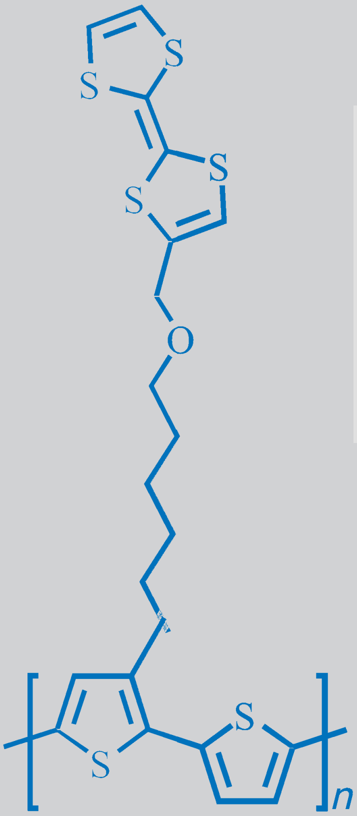
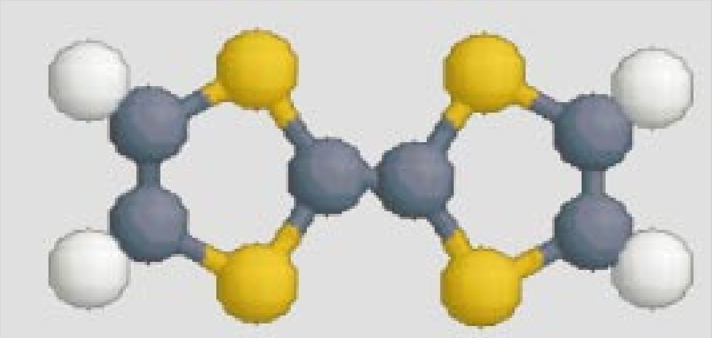
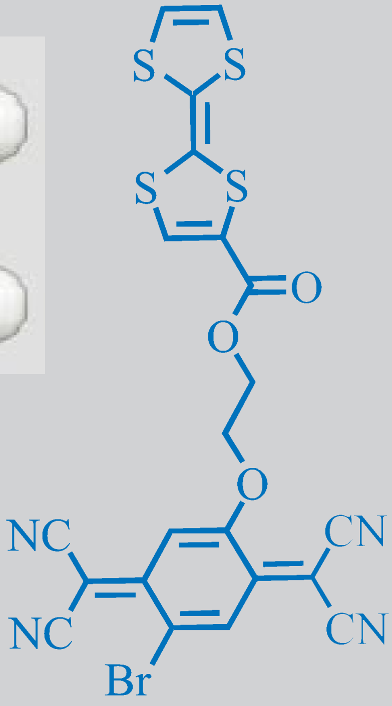
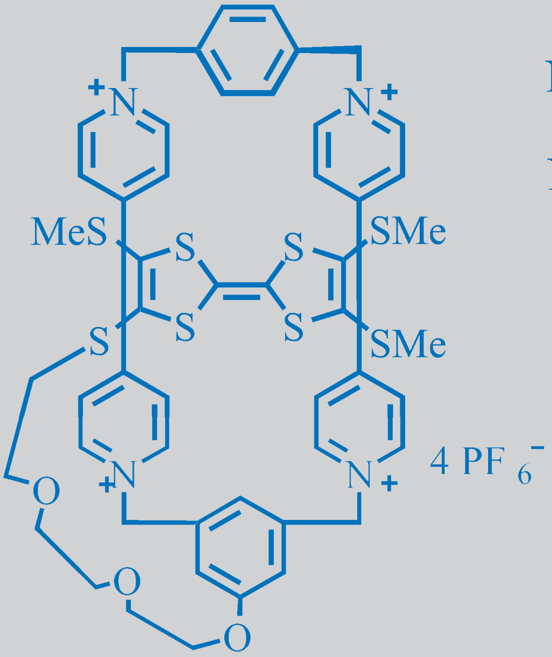












Tetrathiafulvalene and its derivatives offer new possibilities at the molecular to the supramolecular levels, as well as in macromolecular aspects.

ANGEWANDTE
CHEMIE

New Concepts in Tetrathiafulvalene Chemistry

José L. Segura and Nazario Martín*

Dedicated to Professor Michael Hanack
on the occasion of his retirement

Tetrathiafulvalene (TTF) and its derivatives were originally prepared as strong electron-donor molecules for the development of electrically conducting materials. This Review emphasizes how TTF and its derivatives offer new and in some cases little-exploited possibilities at the molecular to the supramolecular levels, as well as in macromolecular aspects. TTF is a well-established molecule whose interest goes beyond the field of materials chemistry to be considered an important building block in supramolecular chemistry, crystal engineering, and in systems able to operate as machines. At the molecular level, TTF is a readily available molecule which displays a strong electron-donor ability. However, its use as a catalyst for radical–polar crossover reactions, thus mimicking samarium iodide chemistry, has only recently been addressed. Important goals have been achieved in the use of TTF at the macromolecular level where TTF-containing oligomers, polymers, and dendrimers have allowed the preparation of new materials that integrate the unique properties of TTF with the processability and stability that macromolecules display. The TTF molecule has also been successfully used in the construction of redox-active supramolecular systems. Thus, chemical sensors and redox-switchable ligands have been prepared from TTF while molecular shuttles and molecular switches have been prepared from TTF-containing rotaxanes and catenanes. A large synthetic effort has been devoted to the preparation of the so-called organic ferromagnets, many of which are derived from TTF. The main task in these systems is the introduction of ferromagnetic coupling between the conduction electrons and localized electrons. TTF has also played a prominent role in molecular electronics where TTF-containing D-σ-A molecules have allowed the preparation of the first confirmed unimolecular rectifier. Recently, it has been confirmed that TTF can display efficient nonlinear optic (NLO) responses in the second and third harmonic generation as well as a good thermal stability. These findings can be combined with the redox ability of TTF as an external stimuli to provide a promising strategy for the molecular engineering of switchable NLO materials. Fullerenes endowed with TTF exhibit outstanding photophysical properties leading to charge-separated (CS) states that show remarkable lifetimes.

Keywords: donor–acceptor systems · electron transfer · materials science · supramolecular chemistry · tetrathiafulvalene

1. Introduction

Shortly after Wudl reported the synthesis of tetrathiafulvalene (TTF, **1**) in 1970,[1] the first "organic metal" tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF–TCNQ) was discovered.[2, 3] In 1979, the first molecule-based superconductor based on the Bechgaard salts $[\mathrm{TMTSF}]_2\mathrm{X}$ ($\mathrm{X} = \mathrm{PF_6}^-$, $\mathrm{AsF_6}^-$)[4, 5] was prepared by using a selenium-containing TTF analogue, namely tetramethyltetraselenafulvalene (TMTSF). Since then, and during almost two decades, a huge amount of work has been carried out to enhance the electron-donating power of TTF analogues in order to improve the conductivities of salts and charge-transfer (CT) complexes derived from them. However, during the last few years, the utility of TTF derivatives as building blocks in macromolecular and supramolecular structures, as molecule-based ferromagnetic compounds, as synthetic intermediates in organic chemistry, as a donor moiety in intramolecular donor–acceptor (D-A) systems in nonlinear optic (NLO) materials and in association with the fullerene core, as well as in the preparation of liquid crystalline materials and Langmuir–Blodgett (LB) films has made TTF one of the most extensively studied molecules. Thus, during the last few years,

---

[*] Prof. Dr. N. Martín, Dr. J. L. Segura
Departamento de Química Orgánica
Facultad de Química
Universidad Complutense, 28040 Madrid (Spain)
Fax: (+34) 91-3944103
E-mail: nazmar@eucmax.sim.ucm.es

partial aspects of the synthesis and properties of tetrathiafulvalenes have been reviewed (Table 1).[6–24].

Table 1. Recent reviews on specific aspects of TTF.

Main author	Title
M. R. Bryce	Recent progress on conducting CT salts[6]
V. Khodorkovsky	Molecular design of organic conductors[7]
M. R. Bryce	Increasing dimensionality in the solid state[8]
G. Schukat	TTF chemistry[9]
J. Garín	Reactivity of TTF and TSeF[10]
K. B. Simonsen	Functionalization of TTF[11]
T. Otsubo	TTF dimers[12]
M. Adam	TTF oligomers[13]
J. Becher	TTF oligomers[14]
M. R. Bryce	Macromolecular TTF chemistry[15]
T. Jørgensen	Supramolecular TTF chemistry[16]
K. B. Simonsen	Macrocyclic and Supramolecular TTF chemistry[17]
M. B. Nielsen	Two- and three-dimensional TTF macrocycles[18]
E. Coronado	Hybrid polyoxometalates-TTF materials[19]
J. Roncali	Linearly π-extended TTF derivatives[20]
P. Day	Molecular magnetic semiconductors, metals and superconductors[21]
M. R. Bryce	TTF as π-donors in intramolecular CT-materials[22]
M. B. Nielsen	Tetrathiafulvalenes as building blocks in supramolecular chemistry[23]
M. R. Bryce	Functionalised tetrathiafulvalenes: new applications as versatile π-electron systems in materials chemistry[24]

The purpose of this account is not to duplicate those aspects previously reviewed in the different fields but to give an overview of recently synthesized TTF-containing systems and to summarize their new applications which are different from the extensively studied electrical conductivity. Thus, we will briefly mention the most recent developments on the chemical modifications of TTF-containing materials and concentrate on the new applications of this unique molecule.

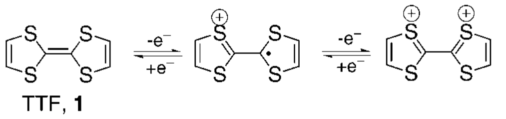
2. Current Trends in the Development of New TTF-Containing Materials

Tetrathiafulvalene is a nonaromatic 14-π-electron system in which oxidation to the cation radical and dication occurs sequentially and reversibly at relatively low potentials ($E^1_{1/2} = 0.37\,\text{V}$ and $E^2_{1/2} = 0.67\,\text{V}$ in dichloromethane versus the saturated calomel electrode). In contrast to the neutral TTF molecule, both the cation radical and dication are aromatic in the Hückel sense as a result of the 6π-electron heteroaromaticity of the 1,3-dithiolium cation, and, therefore, while $\text{TTF}^{+\bullet}$ and TTF^{2+} have a planar D2h symmetry, neutral TTF has a boatlike equilibrium structure with C2v symmetry.[25] However, because of the small difference between planar and boatlike conformations, TTF (**1**) is very flexible and can

N. Martín J. L. Segura

Nazario Martín studied chemistry at the Universidad Complutense de Madrid (UCM), where he obtained his Doctorate at the Department of Organic Chemistry under Professor C. Seoane in 1984. After spending a year working on X-ray contrast agents in a pharmaceutical company, he worked as a postdoctoral fellow (1987-1988) at the Institut für Organische Chemie der Universität Tübingen under Professor M. Hanack on electrically conducting organic materials. In 1994, he was a visiting Professor at the Institut for Polymers and Organic Solids (IPOS) at the University of California, Santa Barbara (UCSB) working with Professor F. Wudl on modified fullerenes. Since 1989, he has been Associate Professor of Organic Chemistry at the University Complutense (UCM). His research interests range over electroactive molecules with emphasis on the optoelectronic properties of electron-donor tetrathiafulvalene (TTF) derivatives and electron acceptors, the chemistry of fullerenes, and, in particular, the design and synthesis of electroactive organofullerenes. He is also active in the asymmetric synthesis of heterocyclic systems and reactive intermediates. He has published around two hundred papers, and he is currently a member of the International Advisory Editorial Board of The Journal of Materials Chemistry and Editor of the spanish journal Anales de la Real Sociedad Española de Química.

José L. Segura studied chemistry at the Universidad Complutense de Madrid, where he obtained his diploma in 1989 and his Ph.D. in 1994 under Professor N. Martín and Professor C. Seoane working on the synthesis of inter- and intramolecular charge transfer complexes derived from TTF, TCNQ, and DCNQI. In 1993 he visited the group of Professor W. Daily (University of Pennsylvania) where he worked in the area of strained-ring organic syntheses. After post-doctoral stays in the group of Prof. M. Hanack (University of Tübingen) working on the syntheses of electroluminescent conjugated polymers and in the group of Professor F. Wudl (University of California at Santa Barbara) working on the functionalization of C_{60} fullerene, he joined the faculty in the Department of Organic Chemistry at the Universidad Complutense de Madrid in 1995.



TTF, **1**

appear in various conformations depending on the donor–donor and donor–acceptor interactions in the crystals.

In the following sections we will outline the main research lines towards the development of new TTF-containing systems at the molecular, macromolecular, and supramolecular level.

2.1. Molecular Level

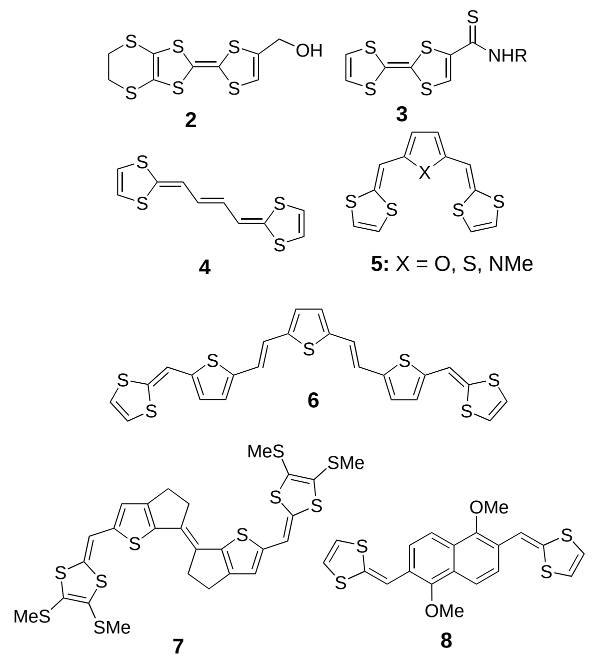
As Bryce has pointed out,[22] recent progess in the syntheses of TTF-containing systems can be divided into the four following points:

- The possibility of synthesizing TTF in multigram quantities.[26]
- The availability of a great amount of monosubstituted TTF derivatives by electrophilic substitutuion of lithiated TTF.[10]
- The new selective protection/deprotection chemistry of the thiolate groups of the 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) system which provides a number of versatile TTF building blocks.[27]
- The discovery of the cyanomethyl protecting group.[11]

The reading of the comprehensive review articles by Schukat et al.[9] and Garín[10] is highly recomended to get insight into the rich chemistry of tetrathiafulvalene.

Although in recent years different chemical modifications have been carried out on the TTF unit to prepare building blocks for macro- and supramolecular chemistry at the molecular level, the "classical" chemical modifications carried out on the TTF skeleton are aimed at increasing the electrical conductivity[6] and are related to the above outlined properties: on the one hand by the fine tuning of the donor ability by changing the substitution pattern and, on the other hand, by changing sulfur to other chalcogens or by introducing chalcogens in a peripheral position on the TTF moiety. These modifications increase the overlap between the chalcogen atoms and result in the formation of dimers, highly ordered stacks, or two-dimensional sheets.

The increase in the dimensionality of the charge-transfer materials has been identified as a priority provided that low-dimensional conductors are unstable and a suppression of the metallic state is produced as the temperature decreases. Thus, during the last few years, the large development in the chemistry of TTF[9–11, 28] has been taken advantage of to develop different alternative routes for the replacement of sulfur by other chalcogen atoms so as to increase the dimensionality in tetrathiafulvalene chemistry. In 1995, Bryce reviewed some of these strategies[8] including hydrogen bonding in functionalized TTF derivatives (**2**, **3**) and the syntheses of TTF analogues with extended π conjugation (**4**–**8**).[29] The syntheses and properties of TTF analogues with polyalkenic (**4**), heterocyclic (**5**), π-conjugated heterocycles such as oligoheteroarylenevinylene (**6**), and other rigid π-conjugated spacers (**7**) have been reviewed in more detail by Roncali.[20] More recently, conjugated carbocyclic spacers (**8**) have also been used. Roncali points out that by precise control of the spacer length it should be possible to tune the conduction mechanism between the "vertical" mixed-valence conduction of TTF charge-transfer salts to the "horizontal" polaron/bipolaron conduction of linear systems.[20]



2 **3** **4** **5:** X = O, S, NMe **6** **7** **8**

Otsubo et al.,[12] and more recently Becher et al.,[14] reviewed the different TTF dimers.[30] As a result of the intramolecular through-bond or through-space interactions between the TTF units, these kinds of TTF derivatives display multi-stage redox behavior which might provide the possibility of controlling the stoichiometry, band filling, and molecular assembly in desired conductive complexes.[12] The intramolecular interaction between the two redox moieties, and hence between the stacks or slabs, can be modified in a controlled way by changing the nature of the bridging group between the TTF units. Figure 1 shows the different types of bis-TTF derivatives.

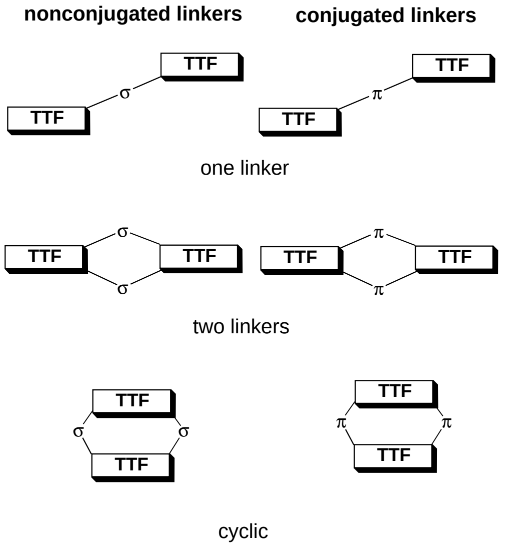
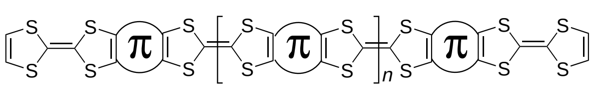
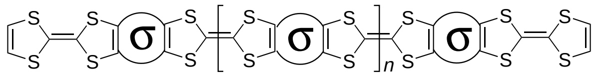


Figure 1. Different types of bis-TTF derivatives.[14]

This approach has been developed by Adam and Müllen.[13] They proposed the syntheses of monodisperse TTF oligomers by linking TTF subunits through two bridges at positions two and three of the tetrathiafulvalene molecule using either π or σ bonds (**9** and **10**, respectively). The possibility of introducing functional groups on the oligotetrathiafulvalenes allows soluble materials to be obtained and also makes polycondensation and polyaddition reactions accessible.[13] Thus, the compounds can be used as electroactive conducting rods.[31] Other kinds of TTF oligomers and polymers will be discussed in Section 2.2.5.



9

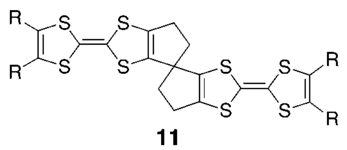


10

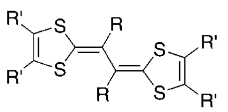
A further approach towards the increase of dimensionality involves the syntheses of nonplanar TTF derivatives.[32] Although for many years there has been a general trend to design planar TTF analogues for conducting CT complexes in order to attain efficient intermolecular interaction, it should be noted that CT complexes of nonplanar molecules still show conductivities comparable to CT complexes derived from related planar molecules.[32] Some representative examples of nonplanar TTF derivatives are **11**–**17**. The use of spiroconjugation has been claimed as a way of adding dimensionality in the design of organic molecular materials.[33] Thus, TTF spirodimers such as **11**[34] and **12**[35] have been synthesized in which two TTF units are annelated on spirocyclic systems and hence are rigidly fixed in orthogonal directions.

We have recently reported the first optically active TTF dimers.[36] These chiral TTF dimers (**13a**,**b**) were prepared by Wittig or Wittig–Horner reactions from the bis(triphenylphosphonium) salt of a binaphthyl system and the respective formyl-TTF unit. Although no X-ray data are available to confirm their ability to form materials with enhanced dimensionality, they are able to form CT complexes.

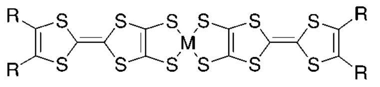
Contrary to the unsubstituted vinylogues **14** (R = H), derivatives containing bulky substituents, such as phenyl (Ph) or thienyl (Th) groups, exhibit a highly twisted structure.[37] These types of compounds can be synthesized electrochemically by using 1,4-dithiafulvenes as starting materials. As a result of this lack of planarity, neither the formation of radical cation[38a] and dication salts[38b] of these compounds nor their use as components for organic conductors had been reported until recently. Yamashita et al. reported in 1998 the first examples of cation radical salts of TTF vinylogues containing substituents at the vinyl positions (**14**, R = Ph, R′ = (CH=CH)$_2$).[38a] Interestingly, although the X-ray data observed for this phenyl-substituted vinylogue show a highly distorted structure, the molecular structure is drastically changed upon oxidation. Thus, the cation radical salt **14**·PF$_6$ has a planar TTF vinylogue skeleton with the aryl groups twisted and amost orthogonal to the framework of the TTF vinylogue. The donor molecules form an interesting two-dimensional columnar structure.



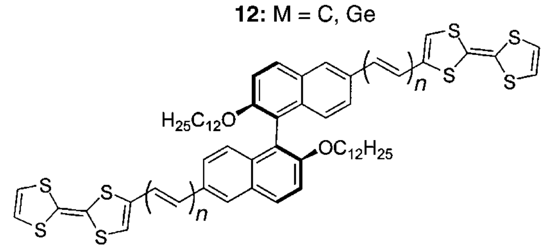
11



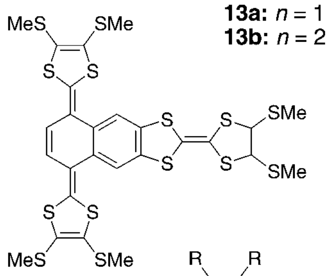
14: R = Ph, Th, H



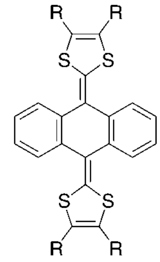
12: M = C, Ge



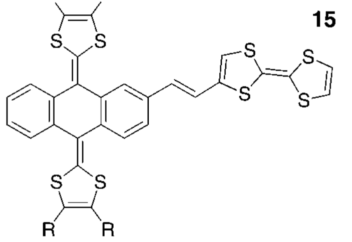
13a: *n* = 1
13b: *n* = 2



16



15



17: R = H, SCH_3,
or $\widehat{\mathrm{R}\ \mathrm{R}}$ = SCH_2CH_2S

The incorporation of cyclic "spacer" groups between two 1,3-dithiafulvenyl rings has also been used to extend π conjugation in TTF-based systems. Similarly to the previously studied TTF vinylogues **14**, derivatives **15** exhibit highly distorted geometries with the central quinoid ring bent into a boat conformation. This distorsion allows the relief of the steric congestion between the *peri*-hydrogens and the sulfur atoms.[39] Upon oxidation, donors **15** adopt an almost planar conformation with the two dithiolium cation rings nearly orthogonal to the anthracene moiety, thereby preventing conjugation between the two heterocyclic rings.[8] We have recently reported the preparation and redox properties of more π-extended TTF analogues of **15**[40] as well as of related dimeric compounds.[41] These compounds exhibit a first oxidation wave involving two electrons, and lead directly to the formation of the dication as a result of the corresponding radical cation having a high instability because of the above-mentioned steric interactions. Hudhomme, Gorgues, et al.

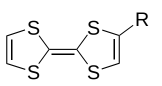
have reported the synthesis of **16**, which contains a TTF unit fused to a π-extended TTF system.[42] Cyclic voltammetry (CV) investigations on **16** showed three reversible oxidation peaks, the first one corresponding to a 2 e^- process arising from the π-extended *p*-quinodimethane analogue of TTF, while the following two correspond to 1 e^- oxidation peaks related to the TTF moiety. These are of interest for studying the possible formation of radical cation salts.

New hybrid TTF dimers (**17**) formed by the parent TTF molecule in conjugation with the π-extended TTF **15** have recently been reported. Electrochemical studies show that these compounds mainly retain the electrochemical properties of both the TTF and the π-extended TTF components. Interestingly, the CV studies reveal an intramolecular electronic interaction between the two moieties. These strong electron donors were able to form CT complexes with dichlorodicyano-*p*-benzoquinone (DDQ), with a donor:acceptor stoichiometry of 1:3.[43]

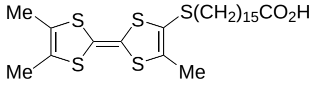
Yamashita et al. have reported heterocyclic analogues of **15** in which heterocyclic rings are fused to the central quinonic core.[44] Substitution of the fused benzene rings by the less sterically demanding thiadiazole rings results in planar π-extended TTF derivatives. Yamashita et al. have also prepared derivatives containing a fused benzene ring and a thiadiazole ring; these molecules have a nonplanar structure and form metallic radical cation salts.[45] The cyclic voltammetric measurements on these compounds show one reversible oxidation wave involving two electrons, which indicates that the cation radical states are thermodynamically unstable. However, their radical cation salts were isolated as single crystals when they were electrochemically oxidized in the presence of Bu_4NPF_6 in tetrahydrofuran. These radical cation salts show electrical conductivity, and the solvent molecules seem to play an important role in the construction of the crystal structure.[46]

To finish with this short resume of the lastest trends in the development of new TTF derivatives as electrically conducting materials, it is worth mentioning that in spite of the fact that studies of conducting charge-transfer complexes have concentrated almost exclusively on single crystals, other alternatives have appeared during the last few years. The Langmuir–Blodgett (LB) technique offers the possibility of assembling organic molecules with a greater level of structural control than in the corresponding crystalline material, and makes it possible to incorporate conducting CT salts into practical devices.[47] With this aim, amphiphilic TTF derivatives have been prepared by attaching hydrophobic tails (**18**–**29**) or charged aromatic substituents (**30**) to the TTF core and used to make LB films of CT complexes and CT salts.[48]

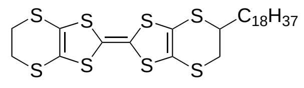
Organic chemical vapour deposition has been used to grow TTF–TCNQ layers.[49] The stoichiometry of the deposits can be controlled by varying the evaporation temperature of the precursors. While the use of amorphous substrates does not induce in-plane textures and the microcrystals are randomly distributed, the use of substrates such as KCl or KBr induce in-plane orientations. Therefore, the influence of the substrate on the in-plane texture of the film is very important in providing a way to control the growth of films of charge-transfer complexes.[50]



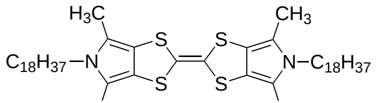
18: $R = C(O)C_{15}H_{31}$
19: $R = C(S)O\text{-}C_{16}H_{33}$
20: $R = C(O)OC_{16}H_{33}$
21: $R = CH_2OC(O)C_{17}H_{35}$
22: $R = S(CH_2)_2OC_{18}H_{37}$
23: $R = C(S)NHC_{18}H_{37}$
24: $R = SC_{16}H_{33}$



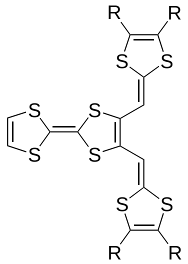
25



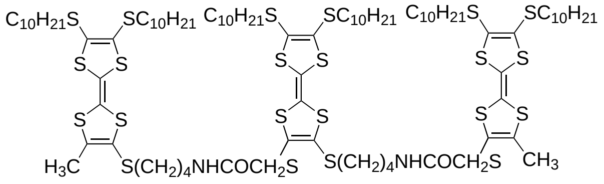
26



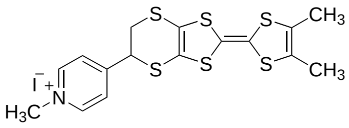
27



28: $R = CO_2C_nH_{2n+1}$
$n = 1,2,4,8$



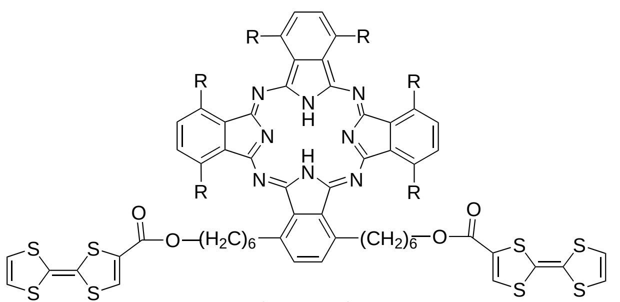
29



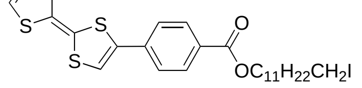
30

An alternative to the above methods for obtaining an assembly of ordered arrays of TTF-containing molecules is based on the preparation of mesogenic derivatives by either attaching a TTF unit to a mesogenic liquid crystalline center or by incorporating substituents which show mesomorphic behavior with the TTF moiety.[51–55] Some of the early citations[51] presented poorly characterized liquid crystal behavior. In contrast, **31**–**35** are representative recent examples of TTF derivatives exhibiting "proper" liquid crystal behavior.

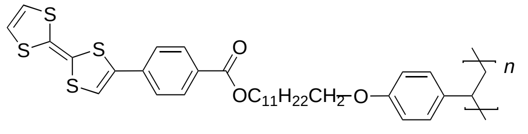
Cook et al. attached the TTF unit to a discotic phthalocyanine liquid crystalline center to obtain the first discotic liquid crystalline tetrathiafulvalenylphthalocyanine derivative (**31**). They observed by UV/Vis spectroscopy of spin-coated films that the molecular architecture of this material can be changed by oxidation with iodine vapor and heating to within the mesophase region.[54] In 1995 Müllen et al. reported the synthesis of the TTF derivative **32**. Although the available data could not distinguish between a nematic or smectic phase, the mesogenic behavior of **32** was used by incorporating it as a side chain into a polymer, thus enabling the electron-donating properties of TTF systems to be combined with the general characteristics of high molecular weight



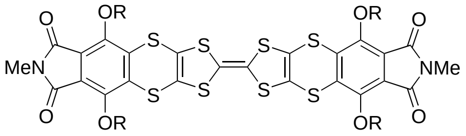
31: R = C_8H_{17}



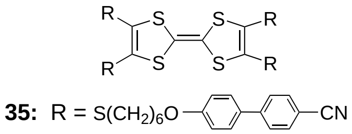
32



33



34: R = $(CH_2)_2CH[(CH_2)_8CH_3]_2$



polymers, such as film forming and processability.[53] Unfortunately, polymer **33** exhibited no liquid crystalline phase after polymerization, which indicated that the TTF moieties act as separate and independent molecules.

In 1998 Bushby et al. reported on the enantiotropic liquid crystalline behaviour of TTF derivative **34**.[55] However, upon p-doping with 2 mol% of antimony pentachloride to give a radical cation concentration of about 10^{20} cm^{-3} (EPR), the conductivity of the alternating current was lower than is normally found in doped discotic liquid crystals. This result probably indicates that the radical cations formed are highly localized and/or fixed by the counterions.

Compound **35** is a thermotropic liquid crystal which displays monotropic behavior and gives the complex $\mathbf{35}\cdot I_{10}$ on mixing solutions of **35** and I_2 in CH_2Cl_2.[52] The results of microscopy observations and X-ray data unambiguosly indicate a nematic phase for the iodine-doped compound. The fact that this compound shows mesomorphic behavior after doping with iodine is a very promising result for the use of liquid crystalline TTF derivatives in forming highly ordered supramolecules and new multiproperty materials.

This section should not conclude without mentioning the great amount of work devoted to the obtention of tetrathiafulvalenes as π-electron donors for intramolecular donor–acceptor materials. However, this topic was thoroughly reviewed by Bryce in 1999,[22, 24] and the reader is referred to these excelent review articles for complete coverage of the field. Some of the most interesting aplications of this type of material will be presented in Section 3.2.

2.2. Macromolecular Systems

In this section we will consider dendrimers, polymers, as well as macrocyclic systems containing one or more TTF units.

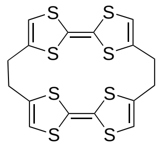
2.2.1. TTF-Containing Macrocycles

Tetrathiafulvalenophanes (cyclophanes containing one or more TTF units) have been extensively studied. These types of compounds could have been included in the previous section devoted to the nonplanar TTF derivatives. However, the interest in these compounds arises not only for the increased dimensionality of their charge-transfer salts but mainly because of their implications in macro- and supramolecular chemistry where they might act as receptors for electron-defficient compounds and, therefore, might be used for electroactive recognition.

In 1997 Nielsen and Becher reviewed[18] the two- and three-dimensional TTF macrocycles and classified them into seven classes:

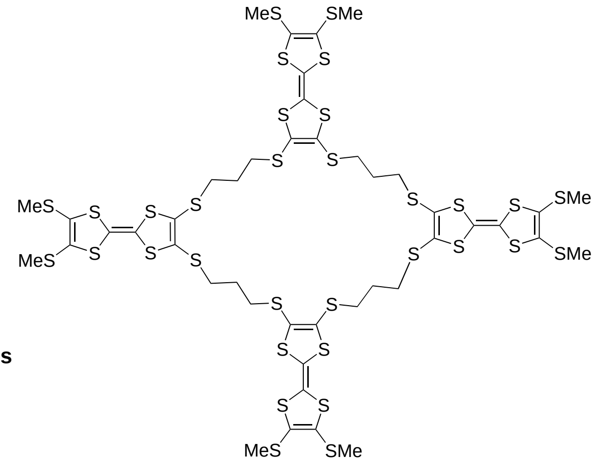
1. Monomacrocycles, such as **36**, which include macrocycles containing one or two TTF units with different spacers.
2. Oligomeric monomacrocycles including tris-, tetra- (**37**), and pentameric TTF monomacrocycles.
3. Bismacrocycles where the central TTF unit can be cyclized either in the peripheral or the lateral positions and which include TTF crowns, such as **38** and **39**, which contain two crown ether moieties annelated to the central TTF unit, and oligomeric bismacrocycles, such as **40**, which are similar to the previous ones but contain more than one TTF unit.
4. Ribbon compounds, such as **41**, in which the tetravalency of the TTF unit is used to prepare ribbon-type systems.
5. Quadruple-bridged tetrathiafulvalenophanes in which the TTF units can be either stacked in a face-to-face arrangement (**42**) or crisscross overlapped (**43**).
6. Cage molecules, such as **44**, which are macrobicyclic tetrathiafulvalenophanes with three bridges.
7. Donor–acceptor cyclophanes, such as **45**, in which the TTF moiety and an acceptor unit are incorporated into the same cyclophane.[23]

Recent research into these types of compounds includes the syntheses of new bis(tetrathiafulvalene)cyclophanes[56] and crisscross-overlapped tetrathiafulvalenophanes,[57, 58] the synthesis and characterization of the first double-bridged tetraselenofulvalenophanes synthesized by Otsubo et al.,[59] the convergent synthesis of rigid macrocycles containing one or two TTF units,[60] and the synthesis and characterization of geometrically constrained tetrathiafulvalenophanes[61] by Becher et al. For a comprehensive treatment of this specific



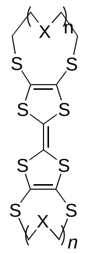
36

Monomacrocycles

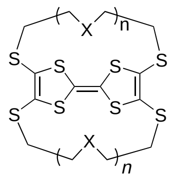


37

Oligomeric macrocycles

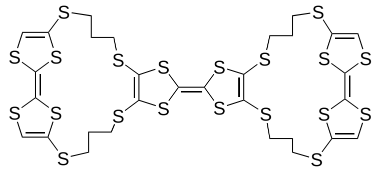


38



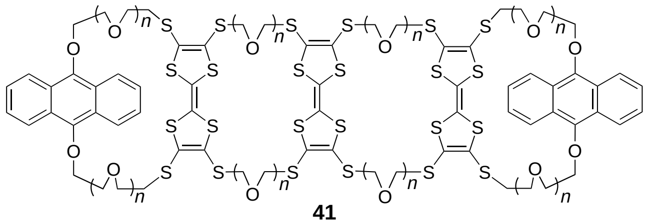
39

TTF crowns



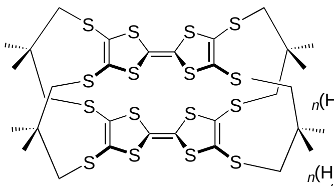
40

Oligomeric bismacrocycles



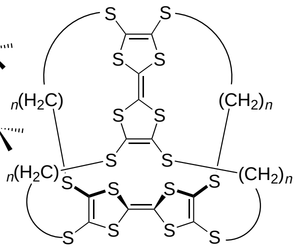
41

Ribbon compounds



42

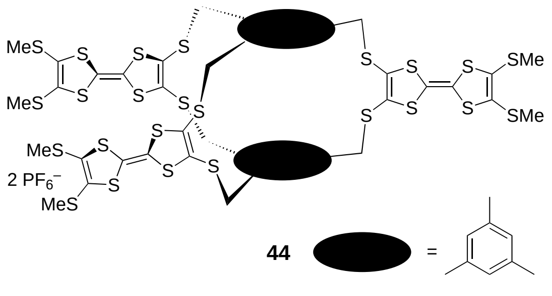
Face to face



43

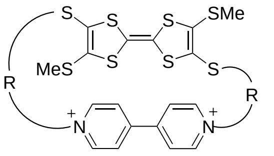
Crisscross overlapped

Quadruple-bridged tetrathiafulvalenophanes



44

Cage molecules



45

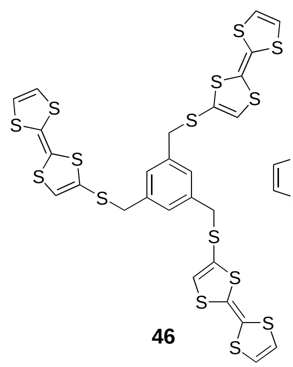
Donor-acceptor cyclophanes

topic the reading of the review article by Nielsen and Becher[18] is highly recommended.

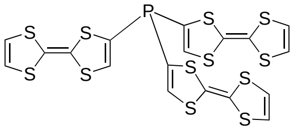
2.2.2. TTF Trimers

In Section 2.1 we explained how TTF dimers and oligomers are of interest because they display multi-stage redox behavior which might provide the possibility of controlling the stoichiometry, band filling, and molecular assembly in desired conductive complexes.[12] Thus, other researchers have concentrated their efforts on the syntheses of systems containing three or more TTF units. The oligomeric bismacrocycle **40**,[62] the ribbon compound **41**[63] and the cage molecule **44**[64] are examples of systems containing three nonconjugated TTF units. Other examples of systems containing three nonconjugated TTF moieties are **46**,[65] **47**,[66] and **48**,[67] while **49**,[68] **50**,[69] **51**,[70] **52**,[71] **53**,[72] and **54**[73] contain three conjugated TTF units.

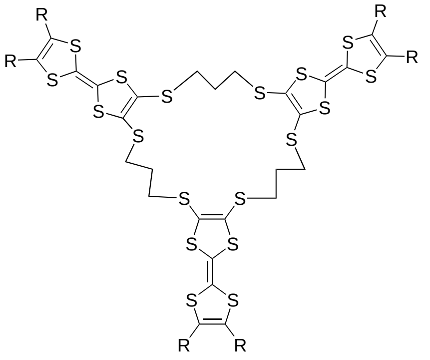
Different degrees of interactions between the TTF units are observed depending upon the geometry of the molecule and the spacer connecting the TTF units. As these donor molecules contain three redox-active moieties and each TTF unit can release two electrons, they should be oxidizable up to the hexacation. However, in general, the electrochemical redox properties of the nonconjugated TTF derivatives correspond to the formation of trications and hexacations, with no intermediate oxidation states detected. These findings suggest that there are no Coulombic repulsion effects between the charged TTF moieties, and that the individual TTF units are electronically isolated by the spacer groups and do not interact to any significant extent. Thus, for derivatives **40**, **44**, **46**, and **47** only two oxidation waves were observed, which



46



47

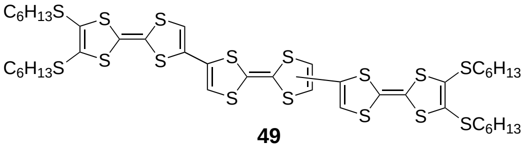


48: R = H, SCH_3

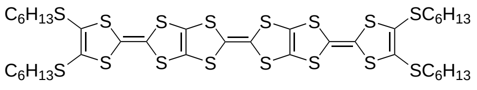
correspond to the oxidation to the trications and hexacations. However, it is worth mentioning the impact that the molecular geometry has on the electrochemical behavior. The cyclic voltammogram of the triple-layered TTF-phane **40** in which the central TTF unit is perpendicular to the peripheral ones shows two redox waves: the first process involves a two-electron process and the second one involves a four-electron process. It is reasonable to assign the first two-electron process to the oxidation of the two outer TTF units while the second wave remains unresolved and appears as a coalescence of the remaining oxidations.[62] On the other hand, the cyclic voltammetric measurements of an isomeric compound of **40** in which the three TTF units are not perpendicular but parallel show three waves: the first two-electron wave corresponds to the oxidation of the outer TTF units, the second one-electron wave to the oxidation of the inner TTF unit, and the third three-electron wave to the simultaneous oxidation of all the TTF units.[62] The different electrochemical behavior of these two isomeric compounds indicates that the columbic repulsion between the TTF units is less important in the perpendicularly oriented TTF-phane and gives an idea of the importance of the molecular structure on the electrochemical behavior.

Another example showing the influence that the molecular geometry has on its redox properties can be seen with the cage molecule **44**. It is a rigid molecule in which the TTF moieties are linked to the spacer through the 2,3 positions, with the three TTF groups pointing out of the cavity. Only one broad first redox wave is visible, which indicates there are weak interactions between the redox centers.[64] An isomeric cage compound in which the TTF groups are linked through the 2,7 or 6 positions exhibits three redox waves for the generation of the radical cation state. This result indicates that there are strong through-space Coulombic interactions as a result of the close proximity of the three redox moieties.[64]

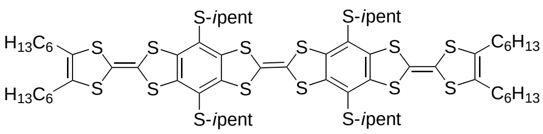
In the case of some conjugated systems containing three TTF moieties, six possible electrochemical processes have been observed which indicate the strong interaction between the conjugated TTF units. This is the case for trimer **51**, for



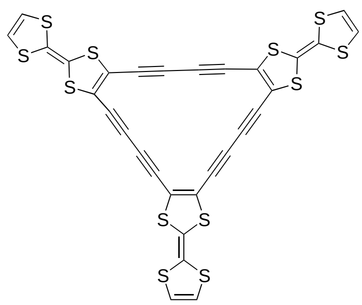
49



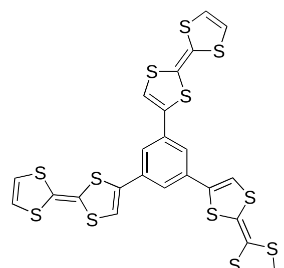
50



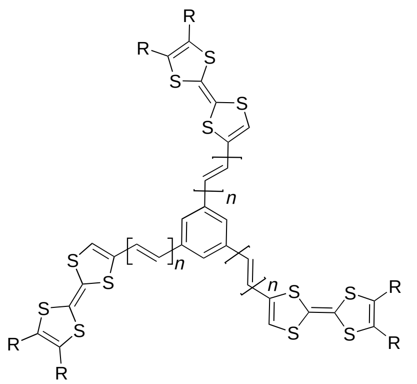
51



52



53



54: R = H, SC_6H_{13}, $SC_{12}H_{25}$; n = 1, 2 which six oxidation waves can be observed in the cyclic voltammogram. This compound represents the first example of a fully reversible stepwise oxidation of a donor containing three redox-active TTF subunits up to a hexacation.[70]

Single-bonded TTF trimers **49** show five reversible waves in their cyclic voltammograms, while in the double-bonded analogue **50**, the redox process is composed of three stages of two-electron transfer to form the hexacation. In this last case, it is worth mentioning how the electron-donating ability of this type of fused-TTF system decreases as the number of fused TTF moieties increases. Thus, under the same conditions, the first oxidation wave was observed at +0.62 V for the tetrahexylthio-substituted TTF, at +0.67 V for **50**, and at +0.65 V for the analogue containing only two fused TTF units. Moreover, while one-electron processes were observed for the first oxidation wave in the case of the substituted TTF molecule and the analogue containing two fused TTF units, a two-electron process was observed for **50**. This result occurs because of the small orbital energy difference between HOMO and HOMO-1 in **50** which may cause HOMO–HOMO-1 mixing in the dicationic state. As a result, on-site coulombic repulsion in $\mathbf{50}^{2+}$ should considerably decrease because they are mainly located on the outer TTF moieties as a consequence of the participation of HOMO-1 (which is mainly localized in the outer TTF units, Figure 2). As a consequence, the dicationic state of **48** is largely stabilized, which justifies the double-electron transfer observed for the first redox stage in the cyclic voltammogram.[67]

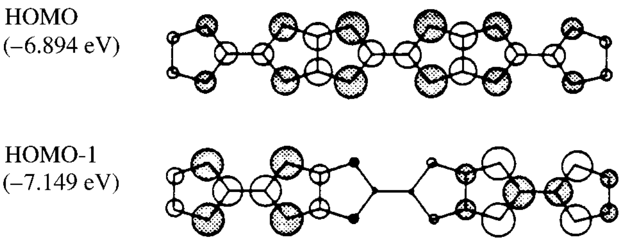


Figure 2. HOMO and HOMO-1 (HF/6-31G* level) of **50**. The radii of the circles are approximately proportional to the LCAO coefficients. (Reprinted with permission from ref. [69].)

Rubin et al. have recently reported the synthesis of tetraethynyltetrathiafulvalenes as precursors to the highly unsaturated tetrathiafulvalene trimer **52**. This compound will have the potential to form CT salts with enhanced dimensionality provided that the overall π-rich surface can enhance the lateral and π-stacking interactions between the individual units.[71] However, to the best of our knowledge, the synthesis of **52** has not yet been reported.

TTF trimers in which the TTF units are located at the 1,3,5-positions of a benzene ring have also been synthesized to examine the interactions of the TTF radical cations in the triradical trication states. If a ferromagnetic interaction between TTF units could occur in the CT complex or radical–cation salts of molecules such as **53**, a quartet ground state would be expected and a ferromagnetic CT complex might be generated.[72] Compound **53** possess oxidation potentials similar to that of TTF: it is oxidized by two three-electron steps, which indicate that small interactions occur between the TTF units as a consequence of the lack of conjugation through the *meta* positions of the benzene ring. This compound forms a conducting CT complex with TCNQ ($\sigma_{RT} = 30\,\mathrm{S\,cm^{-1}}$, compressed pellet, 4 samples).[72] To the best of our knowledge, no report about the interactions of TTF units in the radical cation species have yet been published.

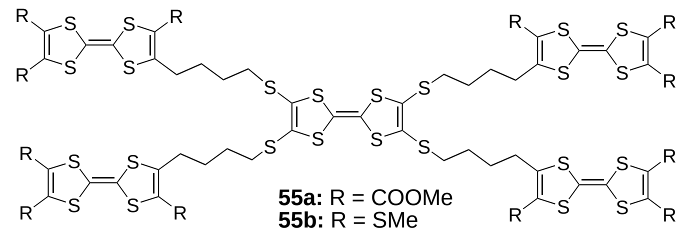
Syntheses of the trimeric system **54** (R = H, $n = 1$) have also been attempted. However, the product obtained was highly insoluble, which prevented its characterization.[73a] We have recently synthesized soluble derivatives of **54** and its magnetic and liquid crystalline properties are currently under investigation.[73b]

2.2.3. Donor Systems With a High Number of TTF Units

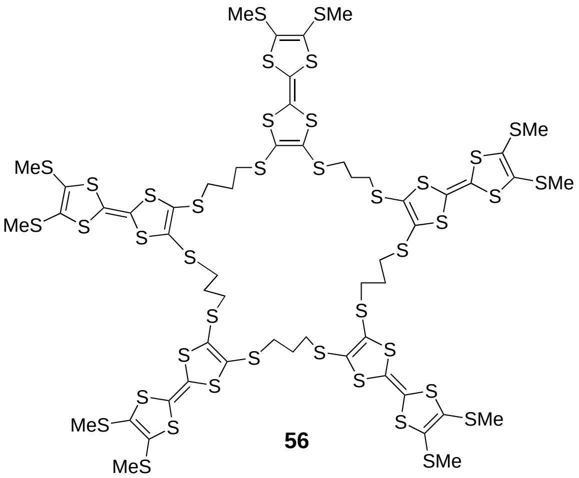
The trends outlined above for systems containing three TTF units are also followed by systems containing more TTF moieties. Thus, in pentakis(TTF) compounds **55**, in which the TTF units are linked through nonconjugated spacers, no interaction between the TTF units is observed by cyclic voltammetry and hence **55a** (R = CO_2Me) exhibits four reversible redox couples.[74] The first one corresponds to the formation of the radical cation of the central TTF unit. The second redox wave can be assigned to the formation of the penta radical cation by the loss of one electron from each of the four peripheral TTF units. The third redox couple corresponds to the formation of the dication of the central TTF unit, and the fourth redox couple arises from the second oxidation of the peripheral TTF units. Only two reversible redox couples are observed in the case of **55b** (R = SMe), probably because the central and the peripheral TTF units are almost equivalent in regard to their redox behavior.

Further multi-TTF systems reported in the literature are **56**[67] and **57**.[75] In 1996 Bryce et al. reported on the synthesis of **57a**, which was the first phthalocyanine bearing TTF substituents to be prepared in the search for novel optoelectronic materials. Although this compound was extremelly insoluble in most organic solvents, a combination of UV/Vis and CV studies allowed the conclusion to be drawn that the molecular design of this system does not prevent the strong tendency of phtahlocyanine units to assemble in solution and does not inhibit the redox behavior of the appended TTF units. Thus, this work paved the way for the study of other systems with phthalocyanine and TTF units[76] which combine the versatile electrochemical, optical, and coordination properties of phthalocyanines with the redox properties of many TTF units.[15] Bryce et al. have reviewed some of the most interesting results in an article concentrating on multi-TTF systems[15] in which different phthalocyanine-TTF systems are studied and the results compared with that for a pyrazinoporphyrazine system endowed with eight appended TTF groups.[77]

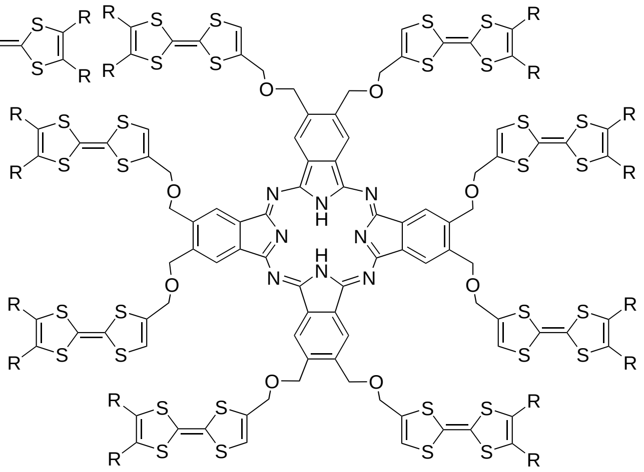
Two recent and outstanding examples of multiple TTF containing molecules are the hexakis(TTF) derivative **58** and the TTF tetramer **59**. Compound **58** was prepared by the groups of Bryce and Becher in an efficient one-pot synthesis in which a sixfold reaction occurs to open the way to the



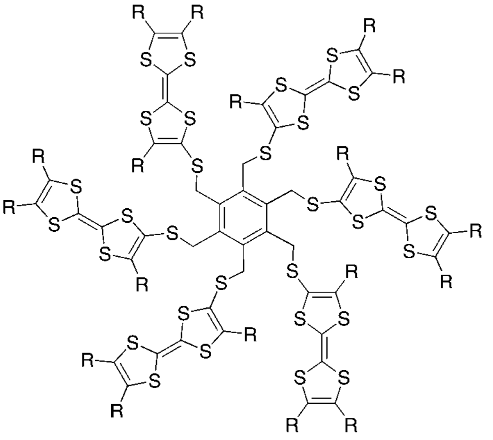
55a: R = COOMe
55b: R = SMe



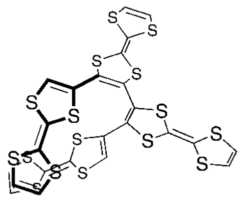
56



57a: R = H
57b: R = C_6H_{13}



58: R = SMe



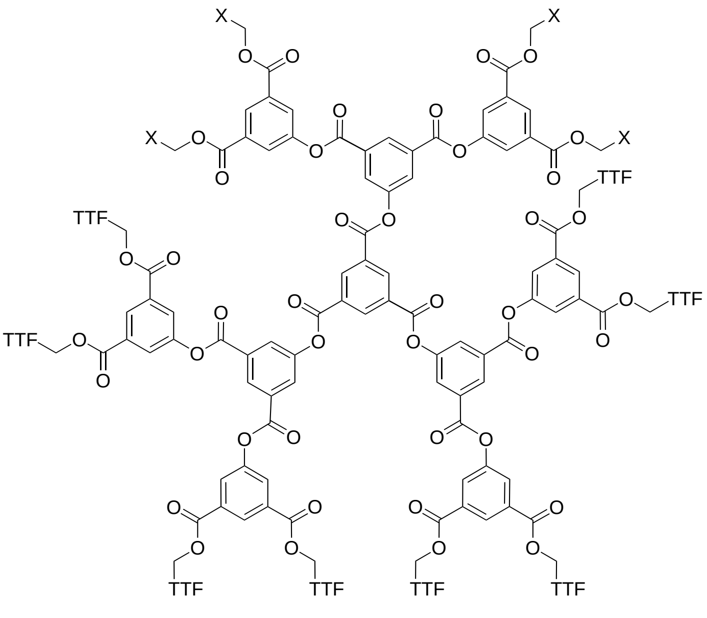
59

convergent construction of higher TTF oligomers and dendrimers.[78] Compound **59** is the first example of a helical tetrathiafulvalene tetramer and was prepared by Iyoda et al.[79] Both compounds were synthesized by using cross- and homocoupling reactions of tetrathiafulvalenylzinc derivatives, and in their neutral state have a tight helical conformation with closely situated terminal TTF rings. Interestingly, the cationic charges in the dication are mainly localized on the inside TTF rings and are stabilized by the face-to-face intramolecular stacking of the two terminal TTF rings. The same situation is observed for the tetracation. On the contrary, the third and fourth oxidations are restrained by the repulsion of positive charges on the terminal TTF units, which makes it more difficult to form the hexa- and octacations.

2.2.4. TTF-Containing Dendrimers

The macrocyclic systems with peripheral TTF units described in Section 2.2.3 can be considered a special case of dendrimeric materials in which the central macrocyclic system acts as the nucleus. Ideally, dendrimers are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture.[80] In recent years, they have developed from curiosities into new technologies.[81] During the last few years, the research group of Bryce has been very active in the syntheses and study of different soluble dendrimeric materials containing TTF units such as **60** and **61**. Dendrimeric materials offer the possibility of controlling the number and placement of TTF groups with well-behaved solubility features that facilitate characterization, as well as to integrate the unique properties of the TTF molecules with the characteristic properties of polymers, such as film formation and processability.

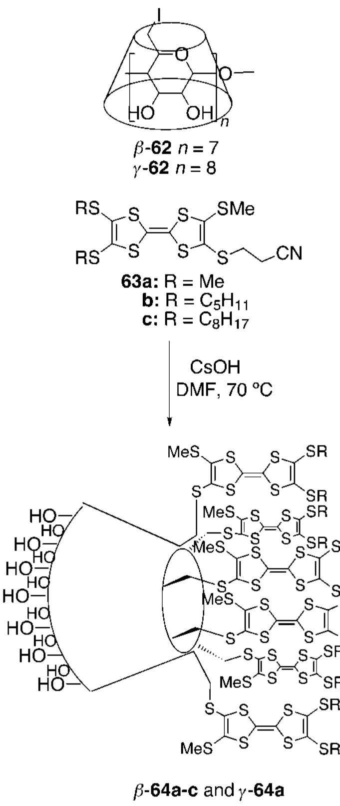
Compound **60** is a dendrimer containing a benzene 1,3,5-triester core and a surface functionalized with twelve TTF units. It is an oil which is readily soluble in polar organic solvents and stable when stored below 0 °C. Dendrimer **60** was synthesized by using a convergent strategy based on a repetitive coupling/deprotection sequence with 4-(hydroxymethyl)-TTF as the starting monomer.[82] The stability of this type of macromolecule decreases with increasing molecular weight as a result, at least in part, of the steric crowding imposed by the trifunctionalized core. Thus, more "open" bifunctional cores (terephthaloyl chloride, biphenyl-4,4′-dicarbonyl dichloride, 4,4′-oxydibenzoyl dichloride) have been



60: X = TTF
61: X = Anthraquinone

used to synthesize hyper-branched multi-TTF derivatives that have good shelf stability, display reversible redox activity in solution, and form semiconducting CT complexes with TCNQ.[83] More recently, a $(TTF)_{21}$ dendrimer has been synthesized which contains TTF units not only at peripheral sites but also within the branches of the structure.[84] Glycol chains were incorporated into the branches to impart solubility in organic solvents, to give air stability, and to provide a flexible structure to facilitate interactions between the TTF units.[84] TTF itself has been used as the nucleus in a different approach towards TTF-containing dendrimers in which the TTF units are placed at all layers of the structural hierarchy.[85] More recently, the convergent synthesis of $(TTF)_x(AQ)_y$ (AQ = anthraquinone), polyester dendrimer **61**, has been reported.[86] This molecule undergoes amphoteric redox behavior as a consequence of the presence of the electron-donating TTF moiety and the electron-accepting anthraquinone system. These types of donor–acceptor systems are specially attractive since the incorporation of stronger π-acceptor groups[87] will enable the study of intramolecular charge-transfer interactions within a dendritic microenvironment.[86] A more in-depth study of dendrimers containing TTF units can be found in the recent feature articles of Bryce et al.[15, 24]

Cyclodextrins (CDs) have been also used as platforms to carry TTF units.[88] Cyclodextrins are cyclic oligosaccharides consisting of six, seven, or eight (α-CD, β-CD, γ-CD, respectively) α-1,4-linked D-glucopyranose units forming a truncated cone. They were used as platforms to carry TTF units, and were shown to form LB films when various amphiphilic β- and γ-cyclodextrins functionalized with alkyl chains at the primary hydroxy positions or modified on the secondary face were used. Thus, Sallé and co-workers carried out the synthesis and electrochemical characterization of molecular blocks, Langmuir monolayers, and LB films built from the association of CD and TTF moieties.[88] The target compounds **64** were achieved according to a convergent synthesis involving nucleophilic persubstitution of the 6-deoxy-6-iodocyclomaltooligosaccharides **62** with the free thiolate derivative **63** (Scheme 1). These systems are interesting since they are designed to combine the complexing ability of the CD cavity with the redox properties of the TTF core. Furthermore, the ability of the CD fragment to promote film transfer has been successfully transposed to produce good quality LB films incorporating electroactive TTF units. Thus, the covalent grafting of appropriate electroactive units onto the CD entity can be envisaged as a good way to produce LB films with physical properties that require a high degree of molecular organization in the material, such as electroconductivity or second-order nonlinear optics.[88]



Scheme 1. Convergent synthesis of **64** by a complete nucleophilic substitution of **62** with the TTF derivative **63**.

2.2.5. TTF-Containing Polymers

In the last part of this section dedicated to the macromolecular chemistry of tetrathiafulvalene we will focus on the most recent developments of polymers containing TTF units both as side chains or as a part of the main chain (Figure 3).

The incorporation of TTF into polymeric matrices for improving the processability of TTF-based conductors was investigated several years ago, and different research groups developed the synthesis of polymers **65** with spacers such as polyamide, polyurethane, polyphenylene, polystyrene or

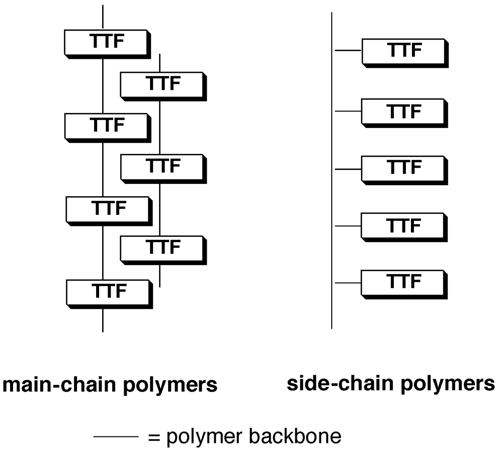
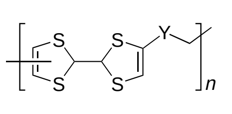


Figure 3. Different types of TTF-containing polymers (redrawn from ref. [53]).



65

Y = $(CH_2)_n$
= $COO(CH_2)_n$
= $CONH(CH_2)_n$
= $C_6H_4OCONH(CH_2)_n$
= $C_6H_4SO_3mC_6H_4$

polyesters.[89] However, it was generally accepted that although such linkages do provide spatial proximity of the redox centers, they cannot ensure a well-defined orientation of the TTF groups relative to one another because the torsion around the bridging bonds allows a great number of different conformations. Thus, these polymers are deficient both in the order of the TTF subunits and in the dimensionality of the conduction process in the doped state.[53] Polymers **65** were poorly characterized and, as a consequence of the above drawbacks, they have attracted little attention for further studies.

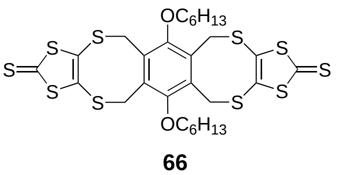
One way to reduce the conformational freedom would be to bridge the TTF units on each side with two σ bonds. Röhrig and Müllen have used dithiones such as **66** as precursors to σ-bonded tetrathiafulvalene oligomers and polymers. When dithione **66** was subjected to a phosphite-induced[90] coupling reaction, polymer **67** was obtained in yields of less than 15%; instead, the formation of a macrocycle by the self-coupling of both thione groups took place.[91] However, the synthesis of **67** can be achieved starting from dithione **66** by using a four-step reaction sequence. By changing the concentrations in the four-step sequence, the formation of the macrocycle can be inhibited and the polymer is obtained as the main reaction product.[53]

Elsenbaumer and co-workers have developed a different and recommended strategy for producing ladder-type polymers based on TTF that circumvents the generation of the TTF system in the last step.[92] They used a tetraanion of tetrathia-TTF derived from tetrakis(cyanoethylthio)tetrathiafulvalene and the two different building blocks tetrakis(bromomethyl)benzene and 2,3-bis(bromomethyl)-1,4-dibromo-2-butene to generate polymers **68**–**70**. The overall yield of these new organic metals is very high (>90%), which means that this kind of coupling is applicable to the synthesis of high molecular weight bulk materials. Polymers **68** and **70** can be doped with $FeCl_3$ to give blue/black CT materials with pressed pellet conductivities of 6×10^{-4} and $2\times10^{-4}\,S\,cm^{-1}$, respectively.

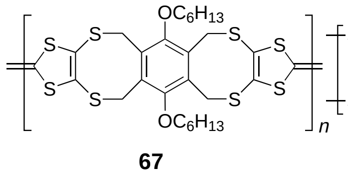
A different way of inducing some order into TTF-containing polymeric materials would be to induce a regular arrangement of the TTF subunits in an eventual liquid crystalline phase of the polymers in order to achieve π-stacking interactions in the polymer matrix. Thus, Müllen and co-workers have reported on the syntheses of a variety of polymeric materials, such as **33**, with TTF units either taking part of the main chain or as side chains.[53] TTF was incorporated quantitatively into the polymer chain by reaction of the precursor TTF-containing molecule **32** with poly(*p*-hydroxystyrene). Unfortunately, they have not been able to induce a liquid crystalline phase in this type of polymer. However, it may not be necessary to achieve a liquid crystalline phase with the undoped TTF-containing polymer and the possibility has to be considered that smectic phases can be induced by introducing complex formation between donor and acceptor pairs in separate mesogenic units. Thus, undoped TTF-containing polymers should be potentially liquid crystalline and may exhibit mesogenic behavior when doped with an acceptor.[53]

In recent years the major interest has focused on the association of TTF-based conductors with linear π-conjugated structures.[13, 20, 93] There are different reasons for this interest:[20]

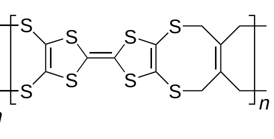
1. The possibility of combining the outstanding electron-donating properties of TTF systems with the general characteristics of high molecular weight polymers, such as



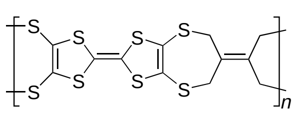
66



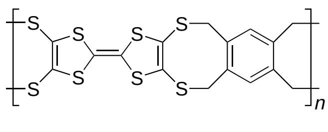
67



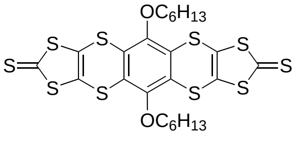
68



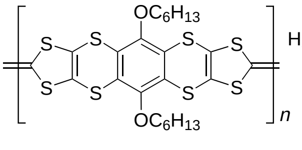
69



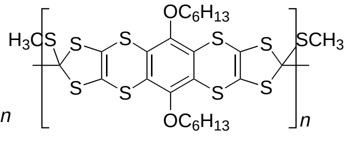
70



71



72



73

film formation and processability, to obtain polymers that could be doped with strong acceptors.[53]

2. The propensity of TTF to form ordered stacks can represent an interesting tool for controlling the long-range order of a conjugated backbone.
3. The combination of TTF with a conjugated polymer chain can contribute to an increase in the dimensionality of the conduction process and might eventually lead to materials presenting hybrid conduction. In this regard, two parallel charge-transport mechanisms might be possible: the intrastack transfer of aromaticity associated with the mixed-valence interactions in TTF stacks[94] and the polaron/bipolaron conduction in the π-conjugated chain.[95]

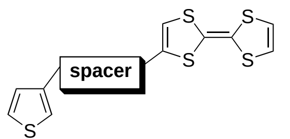
72 is a fully conjugated ribbon-structure polymer in which conductivity along the polymer chain through π-conjugation as well as along the stacking direction through π-orbital overlap might be expected. Compound **72** can be obtained starting from dithione **71** using a four-step synthetic route similar to that used for the synthesis of **67**.[53] Polymer **72** is an orange TTF material that can be doped with iodine to give a black material. However, characterization methods are very limited because of its poor solubility. A new route involving the film-forming precursor polymer **73** has been proposed as an alternative route for casting a thin self-supporting film that could generate a thin film of the conjugated polymer **72** after thermal extrusion.[53] This type of conjugated polymer can be used as an electroactive conducting rod in which the TTF group permits the rods to bend easily in the direction perpendicular to the ring plane.[31]

Other attempts have been made to incorporate TTF moieties on a conjugated polymer backbone. One approach in this direction involves the grafting of a TTF moiety onto an electropolymerizable monomer to yield conjugated polymers with pendant TTF groups. This strategy was originally developed by Bryce et al. as a possible way to indirectly control the long-range order of electrogenerated poly(thiophene) (PT) by using the strong propensity of TTF to self-assemble into regular π stacks.[96] After the seminal work of Bryce et al. reported in 1991, other thiophenic precursors **74**–**79** have been synthesized.[97, 98, 99]

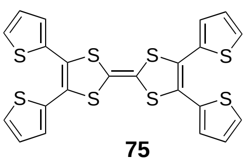
Unequivocal evidence for electropolymerization was reported in one case[97] although the large potential difference between the first TTF oxidation (ca. 0.40 V/SCE) and the potential needed to polymerize the substituted thiophene (1.80 V) has been identified as a serious problem.[97] The cyclic voltammogram of the resulting polymer exhibits a splitting of the first TTF reduction wave typical of the occurrence of the mixed-valence dimer (TTF)$^{2+}$,[100] which indicates that self-assembly of the oxidized TTF moieties already takes place in the material.[97] Roncali and co-workers have recently shown that as a consequence of a much lower electropolymerization potential,[101] TTF-substituted bithiophenic precursors are readily converted into extensively π-conjugated TTF-derivatized poly(thiophenes) **80** and **81** with interesting electrochemical properties.[102]

The cyclic voltammogram of these polymers have revealed a hitherto unknown additional oxidation wave at a potential intermediate between those corresponding to the generation of the TTF radical cation and the dication.[100] This electrochemical behavior has been studied in more depth on equilibrated films and in dynamic conditions by Roncali and co-workers using classical and time-resolved spectroelectrochemical techniques.[93] The results obtained provide evidence for the occurrence of large amounts of mixed-valence dimers and π dimers in these polymers. At the potential needed to electropolymerize the attached bithiophene precursor, initially formed mixed-valence dimers are successively converted into π dimers and dications. Therefore, mixed valence interactions must be reconstructed by subsequent undoping and controlled reoxidation of the polymer. This process will probably result in a partial loss of the initial order.[93] Thus, different strategies have been proposed by Roncali and co-workers[93] to design more appropriate precursors:

- a further increase of the electropolymerization potential,
- an increase in the first oxidation potential of the attached TTF by electron-withdrawing substituents, and
- an increase in the TTF concentration within the polymer by grafting more than one TTF unit onto the precursor structure.

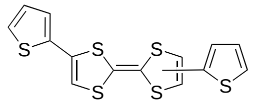


74

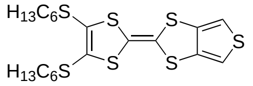


75

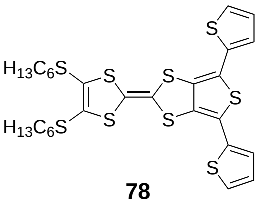
spacer = OCH$_2$CH$_2$OCO
CH$_2$CH$_2$OCO
CH$_2$CH$_2$Se
CH$_2$(CH$_2$)$_7$O-CH$_2$
CH$_2$CH$_2$OCH$_2$



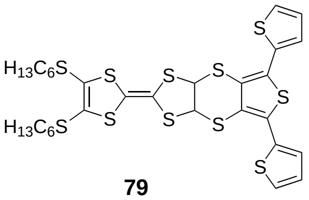
76



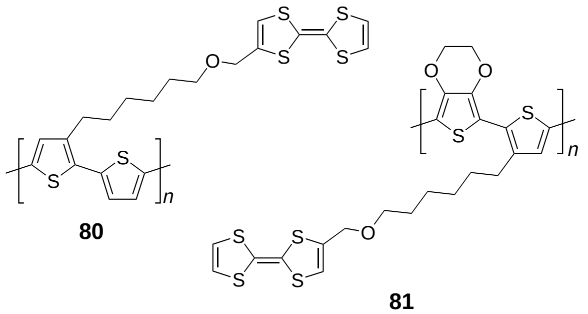
77



78



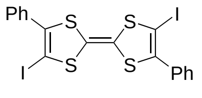
79



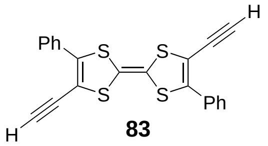
80

81

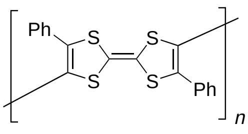
Yamamoto et al. have reported on the syntheses of four kinds of poly(arylene) and poly(aryleneethynylene) polymers containing TTF units in the π-conjugated main chain by using organometallic polycondensation.[103] The Ni-[104] and Pd-promoted[104a, 105] polymerizations and copolymerizations of monomers **82** and **83** with substituted diiodothiophene give π-conjugated polymers **84**–**87** in high yields. Among these polymers, the poly(aryleneethynylene) polymers **86** and **87** have well-expanded π-conjugation systems as a result of the acetylenic spacer groups, and because of the presence of the TTF moieties they are active for both chemical and electrochemical oxidation even when containing strongly electron-withdrawing acetylenic groups. They are the first examples of poly(aryleneethynylene) polymers which are active for electrochemical oxidation.



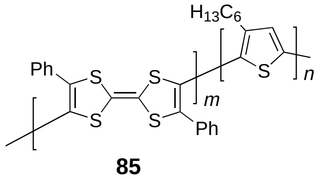
82



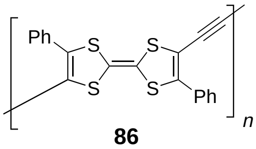
83



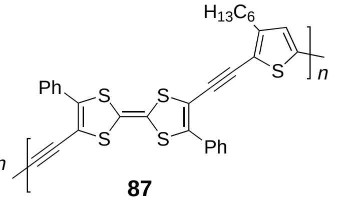
84



85

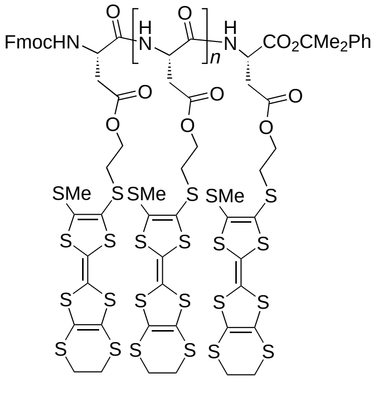


86



87

To conclude with the study of TTF-containing polymers, it is worth mentioning the recent work by Kilburn and co-workers. This work is at the frontier between macro- and supramolecular chemistry and deals with the possibility of incorporating TTF-bearing amino acids into a polypeptide, where the role of the peptide backbone would be to control the spatial arrangement of the TTF units.[106] They propose that the incorporation of TTF-bearing amino acids into an α-helical structure might allow the alignment of the TTF units into a conducting stack on one face of the helix or even a helical arrangement of conducting TTF units to give rise to a molecular solenoid. The packing of the individual helical units in the solid state, and hence the degree of interaction between TTF units on adjacent helices, would be influenced by the substitution pattern of the TTF units on the peptide backbone.[106] With this aim, Kilburn and co-workers have prepared unnatural TTF-bearing amino acid derivatives and have incorporated them into small peptide structures (**88**, Fmoc = fluoren-9-ylmethoxycarbonyl). Although they have not been able to prepare characterizable CT salts of these peptides, the electrochemical studies indicate that they may well undergo conformational reorganization upon oxidation of the TTF moieties, presumably in response to interactions between the oxidized TTF units.



88

2.3. Supramolecular Systems

As Fitzmaurice and co-workers pointed out "supramolecular chemistry is distinguished from large-molecule chemistry by the fact that the intrinsic properties of the molecular components are only slightly perturbed within the supermolecule, and the properties of the supermolecule are not a simple superimposition of the properties of the molecular components (that is, there exists a supramolecular function)".[107] In the words of Lehn, "supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond".[108] During the last few years, the influence of supramolecular chemistry in the realm of materials science has been enormous.[109] The supramolecular approach in regard to the TTF moiety has been considered in two different ways:

- The construction of supramolecular assemblies in the solid state as a pathway to new and desired materials by using different types of intermolecular interactions.
- The construction of redox-active supramolecular systems with applications in different areas such as electroactive sensors, molecular shuttles, or molecular switches.

One of the great challenges for materials science is the creation of supramolecular materials in which the constituent units are highly regular molecular nanostructures. Learning how to create large supramolecular units, and the elucidation of rules that mediate their macroscopic organization into functional materials, offers a fascinating prospect for technology.[110] The ability to control the supramolecular assembly over the molecular arrangement is especially effective in the solid state because of its rigidity and infinity. Thus, the concept of "crystal engineering" proposed by Sharma and Desiraju in 1989[111] has been applied in the field of molecular conductors to construct supramolecular assemblies by using several types of intermolecular interactions.[112] Classical methods towards the obtention of different donor packing motifs in the CT complexes and/or salts are:[8]

- Introducing heavy heteroatoms as chalcogenides[51e, 113–116] and halogenides[117] at peripheral positions of the TTF moieties.

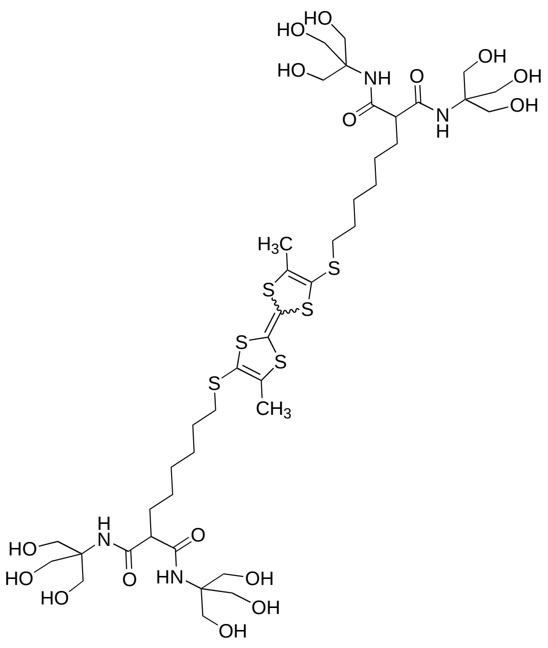
- Functionalizing the TTF ring with OH[118] and/or NRH[119] groups that would enable intermolecular hydrogen bonding to occur.

Together with these strategies, other less conventional methods such as supramolecular arrangements have been attempted. Thus, incorporation of TTF species in calix[4]arenes, which are well known in supramolecular chemistry for acting as organizing platforms for various kinds of substituents, has also been carried out.[120] A more recent approach which is also related to "crystal engineering" has been developed by Yamamoto et al. which utilizes Lewis acid/base interactions between anions and iodine-containing neutral molecules to accomplish multicomponent molecular conductors with supramolecular assemblies.[121] By using this strategy they obtained radical–cation salts with new types of donor arrangements. The authors claim that examination of many cases of different arrangements will allow the design of "tailor-made" anion networks to accomplish desired donor arrangements.

The use of the old, but elegant, Langmuir–Blodgett technique is another way of arranging molecules into organized assemblies. For example, the possibility offered by the LB technique to build noncentrosymmetric architectures has been widely used to achieve nonlinear optical properties in these materials.[47, 122]

It is also worth mentioning how the preparation of mesogenic derivatives by either attaching a TTF unit to a mesogenic liquid crystalline center or by incorporating substituents which show mesomorphic behavior onto the TTF moiety have been used as an alternative to the above procedures to obtain an assembly of ordered arrays of TTF-containing molecules [51–55]

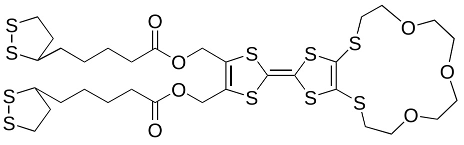
In 1994 Jørgensen et al. utilized self-assembly principles and gel-formation techniques to manufacture a prototype "molecular" wire.[123] Gel formation can usually be best understood as resulting from a competition between the tendencies of the gelator to dissolve in the solvent or to self-assemble and crystallize.[124] Thus, by taking advantage of the work of Newkome et al., who prepared the so-called bis-arborols that readily form gels consisting of stringlike assemblies in water,[125] Jørgensen et al. synthesized the bis-arborol-tetrathiafulvalene **89**, which forms a gel, which consists of string- or bandlike structures with a length of tens of micrometers and diameters in the 300–1000 Å range. UV/Vis-NIR spectroscopy on the oxidized gel revealed a CT band typical of stacked TTF molecules.



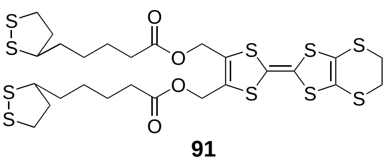
89

One of the most challenging projects in the field of molecular optoelectronics involves the self-assembly of monolayers of electroactive molecular systems on solid supports.[126] The monolayer represents a two-dimensional array on the solid support. TTF compounds containing four thiol groups have been reported to form very robust self-assembled monolayers (SAM) on gold which were stable after repeated voltammetric cycling.[127] Echegoyen and co-workers took advantage of the good results obtained by anchoring SAMs on metal surfaces by using thioctic acid derivatives[128] to synthesize bis-thioctic ester derivatives of TTF units annelated with crown ethers (**90**–**93**) that form stable self-assembled monolayers on gold electrodes (Figure 4).[129] Thus, they have prepared electrochemically active SAMs which are almost indefinitely stable and that show promise as potential thin-film sensors for electrochemically inactive metal ions.[129]

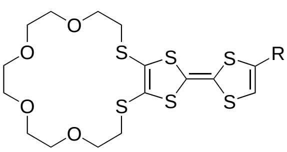
Prior to this work, Bryce and co-workers reported crown-annelated TTF derivatives **94** which also contained single alkyl chains terminated in thiol groups.[130] Monolayers of



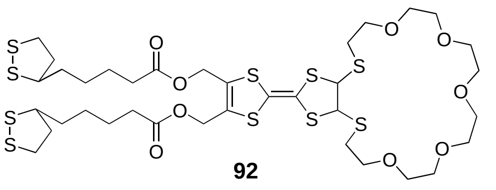
90



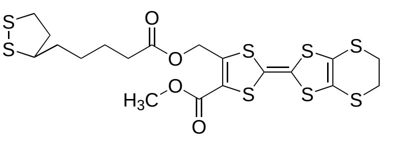
91



94a: R = $C(O)O(CH_2)_nSH$; n = 6, 12
94b: R = CH_2SH



92



93

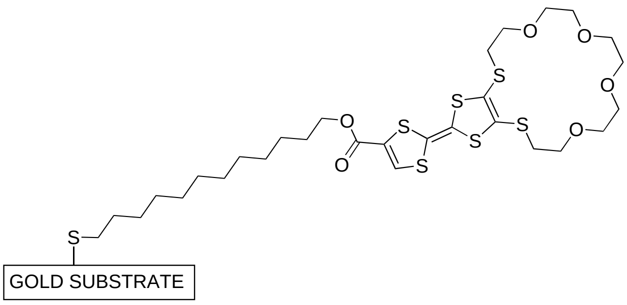


Figure 4. Probable disposition of the SAM of **94a** on a gold surface.

compounds **94** were assembled onto gold or platinum surfaces from saturated acetonitrile or acetonitrile/benzene solutions. Figure 4 shows the probable orientation of a SAM of compound **94a** ($n = 12$). Similar CV responses to metal cations were obtained for SAMs and acetonitrile solutions (electrochemical recognition of Na^+, Ba^{2+}, and Ag^+, with the largest response for Ag^+), which represents an important step forward in the design of thin-layer molecular devices that function as electrochemically responsive detectors for metal cations.[130] Bryce has recently reviewed these SAMs within the context of materials chemistry.[24]

The construction of redox-active supramolecular systems with applications in different areas and the construction of supramolecular assemblies in the solid state has been another important overlap-zone between TTF and supramolecular chemistry. Becher and co-workers have reviewed most of the work in this area. They focused on cation-sensitive TTF systems including TTF-crown ether derivatives, TTF-thiacrown ether derivatives, macrocyclic and bis-macrocyclic TTF units, all of which are molecular systems containing the redox-active TTF functionality together with a host unit capable of cation binding. These types of TTF derivatives as well as those that incorporate the TTF moiety in supramolecular systems, such as rotaxanes or catenanes, have been the origin of some of the most interesting recent applications found for TTF-containing molecules.[23] With the purpose of taking a systematic approach, we will study this type of TTF derivatives within the next section dedicated to the nonconventional application of TTF derivatives.

3. Nonconventional Applications of TTF Derivatives

Although thirty years have passed since the synthesis of TTF was firstly reported by Wudl et al.,[1] an explosive growth of activity in the area of tetrathiafulvalene chemistry has arised during the last decade. Interest has arisen in a variety of new fields by taking advantage of its unique solid-state as well as its solution properties.

The main emphasis of the investigation during almost twenty years was on the solid-state properties of the TTF charge-transfer (CT) complexes and CT salts. It is still a very active field of research and new TTF salts with improved solid-state properties are being reported week by week. However, since there is a great deal of excellent literature[131, 132] dedicated to the study of CT salts, their study will not be included in the present review article, which instead will be more concerned with the less-well known but very promising "nonconventional" applications of TTF derivatives.

3.1. TTF as an Electroactive Unit in Chemical Sensors and Redox-Switchable Ligands

As discussed previously, the construction of macrocycles containing TTF units has received considerable attention since such molecules may act as a host in host–guest chemistry.[133] Figure 5 shows schematically a) a redox-detected sensor molecule and b) a redox-controlled ligand system.

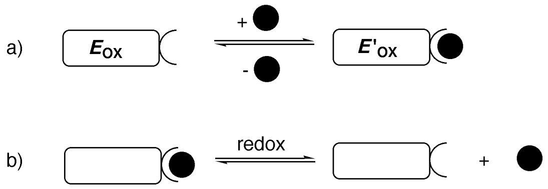
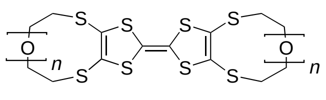


Figure 5. a) Redox-detected sensor molecule and b) redox-controlled ligand system (redrawn from ref. [16]).

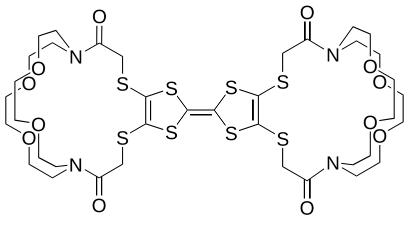
In the first case, a "transducer" built into the molecule responds to complexation in the host by a change in physical properties. In the redox controlled/switchable ligand system the roles of the two parts are reversed so that a physical change of the transducer units is imposed by an external stimulus. A positive charge is created after oxidation of systems containing a TTF unit which inductively decreases the binding ability of the attached host unit towards cations.[16] Although the voltammetric response upon metal binding in this system is quite small (< 100 mV), an advantage of the TTF moiety is that only the first oxidation potential is affected, and the second (unchanged) oxidation potential serves as an internal reference.[134] In addition, both TTF redox steps occur in a convenient potential window.

Since Jørgensen et al. reviewed[16] the literature related to cation-sensitive TTFs prior to 1994 thoroughly, we will only give a brief account of recent examples in order to update the improvements reported in recent years. By using the same classification method used by Jørgensen et al.[16] in their review, cation-sensitive TTFs can be divided into planar TTF derivatives with annelated macrocyclic moieties and distorted macrocyclic TTF systems. Planar derivatives include TTF-crown ether (**95**) and TTF thiacrown ether (**97**) derivatives as well as a TTF-cryptand (**96**). These compounds have been investigated for their potential use as electroactive cation sensors.[16, 23] The ring size of the macrocycle and the extension of the π system of the TTF unit (**98**)[16] have also been the subject of study.

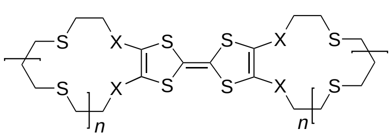
Changes in the ^1H NMR spectrum of the macrocyclic ligand, and the changes in the redox properties of the TTF system as determined by cyclic voltammetry, have been used to monitor metal binding within the crown rings. A shift in the value of the first oxidation potential to more anodic (positive) potentials was observed upon addition of metal salts (M = Li,



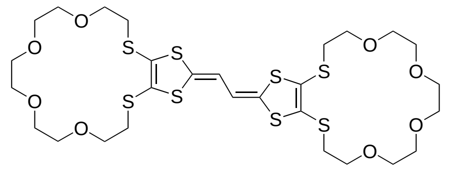
95: n = 1-5



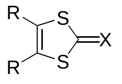
96



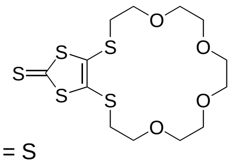
97: X = S, Se; n = 1-3



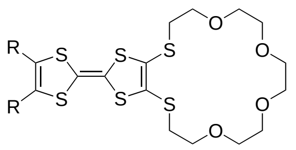
98



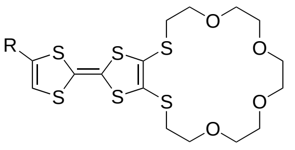
99: R = $SC_{18}H_{37}$; X = S
100: R = H; X = S
101: R = CO_2Me; X = O



102



103: R = $SC_{18}H_{37}$
104: R = CO_2CH_3



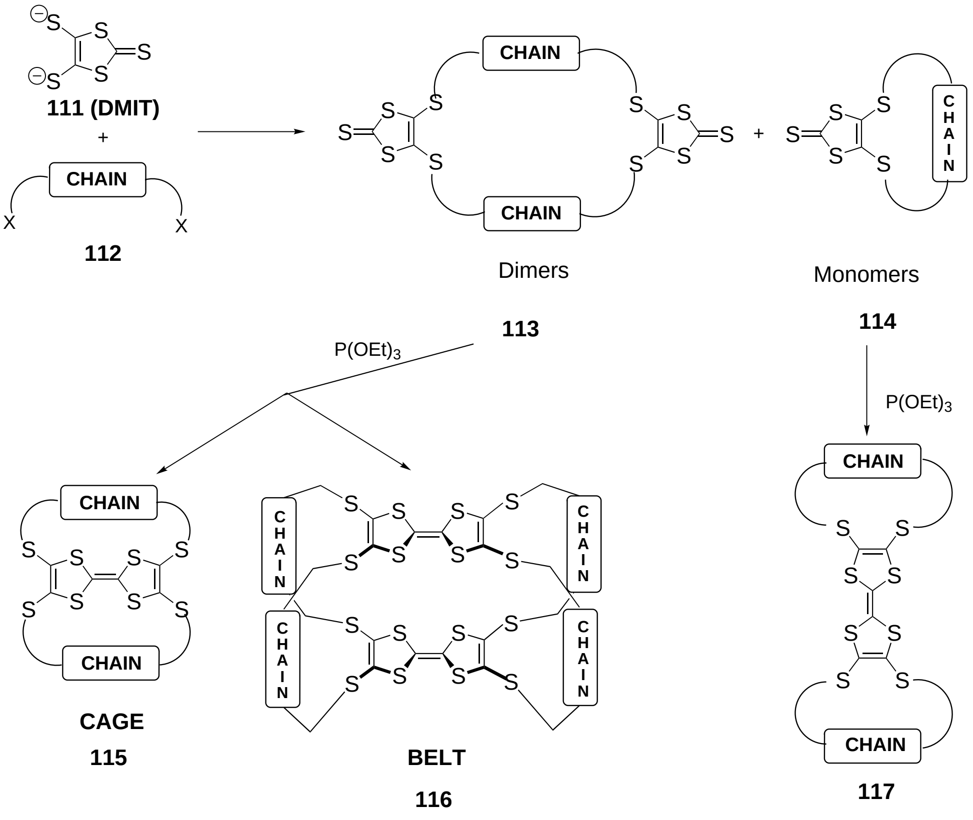
105: R = H
106: R = CHO
107: R = CO_2Me
108: R = CH_2OH
109: R = CO_2H
110: R = $CH_2OC(O)C_{17}H_{35}$

Na, K, Ba, Ag) to a solution of the TTF-crown molecules. This observation indicates that metal complexation has occurred. The scope of this application for TTF-containing systems has been explored by using synthetic approaches previously used in TTF chemistry[10]:

1. cross-coupling reactions to produce functionalized TTF-crown systems, such as the amphiphilic TTF-crown **103** and the diester **104**,
2. electrophilic substitution of TTF-crown compounds, via a lithiated intermediate, to provide derivative **106**, and
3. functional group removal and interconversion to give **107**–**109** as well as **106** again, these derivatives are suitably functionalized for further chemical transformations.[16, 23]

However, a very large proportion of these types of TTF derivatives have been synthesized from macrocycle-fused 1,3-dithiole-2-thione-4,5-dithiolate (DMIT, **111**; Scheme 2).[26] The readily available compound **111** can be treated with a variety of chain-containing electrophiles **112** to generate a variety of monomeric (**114**) or dimeric (**113**) thiones. The coupling of monomeric thiones with themselves or with other thiones by using the standard coupling reaction with trialkyl phosphites yields the corresponding symmetric (**95**–**97**, **117**) and unsymmetric (**103**–**110**) TTF derivatives with annelated macrocyclic moieties.

DMIT (**111**) derivatives have also been directly involved in the second type of TTF-containing systems capable of binding cations; these are the distorted macrocyclic derivatives.[28] By using high-dilution techniques it is possible to maximize the yield of dimeric thione derivative **113** in the reaction of DMIT with chain-containing electrophiles. Subsequent phosphite

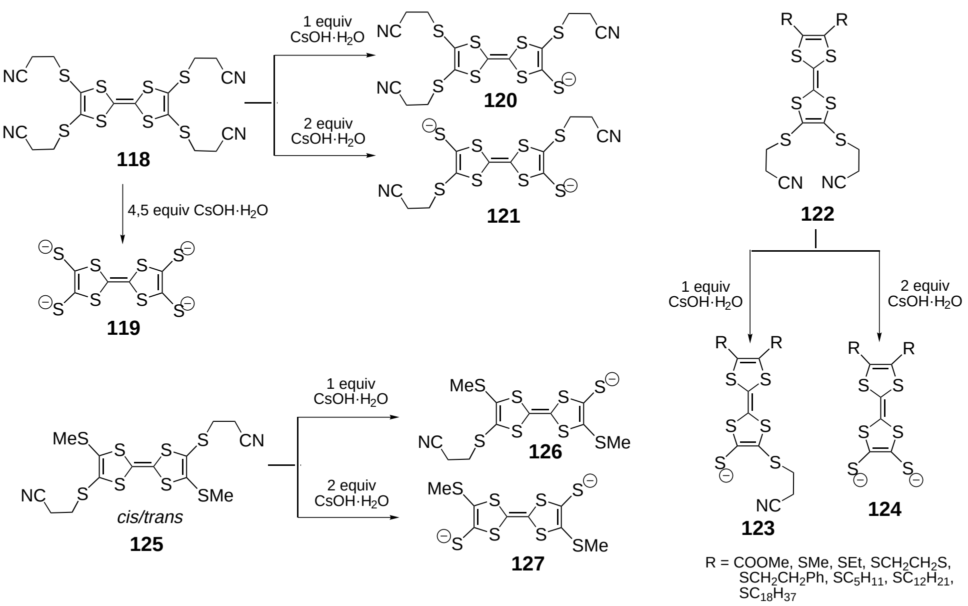


Scheme 2. Synthesis of the macrocyclic TTF derivatives from DMIT **111**.

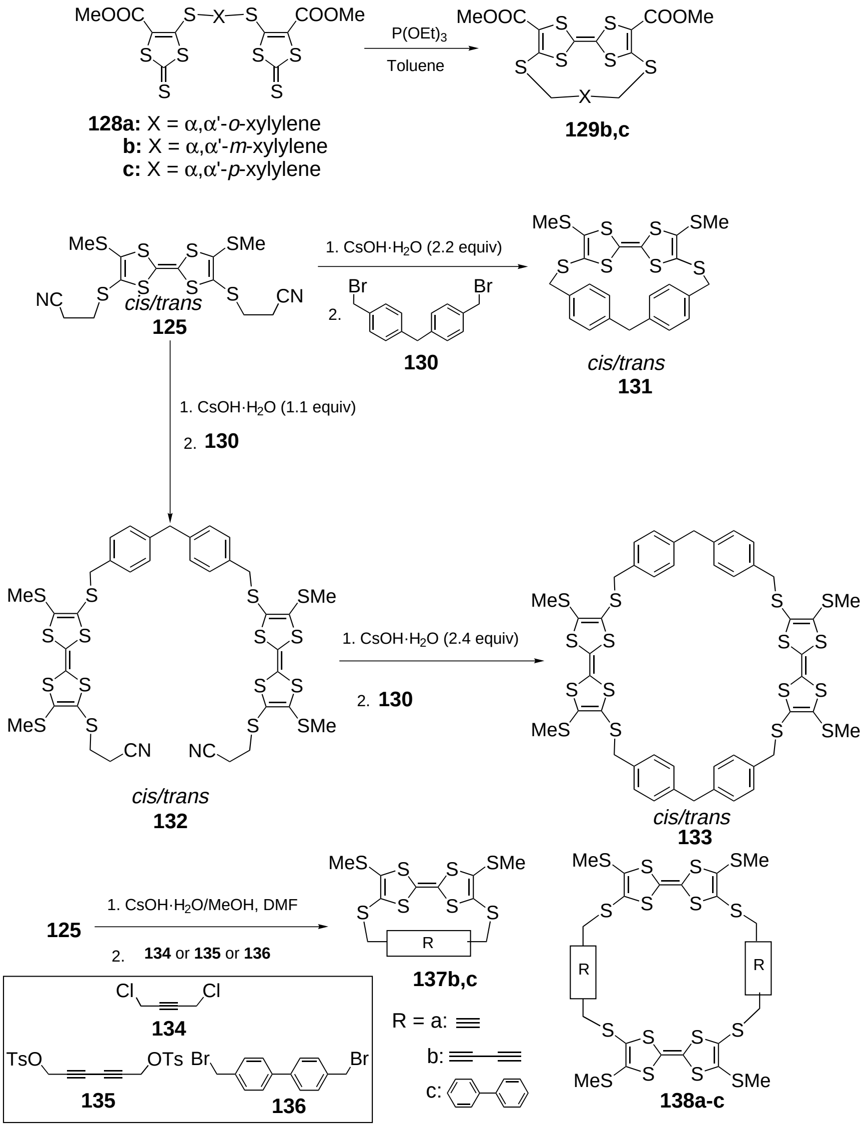
coupling normally proceeds in an intramolecular fashion, to give rise to monomeric cage molecules **115**. Occasionally, intermolecular coupling which produces low yields of larger "belt-type" macrocycles has also been observed.[16] Whether these reactions give inter- or intramolecular cyclization seems to be controlled solely by the length of the linker between the two dithiol units. Very short linkers, namely two,[135] three,[135] four,[136] or five[137] atoms gives intermolecular coupling, whereas longer spacers tend to result in intramolecular reactions.

Special credit has to be given to the effective protection/deprotection methodology for the preparation of tetrathiafulvalene thiolates (TTFTT) developed by Becher and co-workers that use the cyanoethyl group as a versatile protecting group for TTF thiolate groups and which allows the incorporation of preformed TTF derivatives in macrocyclic compounds.[11, 17, 18, 23] Selective monodeprotection makes it possible to carry out stepwise deprotecion of TTF with several cyanoethylthio groups by using caesium hydroxide in the cleavage step. Thus, from only three different TTF units (**118**, **122**, **125**) it is possible to prepare a variety of TTF thiolates bearing one to four thiolate moieties (Scheme 3).[17] By taking advantage of the above reactions, a variety of TTF-containing macrocyclic systems with specific physical and chemical properties have been prepared.

Becher and co-workers have recently revisited the triethyl phosphite coupling of some bis-trithiocarbonates in order to study the influence of the linkers on the course of the reaction.[61] By using triethyl phosphite mediated coupling of the corresponding bis-1,3-dithiole-2-thiones **128b,c**, the *m*- and *p*-cyclotetrathiafulvalenophanes **129b** and **129c** could be isolated (Scheme 4). Treatment of **128a** with triethyl phosphite gave an intractable solid. The λ_{max} value for **129b** is 414 nm whereas that for **129c** is 424 nm, which indicates



Scheme 3. Preparation of different TTF thiolates with one, two, or four thiolate groups.

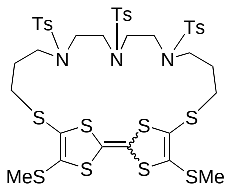


Scheme 4. Synthesis of macrocycles with TTF units.

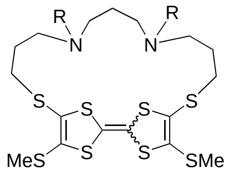
that the *m*-cyclophane has a more distorted TTF group that allows for less π delocalization. The protection/deprotection methodology using the cyanoethyl group was used to generate a TTF bis-thiolate starting from **125** which upon reaction with the bis-bromo reagent **130** yielded the tetrathiafulvalenophane **131** as an orange powder. No trace of dimeric product **133** was detected by plasma desorption mass spectrometry (PD-MS).

The addition of 1,4-dichlorobut-2-yne (**134**) to deprotected **125** under high-dilution conditions gave only the [2+2] addition product **138a**. This occurs because in this case the length of the spacer group is considerably shorter than the thiolate–thiolate distance in the TTF unit.[60] When the length of the spacer group, for example, 4,4′-bis(bromomethyl)biphenyl (**136**) and hexa-2,4-diyne-1,6-diol ditosylate (**135**), is comparable to the thiolate–thiolate distance in the TTF system, the two reaction products **137b,c** and **138b,c** could be isolated after chromatography.[60] Therefore, it can be concluded that 1) the length of the linker as well as its geometry have a profound influence on the course of the coupling reaction of bis-1,3-dithiole-2-thione and 2) that a general method for preparing tetrathiafulvalenophanes with more than one TTF moiety requires strategies involving a preformed TTF building block.[61]

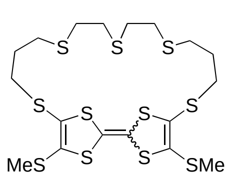
Macrocycles **139** and **140** are cage compounds (Ts = toluene-4-sulfonyl) that have been designed to have the crown complexing part in close proximity to the TTF core and to have a sufficiently large cavity so as to minimize the structural distortions of the TTF moiety previously observed in cage compounds with small crown systems.[138] In comparison with the shorter crown-annelated TTF derivatives for which the first oxidation step is either irreversible or is found at much more anodic E_{pa} values, because of distortion of the central TTF core, derivatives **139** and **140** exhibit two reversible oxidation processes similar to that observed for planar substituted TTF derivatives. The addition of a solution of Ag^+ ions to **139** results in the formation of a 1:1 complex, which can be observed in the FAB mass spectrum. Interestingly, only 70% of **139** is complexed. This observation, together with the fact that a 70:30 Z:E ratio was determined from NMR experiments performed on **139**, indicate that Ag^+ is only complexed by the Z isomer.[138]



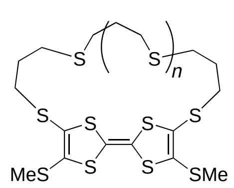
139



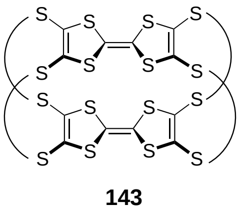
140



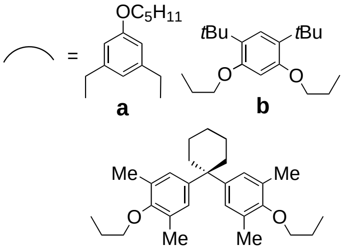
141



142



143



a **b** **c**

Other crown-TTF derivatives with increased chain length relative to the previouly described thiacrown TTF derivatives are compounds **141** and **142**.[139] Two reversible one-electron redox processes were observed upon oxidation which is consistent with the quasi-planar character of the TTF skeleton in these systems. No change was observed in the cyclic voltammograms of compound **142** upon addition of Ag^+. In contrast, the addition of controlled amounts of silver triflate to **141** results in a positive shift of E^1_{ox}. No shift of E^1_{ox} was observed upon addition of a wide variety of Group 1 and 2 or transition metal ions (Na^I, K^I, Cs^I, Mg^{II}, Ba^{II}, Cr^{III}, Ni^{II}, Zn^{II}, Cd^{II}), which illustrates the good selectivity of ligand **141** for Ag^+ ions.

As discussed in previous sections, bistetrathiafulvalenophanes (TTF-phanes) such as **42** and **43** have been studied because the two TTF units can adopt a sandwich structure, which enables intermolecular interactions between the two redox units to occur and increases the likelihood of strong noncovalent inter- and intramolecular interactions occuring.[12, 13, 14] Most of the TTF belts reported by the research group of Otsubo[12, 58, 137b] are based on the coupling of bis-2,3-dithiole precursors to give the TTF core in the final step of the synthesis, while the above studied deprotection/realkylation protocol involving tetrathiafulvalene thiolates developed by the research group of Becher have also been recently applied to the synthesis of belt compounds. Thus, in 1999, the stepwise synthesis of the new TTF belts **143** with well-defined large cavities have been reported.[140] The spacers used were chosen to confer rigidity as well as solubility to the belt molecules. They are stable and isolable compounds which show some promise as host molecules: the solid-state structure of **143c** shows that it crystallizes with two molecules of chloroform inside its spacious cavity (Figure 6). However, no complexation studies have been reported for these interesting systems so far.

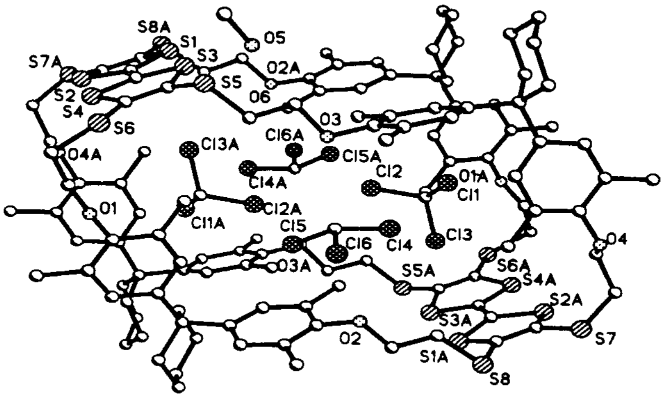


Figure 6. View of the molecular structure of **143c** including solvent molecules. (Reprinted with permission from ref. [140].)

3.2. Molecular Shuttles and Molecular Switches Containing TTF Units

TTF is an ideal building block for the construction of supramolecular systems which can be controlled by external stimuli because its reversible oxidation to its radical cation that can be realized chemically and electrochemically.[141] This type of compound can be used as molecular devices which can operate as machines upon external energy transfer since they may be able to store and process information at the molecular level.[108, 142] Rotaxanes, catenanes, and other intertwined structures and superstructures (Figure 7)[143, 144] are ideally suited for building integrated, multicomponent modular systems.[145]

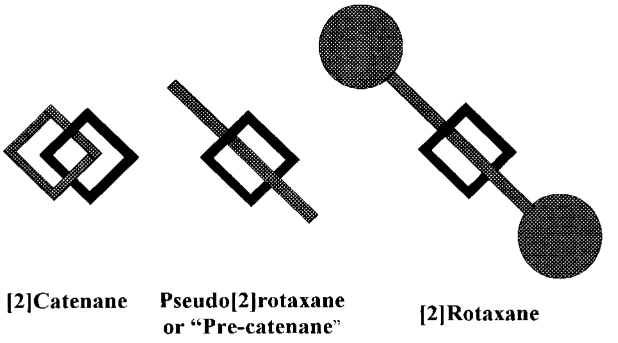
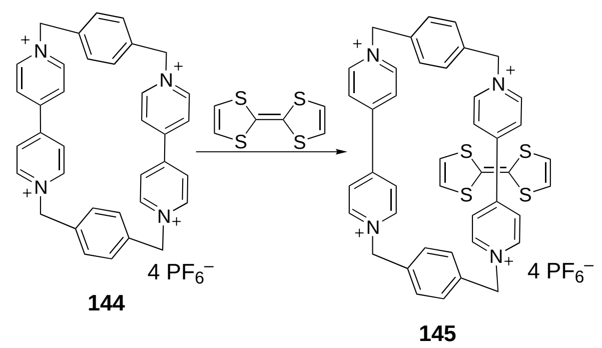


Figure 7. Schematic representation of a [2]catenane, a pseudo[2]rotaxane, and a rotaxane.

Some of these supramolecular systems have been prepared by taking advantage of the experience gained in the syntheses of macrocyclic systems containing TTF units as well as of the self-assembly strategy developed by Stoddart and co-workers which uses the ability of the bis(benzyl)-4,4′-bipyridinium dication to self-assemble with a variety of electron-rich systems.[143] This field has been excellently reviewed by Becher and co-workers in a very recent paper devoted to the use of TTF as a building block in supramolecular chemistry.[23] Different TTF derivatives have been prepared in which the TTF unit is covalently attached to pyridinium and bipyridinium acceptors. The literature related to these systems containing TTF and σ acceptors of pyridinium and bipyridinium cations are studied in detail in the 1999 review by Bryce on the use of TTF derivatives as donors in intramolecular charge-transfer materials.[22]

In 1991, Stoddart and co-workers reported that the receptor cyclobis(paraquat-*p*-phenylene) (**144**) forms a complex[146] with TTF which crystallizes with a pseudorotaxane-like geometry (**145**, Scheme 5). Further studies on this complex carried out by Bryce and co-workers show that the electrochemical oxidation of TTF to the radical cation results in decomplexation, which is accompanied by a visible change in the color of the solution.[147] Moreover, this process is highly reversible over many redox cycles. It therefore seemed that the combination of the TTF residue and the cyclobis(paraquat-*p*-phenylene) moiety is an ideal choice for incorporating into "molecular shuttles" with potential application as electrochemically controlled molecular switches.[143a]



Scheme 5. Formation of a pseudorotaxane-like structure through complexation of TTF with cyclobis(paraquat-*p*-phenylene) (**144**).

When two different π-electron-rich residues ("stations") are connected in a dumbbell-shaped chain structure and encircled by an electron-defficient ring (shuttle) to form a [2]rotaxane, a chemical, electrochemical, or photochemical stimulus can disturb the equilibrium position of translational isomers and the [2]rotaxane can behave as a molecular shuttle (Figure 8). Although other rotaxane-based switches[148] and gates[149] have been previously demonstrated in solution, the TTF moiety is especially interesting for constructing new types of catenanes provided that it is, in principle, tetravalent. Most building blocks hitherto used to construct catenane systems, for example, hydroquinone, phenylene-1,4-diamine, benzidine, and bipyridine, are divalent species.

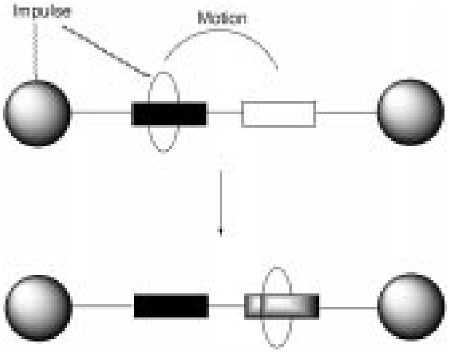
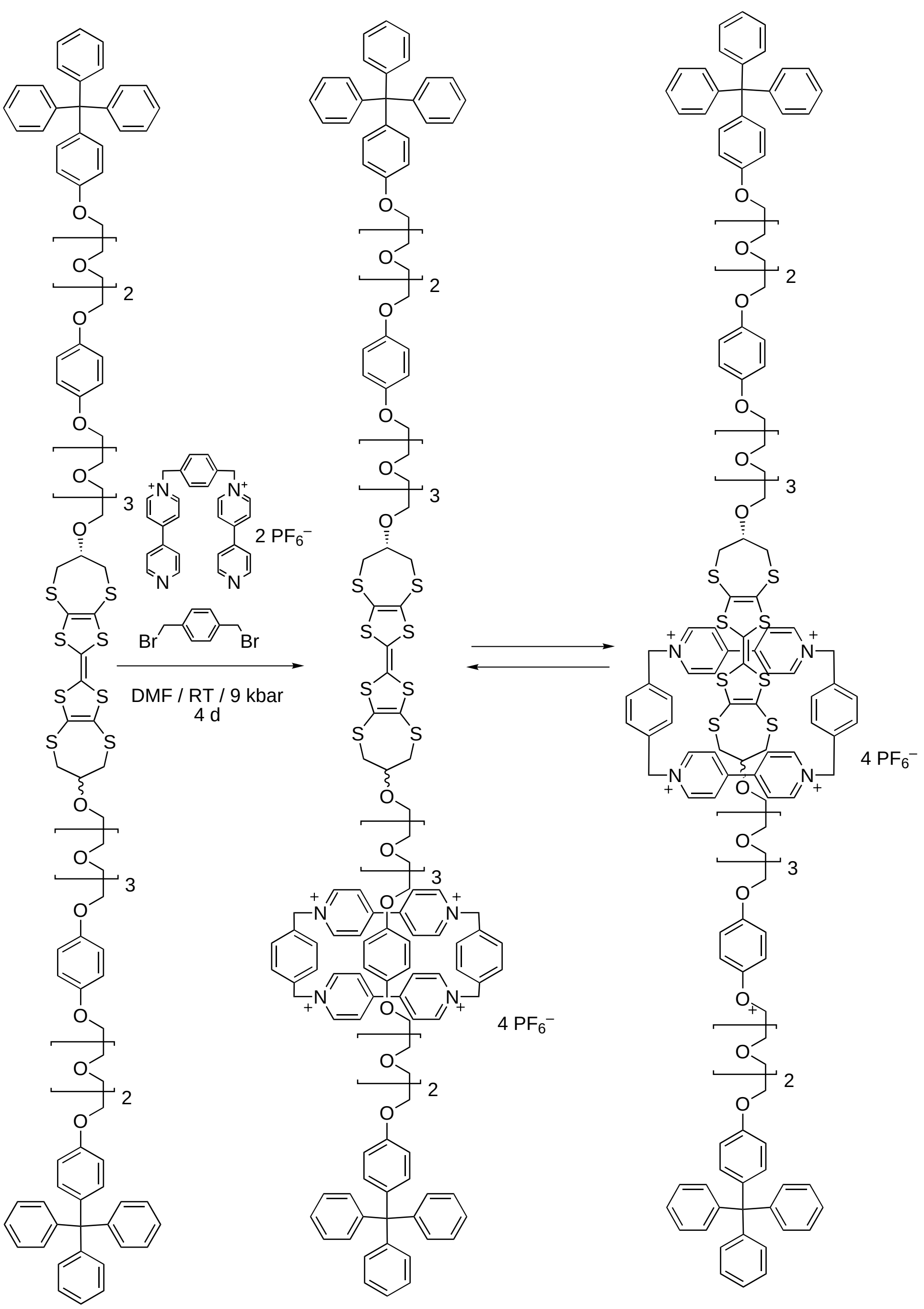


Figure 8. Molecular shuttle obtained from a [2]rotaxane comprised of two different electron-rich units (stations) connected in a dumbbell-shaped chain and encircled by an electron-deficient ring (shuttle).

With the aim of preparing a molecular shuttle, Stoddart and co-workers carried out the self-assembly of the [2]rotaxane **147** with two degenerate stations located on either side of a TTF residue.[146] The two hydroquinone rings are positioned on each side of the TTF residue to ensure that it is the most thermodynamically favorable position for occupation by the π-electron-defficient cyclophane. Two 4-tritylphenyl ether units were used as "stoppers". The TTF residue is the site which is occupied predominantly by the cyclophane. Upon selective oxidation of the TTF unit, the positive charge on TTF^+ (**147b**) repels the tetracationic acceptor macrocycle by coulombic forces, forcing the "shuttle" away from the TTF unit to one of the hydroquinol units (**147a**; Scheme 6).



146 **147a** **147b**

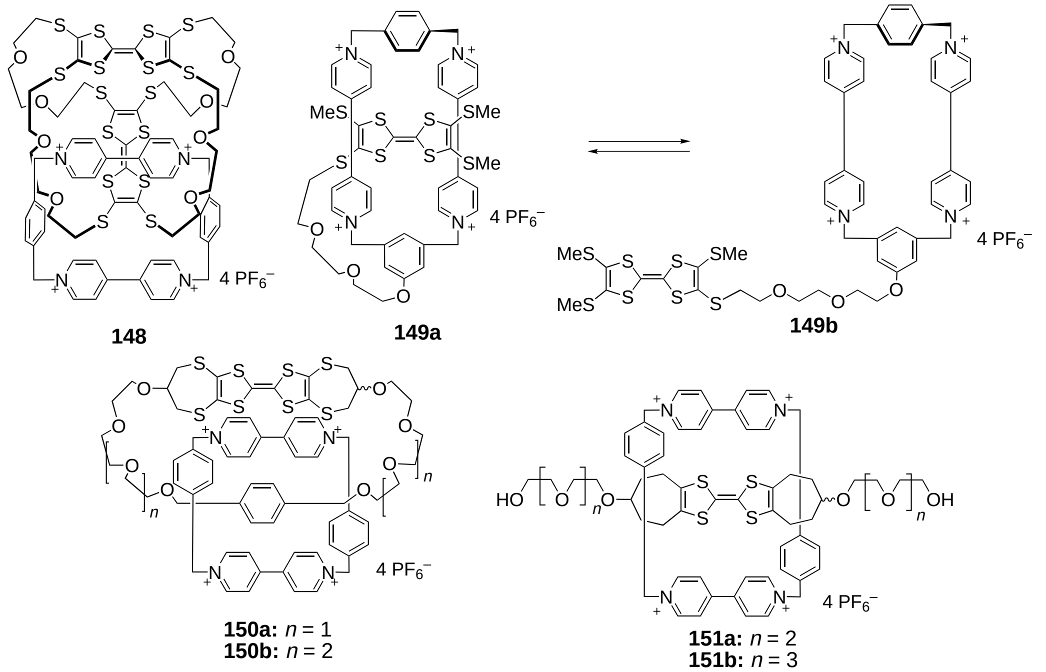
Scheme 6. A molecular shuttle bearing a central TTF unit and two hydroquinone rings as electron-rich residues.

Other interlocking molecular systems containing the TTF unit and the π-electron-accepting cyclophane cyclobis(paraquat-*p*-phenylene) have been synthesized by using the self-assembly strategy developed by Stoddart and co-workers.[23, 59, 63] Some recent examples of these types of materials (**148**–**151**) are depicted in Scheme 7. Since these systems have been very recently reviewed by Becher and co-workers, we refer the reader to this timely and outstanding paper.[23]

We will briefly discuss pseudorotaxane **151**. Thus, a complex having a [2]pseudorotaxane geometry (**151**) was formed by mixing a polyether containing a (2-oxy-1,3-propylenedithio)TTF unit with the cyclobis(paraquat-*p*-phenylene) π acceptor.[141] The TTF unit is oxidized to the radical monocation upon addition of three molar equivalents of I$_2$ and dissociation of the complex occurs as a result of the disruption of the CT interaction and the presence of electrostatic repulsion between the tetracationic host and the monocationic guest. Reduction of the monocationic species to their neutral states is accompanied by the insertion of the regenerated neutral guests into the cavity of the host. Therefore, this is a new example of prototypical molecular-sized machines which can be controlled by external redox stimuli.[141]

Ashton et al. also reported in 1999 a supramolecular system that can be switched between three distinct states through electrochemical manipulation of a guest's redox properties in the presence of two hosts with different π-donor/π-acceptor capabilities.[150] Together with the π acceptor cyclobis(paraquat-*p*-phenylene) (CBPQT)acting as the guest, the π-electron-donating macrocyclic polyether 1,5-dinaphtho[38]-crown-10 (1/5DN38C10) and TTF were used as the hosts in this new supramolecular system (Figure 9).

A new concept was introduced in this study: the reverse role of the TTF moiety. The TTF^{2+} ion generated upon oxidation could play the role of an electron-acceptor (EA) guest in complexes with electron-donor (ED) hosts. Then it should be possible to use TTF as a switchable ED/EA guest, so that its association with EA/ED hosts can be controlled electrochemically. In this supramolecular system, depending on the potential range, TTF can 1) be free when present as the radical cation TTF$^{+\bullet}$, 2) form a complex with CBPQT^{4+} in its TTF(0) state, or 3) be complexed by 1/5DN38C10 when it exists as TTF^{2+}. The authors claim that second-generation three-pole systems can be conceived wherein the occurence of, in addition to the choice of the partner in, energy- or electron-transfer processes can be coordinated by electrochemically driven molecular motions. Such a system may lead to its application as molecular-level signal processors.[150]



Scheme 7. **148**: a catenane with a *cis*/*cis*-configured tetrathiafulvalenophane; **149**: a macrocycle bearing a pendant TTF unit that exhibits "anchimeric complexation"; **150**: a [2]catenane with a TTF unit; **151**: a [2]pseudorotaxane as a prototype for molecular-sized machines.

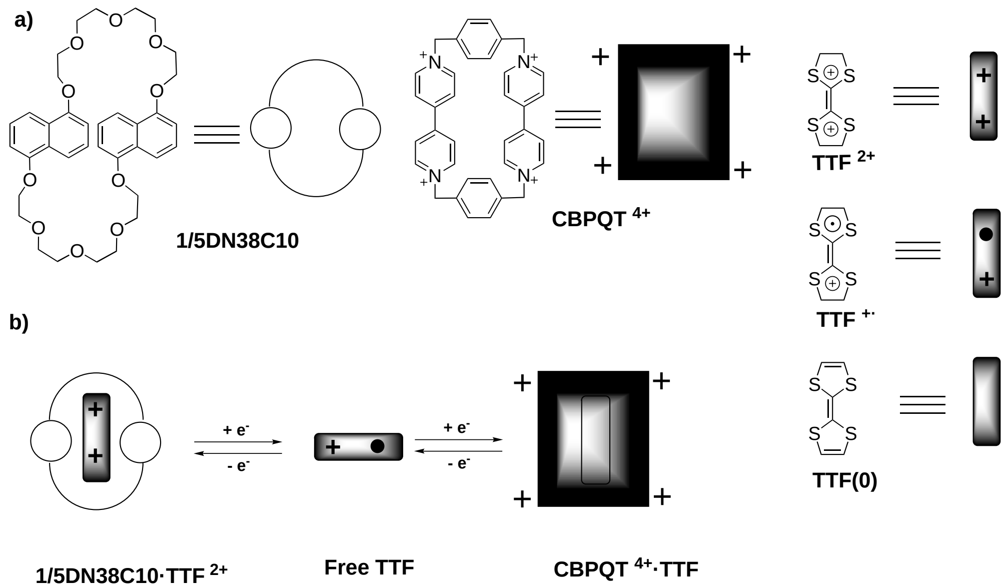


Figure 9. a) Structural formulas and schematic representations of the components of the three-pole supramolecular switch described in ref. [150]. b) Schematic representation of the electrochemically reversible three-pole supramolecular switch based on the three-component mixture $CBPQT^{4+}$-1/5DN38C10-TTF (redrawn from ref. [150a]).

A research group led by Heath at the University of California and Williams at the Hewlett–Packard Laboratories in Palo Alto have described new electronically configurable molecular-based logic gates consisting of a monolayer of redox-active rotaxanes sandwiched between metal electrodes.[151] The switches were read by monitoring the current flow at reducing voltages. The demonstration circuit is not very flexible, because the rotaxanes cannot be restored to their original state once oxidized. Hence turning off any given switch is irreversible. This facility is sufficient for read-only memory and certain kinds of logic circuits.[152] Considering the particular redox behavior of the TTF moiety and the extensive knowledge obtained in recent years on its supramolecular chemistry, TTF-based rotaxanes might be good candidates to be investigated in this type of device in the hope of finding a system that may switch back and forth and create a novel version of computer memory that could be written and erased many times over.[152]

3.3. TTF Derivatives Exhibiting Magnetic Properties

One of current trends in molecular science deals with the investigation of compounds that exhibit, if possible in a synergistic way, multiple physical properties such as electrical conductivity and magnetic interactions, spin crossover and magnetism, optical and magnetic properties.[153] Thus, a contemporary challenge in this field is that of designing, by the wise choice of constituent molecules, new materials that combine properties not normally associated with a single material.[154, 155] It has long been thought that conductivity and magnetism were inimical to one another.[156] However, several attempts have been made to couple interesting conducting and magnetic behaviors in molecule-based compounds.[157] With this aim, different approaches have been followed to design and synthesize new TTF-containing organic conductors exhibiting localized magnetic moments. Since Day et al. reported the first observation of the coexistence of localized and conducting electrons in a metallic charge-transfer salt in 1992,[158] different types of TTF-containing metallic radical cation salts with paramagnetic anions have been prepared to study the possibility of new physical phenomena resulting from the mutual interaction between delocalized conduction electrons and localized magnetic moments.[157, 159] Comprehensive review articles have recently been published that focus on the different magnetic molecular materials based on CT complexes and CT salts of tetrathiafulvalene in which magnetism arises from the presence of magnetic ions. In 1997 Day and Kurmoo reviewed the different molecular magnetic semiconductors, metals, and superconductors based on bis(ethylenedithio)(BEDT)-TTF salts with magnetic anions.[21] In a comprehensive review article Coronado and Gómez-García collected recent results of organic/inorganic hybrid salts in which the electron donors are organic molecules of the TTF type and the electron acceptors are polyoxometalates that can also act as ligands that incorporate one or more magnetically active transition metal ion.[19] Ouahab has also recently reviewed the use of organic/inorganic molecular materials in which the inorganic components are coordination complexes (tetracyanometalates, hexacyanometalates, metal bis(dithiolates), metal bis-(dithiolenes), metallocenium complexes, and polyoxometalates) and the organic part is concerned with TTF and BEDT-TTF derivatives.[153] In these kinds of materials it is possible to couple ferromagnetically isolated and localized spins on transition metals in the inorganic network, as a consequence of the π electrons of the organic network. Rovira has recently reviewed the structural and magnetic characteristics of the recently discovered quantum–spin ladders.[160] In this regard, molecular spin ladders involving some TTF derivatives have been prepared from dithiophenetetrathiafulvalene (DT-TTF) and BEDT-TTF salts. The reading of the above mentioned review articles[19, 21, 153, 160] is highly recommended for a comprehensive coverage of the field.

The second type of TTF derivatives that exhibit magnetic behavior are those which include only organic species, the so-called organic ferromagnets.[161, 162] Enormous efforts have been devoted in recent years towards the obtention of organic magnetic materials composed of molecular species or polymers. This research has been stimulated by the promise of applications in future generations of electronic, magnetic, and/or photonic/photronic devices ranging from information storage and magnetic imaging to static and low-frequency magnetic shielding.[163, 164] The target of this research is the obtention of organic compounds that combine the inherent properties of organic compounds with a usable magnetic property. Some of the foreseeable advantages of the organic and polymeric over the traditional materials have been recently pointed out by Veciana:[165]

1. Their transparency in many spectral regions and the possibility of being obtained in optically active chiral forms might enable them to be used as magneto-optical switches and for the manipulation of polarized light in optical devices.
2. The flexibility and solubility of organic/polymeric compounds makes them easily processable, and they are therefore good candidates for obtaining magnetically active thin films and colloidal dispersions with ferrofluid properties.
3. The possible biocompatibility of organic magnetic compounds allows applications such as selective contrasting agents in nuclear magnetic resonance imaging to be envisaged.
4. The enormous versatility of organic chemistry allows small structural modifications to be performed to obtain desired materials properties which are not usual in most traditional inorganic materials.

Although a number of organic ferromagnets have been reported,[166] the transition temperatures of genuine organic ferromagnets are still extremely low. One promising approach to raise transition temperatures is the above-mentioned strategy of using conduction electrons which itinerate along a stack of organic donor radicals.[167] The main point in this methodology is the introduction of ferromagnetic coupling between the conduction electrons and localized spins. Thus, in order to introduce a ferromagnetic exchange interaction between a localized spin on the radical unit and a π spin generated on the donor unit, Sugawara and co-workers proposed an open-shell donor, where the π-donor and π-radical units are connected through cross-conjugation.[168] They prepared nitronyl nitroxide (NN) derivative **152** bearing a TTF unit at the nodal carbon atom of NN (Figure 10). When **152** was oxidized by excess I_2 in 2-methyltetrahydrofuran (MTHF), the ESR spectrum of the oxidized species in a frozen matrix of MTHF at 100 K showed a set of fine structure signals corresponding to the triplet species along with a signal ($g = 4.030$) of $\Delta m_s = 2$ in a half-field region (Figure 10). The temperature dependence of the signal intensity in the THF glass was measured in the temperature range 50–150 K.

The results show that the ground-state spin multiplicity of the cation radical of **152** is a singlet and the observed triplet signal is derived from a thermally populated species and that two spins interact antiferromagnetically.[168a] In 1999, the research groups of Sugawara and Fujiwara reported on the synthesis of new TTF-based donor radicals **153** and **154** (Figure 10).[169] These radicals were also oxidized with excess iodine in THF solution and the ESR spectra showed a set of fine structured signals corresponding to a triplet species. The results obtained suggest that the triplet is the ground state of these cation diradicals. This result is in sharp contrast with that obtained for **152**. This difference is probably because although the TTF and NN groups in **152** are connected through cross-conjugation, they are considered to be severely twisted as a result of steric repulsion. The delocalization of the HOMO or SOMO′ to the radical site is therefore suppressed, which leads to a breakdown of the electronic feature of a spin-polarized donor. This unfavorable steric hindrance is released by inserting a *p*-phenylene or *p*-thiophenylene group (**153**) as seen from the ESR measurements. If a columnar stacking of these TTF-based donor radicals that afford the ground-state triplet cation radicals upon one-electron oxidation can be realized, an organic conducting ferromagnet is expected to form.[169a]

The cross-conjugated dimeric TTF units **155**[170] and **156**[171] also provide the possibility of a stable triplet ground state, and they can be regarded as simple model compounds for the high-spin system **157**. Mizouchi et al. predicted theoretically that the radical cations of **157** should show a high-spin ground state.[172] The dication radical of **155a** possesses a singlet ground state, which is not in agreement with the prediction of a triplet state from theoretical calculations, presumably because it is fairly well stabilized. The calculations do predict

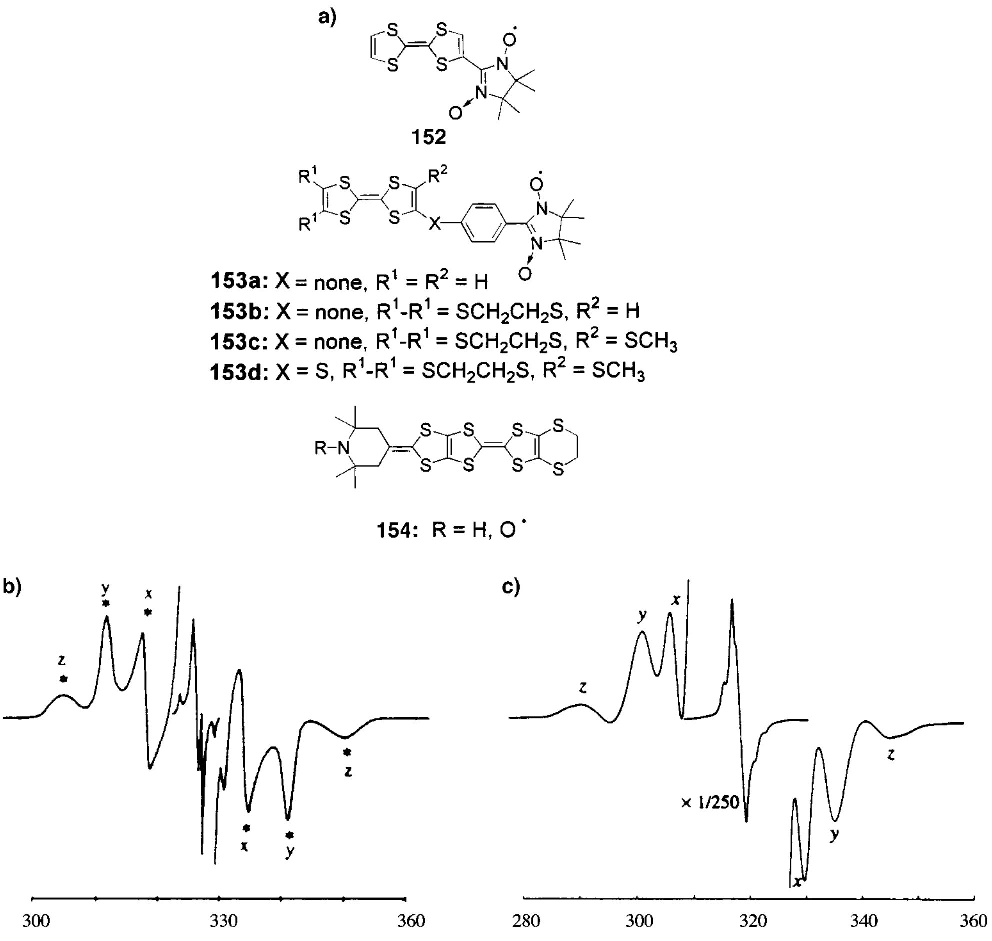
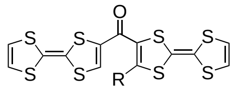
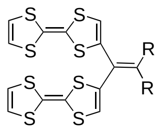
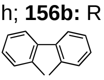
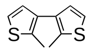


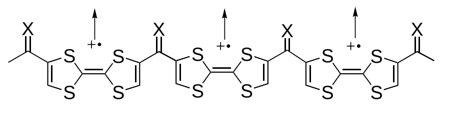
Figure 10. a) TTF-based donor radicals (**152**–**154**); b) ESR spectra of iodine-doped $\mathbf{152}^{+\bullet}$ (reprinted with permission from ref. [168a]) and c) ESR spectrum of iodine-doped **153c** (reprinted with permission from ref. [169a]).



155a: R = H
155b: R = CO_2CH_3
155c: R = $CON(CH_3)_2$



156a: R = Ph; **156b**: R = Me;
156c: R_2 = 
156d: R_2 = 
156e: R_2 = 



157 X = CH_2, O, S

the observed smaller singlet–triplet difference in $\mathbf{155a}^{2+}$ compared with those in other bis(tetrathiafulvalenyl)vinylene and bis(tetrathiafulvalenyl)thioketone dications. Furthermore, the polarization of a carbonyl group might contribute to the stabilization of the singlet species.[170] Therefore, Iyoda et al. have carried out the synthesis of derivatives **156a**–**e** in order to examine the spin–spin interaction in their oxidized state.[171] The redox processes of these dimeric TTF compounds display no separation in either of the two-electron transfers in their cyclic voltammograms, presumably as a consequence of the weak interaction between the two TTF moieties in these molecules. This weak interaction reflects the twisted structure, which could be elucidated by the X-ray analysis of **156a**. Treatment of **156a** with iodine yielded the corresponding radical cation salt which shows interesting magnetic and electrical behavior. The ESR spectrum of the powdered sample of the radical cation salt of **156a** consists of a broad signal at the center and a fine structure ($g = 2.0074$, $D = 108$ G at 163 K) together with signals with $\Delta m_s = 2$ corresponding to a triplet species. The distance between the two spins, as estimated from the D value by the point–dipole approximation (6.36 Å), seems to be comparable to the distance between the two TTF units in the CT salt. This interesting result paves the way towards the synthesis of polymeric analogues exhibiting the more preferential triplet ground state.

A third type of TTF-containing magnetic materials lies at the frontier between the two previous types. They consist of TTF derivatives that incorporate magnetic ions in their structure.

In 1994, McCullough et al. reported on the first synthesis and characterization of metal coordination complexes of TTF as new building blocks (**158**–**161**, Figure 11 a) for new electronic, optical, and magnetic materials.[173] They consist of early and late transition metal homobimetallic coordination complexes of tetrathiafulvalene tetrathiolate ($TTFS_4$); the $TTFS_4$ framework allows spin interaction between the two metal centers by superexchange (Figure 11 b).[174] In addition, a one-electron oxidation should produce a spin ordering of the molecule through an intramolecular antiferromagnetic coupling of the spins (Figure 11 c). The electrochemical characterization of **158** shows two reversible oxidations corresponding to the TTF moiety together with a reduction process at −0.85 V corresponding to the Ti^{IV}/Ti^{III} couple. Compound **158** forms charge-transfer complexes with tetracyano-*p*-quinodimethane (TCNQ) which is important for

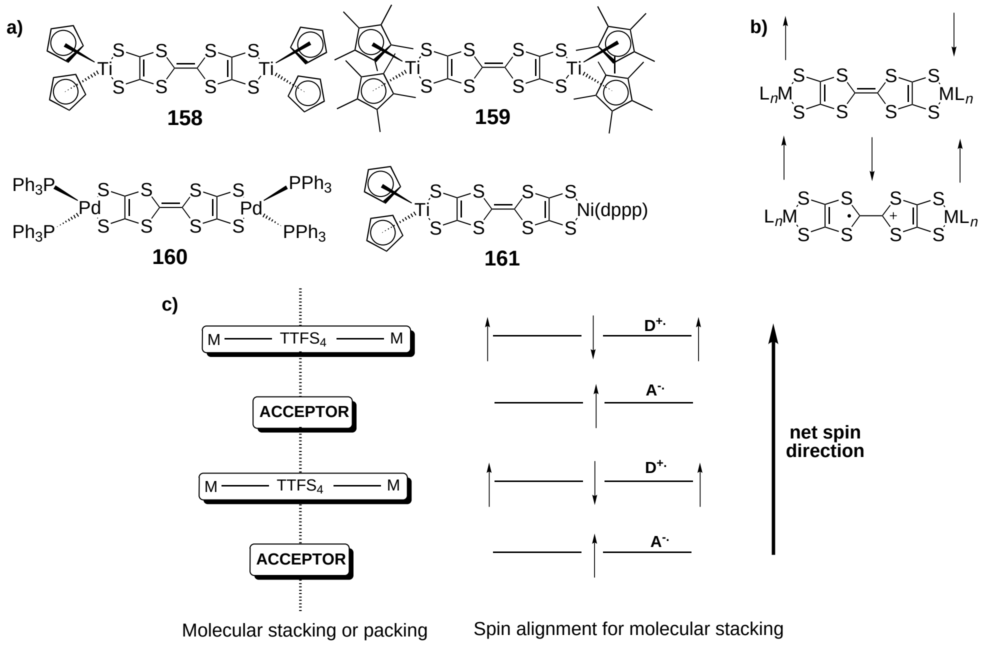
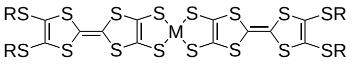


Figure 11. a) New metal coordination complex of tetrathiafulvalene thiolates **158**–**160**. b) Spin interaction in bimetallic TTFS$_4$ complexes. The complexes shown are based on the metal M having a $S=1/2$ ground state. c) Proposal for molecular ferrimagnets based on mixed-stack, charge-transfer complexes. (Redrawn from ref. [173a].) dppp = bis(diphenylphosphanyl)propane.

achieving the mixed-stack complexes required for magnetic materials.[175] However, although the main target in the syntheses of these compounds was the preparation of ferrimagnetic materials based on the use of mixed-stack charge-transfer complexes of the bimetallic TTSF$_4$ complexes, to the best of our knowledge, no report on their magnetic properties have so far been reported.

A similar approach has been more recently followed by Sugimoto and co-workers.[176] They synthesized a new type of TTF-containing organic complex (**162**) with magnetic metal ions incorporated through covalent bonds into the two- or three-dimensional π-conducting network provided by the TTF moiety.



162: M = Cu, Zn, Ni
R = Me, Et or R‿R = CH$_2$CH$_2$

It was expected that unique solid organic systems involving both conducting π electrons and localized d electrons in interaction with each other would be formed. In contrast to this expectation, a large degree of intramolecular electron transfer from the Cu^{II} ion to the TTF radical cation ligands occurs to give rise to almost no spin on the resultant Cu^{III} atom. Interestingly, as the one electron transferred from the Cu^{II} atom can be equally accepted by the two TTF radical cation ligands, a 50% radical cation resides on each TTF ligands; hence a mixed-valence state can be achieved. In fact, the present neutral copper complexes exhibited comparatively high electrical conductivities (single crystal $\sigma_{RT}=10^{-4}$–10^{-1} S cm^{-1}) without any doping. The authors suggest that magnetic metal ions other than Cu^{II}, for example, Cr^{III} ($S=3/2$), Mn^{II} ($S=5/2$ or 1/2), Co^{II} ($S=1/2$), and Fe^{III} ($S=5/2$ or 1/2) could also be used in the preparation of similar neutral complexes. Different electrical conducting and magnetic properties might be observed with these new complexes.

3.4. Molecular Rectification in TTF-σ-Acceptor Materials

In 1974 Aviram and Ratner proposed rectification of electrical current through a single D-σ-A molecule, in which a strong donor moiety is covalently attached to a strong acceptor moiety through a covalent, saturated σ bridge.[177] Molecule **163** was chosen as a prototype material because of the excellent donor and acceptor properties of TTF and TCNQ, repectively. In order to achieve molecular rectification the molecule should exhibit anisotropic electrical properties. Thus, these materials should be aligned uniformly between two electrodes (M$_1$ and M$_2$) so that they would allow electron flow from the cathode M$_2$ to the acceptor end, from there to the donor by electron tunneling through the σ bridge, and then from the donor terminus to the anode M$_1$. Figure 12b shows how such a device is asymmetric because the HOMO of D is relatively low while the LUMO of A is relatively high. The device will work if the inelastic through-bond tuneling is more likely than the elastic through-space tunneling, which is unaffected by molecular orbitals.[178]

Although the research groups of Panetta and Metzger have performed a great deal of work during the last two decades to bring this theoretical project into reality,[179–181] to the best of our knowledge, the D-σ-A structure **163** has not yet been synthesized. However, they have developed a systematic synthetic plan aimed at the obtention of a series of model compounds in which different donor and acceptor moieties as well as σ bridges are incorporated.[179b, 180] This effort has allowed different D-σ-A molecules and several ground-state zwitterions D$^+$-π-A$^-$ to be obtained, one of which became the first confirmed unimolecular rectifier.[182] **164**–**170** are selected examples of TTF-containing D-σ-A molecules proposed as molecular rectifiers.

The first two D-σ-A products prepared (**164**, **165**) containing the strong donor TTF and the strong acceptor TCNQ were metastable materials; they were amorphous, difficult to purify, and readily decomposed. The ^{1}H NMR studies of these products resulted in spectra in which many of the resonances were extremely broad: perhaps indicative of

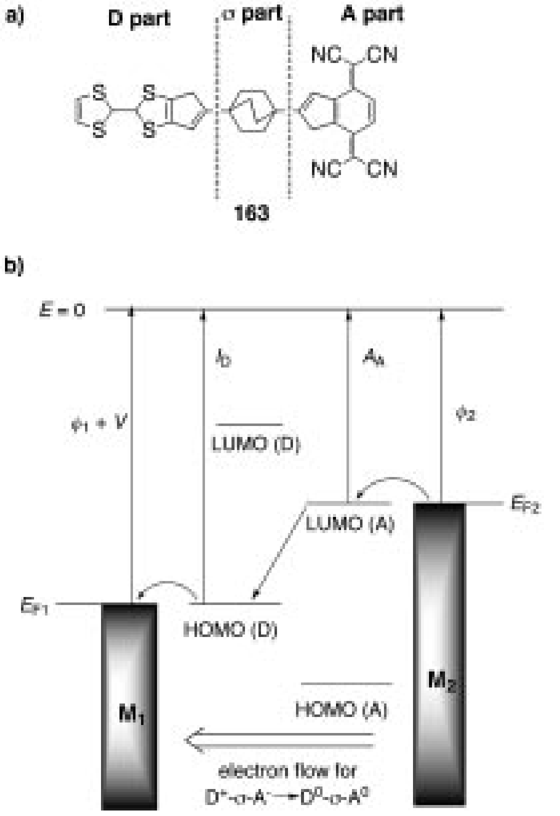
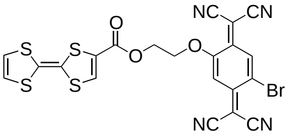
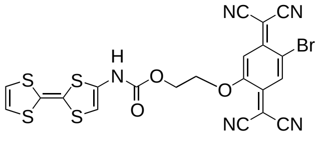


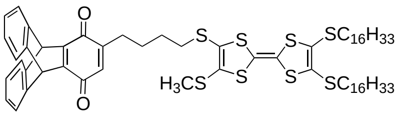
Figure 12. a) Original D-σ-A structure **163** proposed by Aviram and Ratner for a molecular rectifier. b) The Aviram–Ratner mechanism, showing the through-molecule electron flow from the excited zwitterion state D^+-σ-A^- to the ground state D^0-σ-A^0.[180]



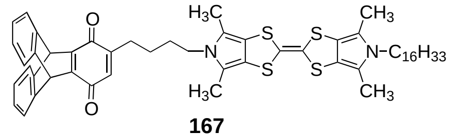
164



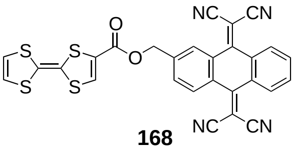
165



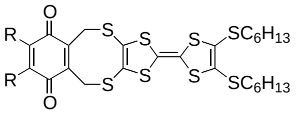
166



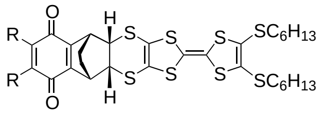
167



168



169a: R = H
169b: R = Br
169c: $\overset{\frown}{\mathrm{R\;R}} = (\mathrm{CH{=}CH})_2$



170a: R = CH_3
170b: R = $C_{10}H_{21}$

paramagnetic species or charge-transfer complexes.[179a)] A ground-state biradical character for these compounds is also suggested by the intense broad signal observed in the ESR spectrum of a powdered sample of **165** recorded at 300 K. In order to avoid these problems, other weaker donor moieties (dialkylamine, pyrene, anthracene) were covalently attached through different bridges (ester, carbamate) to the TCNQ moiety to yield stable D-σ-A systems, with some of them exhibiting rectification.[180] On the other hand, TTF has been incorporated in stable D-σ-A systems by replacing the strong TCNQ acceptor moiety by other moderate acceptors such as the triptycenequinone system (**166**, **167**).[183] Further conversion of the triptycenequinone derivatives **166** and **167** into the triptycene-dicyanoquinonediimines (stronger acceptors) failed.[87, 180, 184] The presence of long alkyl chains in **166** and **167** allows these compounds to form Pockels–Langmuir (PL) films at the air–water interface and can be mostly transferred as LB films onto solid substrates. No charge-transfer band was however observed in the LB films.

In 1998, Bryce and co-workers reported on the synthesis and study of **168** and a related TTF-σ-TCAQ-σ-TTF triad in which the strong donor TTF is covalently attached to the moderate acceptor TCAQ moiety.[185] These are the first readily available, analytically pure, stable TTF-spacer-TCNQ derivatives. In contrast with compound **165**, ESR (no signal) and IR data on powdered samples of **168** suggested a neutral ground state. Simultaneous electrochemistry and ESR experiments provide evidence that the spin-density distribution in the radical cation of **168** was modulated intramolecularly by the adjacent TCAQ moiety. This behavior was significantly different to that observed in a mixture of model TTF and TCAQ derivatives which did not interact in solution when mixed under the same experimental conditions. Derivatives of **168** would therefore be good candidates for preparing macroscopic films to study their potential behavior as bulk rectifiers in suitable devices.

We have also reported on the synthesis of novel single-component donor–acceptor compounds (**169**) containing *p*-benzoquinone-TTF units.[186–187] Since the substitution on the *p*-benzoquinone ring has a striking influence on the acceptor ability of this moiety, we have introduced different substituents to tune the acceptor ability of the quinone moiety. The presence of the long alkyl chains attached to the TTF moiety led to compounds that were highly soluble in common organic solvents, which is very important for obtaining easily characterizable and proccessable materials. The CV data reveal the presence of both donor and acceptor moieties which behave independently and preserve their own redox character. Work is in progress to improve the acceptor ability of the quinone moiety by replacing the *p*-benzoquinone unit with the stronger acceptors TCNQ and DCNQI. The preparation of LB films of **169** and other bisdodecyl-substituted derivatives as well as their possible rectifying behavior is also under study.

Khodorkovsky and co-workers have recently reported on a similar TTF-*p*-benzoquinone system (**170**).[188] The X-ray structure of **170** shows the molecule has a bent configuration with the acceptor *p*-benzoquinone moiety spatially located above the donor dimethylthio-TTF unit. A low charge transfer can be observed in the ground state of **170** because of the short intramolecular face-to-face distances between the planes of donor and acceptor molecules. A photoinduced intramolecular electron transfer takes place after irradiation with sunlight which results in the appearance of broad signals in the EPR measurements. This is one of the first examples of systems with inherent intramolecular through-space charge-transfer properties.[188]

3.5. TTF Derivatives as New Organic Electrooptic Materials

3.5.1. TTF Derivatives as NLO Materials

Recent advances in polymeric electrooptic materials and fabrication techniques for devices have significantly increased the potential incorporation of these materials and devices into modern high-bandwidth (fiber and wireless) telecommunication, information processing, and radar systems.[189] Push–pull systems of general structure D-π-A are being actively studied as NLO chromophores,[190] since they can exhibit large quadratic molecular hyperpolarizabilities (β). These are electrooptic materials whose refraction index can be changed by the application of an electric field and are of interest as a result of their potential use in areas such as optical modulation, molecular switching, optical memory, and frequency doubling.[191]

In this context, we reported in 1998 the first NLO materials containing the TTF unit as the donor moiety in D-π-A systems (**171**, **172**, Table 2).[192] We have studied the influence of different acceptors and spacers in order to optimize the nonlinear optical response of these materials.[193–196] Table 2 shows the $\mu\beta$ values of selected TTF-containing NLO materials (**171**–**177**). The $\mu\beta$ values were measured using the electric-field-induced second harmonic generation (EFISH) technique at 1907 nm.

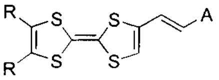
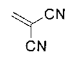
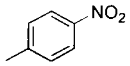
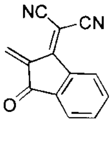
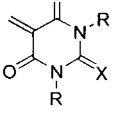
An increase in the NLO properties of these materials has been observed by using stronger electron acceptors attached to the TTF moiety. Low $\mu\beta$ values were obtained for derivative **171** bearing the weak formyl electron acceptor.[192] An improvement in the $\mu\beta$ values was observed when the formyl group was replaced by stronger electron acceptors such as dicyanomethylene (**172**),[192, 193] nitrobenzene (**173**)[194] and (thio)barbituric acid (**175**–**177**),[195] with the best results ($\mu\beta = 1350.10^{-48}$ esu) being observed when the strong acceptor 3-(dicyanomethylidene)indan-1-one was used in combination with the TTF unit.[196]

As in other NLO materials, the $\mu\beta$ values increase in the series **a** < **b** < **c**, which shows the beneficial effects of the extended conjugated chain on the molecular first hyperpolarizability (Table 2).[190c]

The UV/Vis absorptions of the novel compounds were measured in the same solvent used for the EFISH measurements. In all of them, a low-intensity charge-transfer band is observed in the visible region. A bathochromic shift is observed when increasing the acceptor ability of the acceptor moiety. A most interesting observation of these compounds is that they present an increase in their $\mu\beta$ values with substitution on the TTF skeleton and, in spite of their larger π extension, a hypsochromic shift is observed when going from the **a** to the **c** member of a series. Thus the well-known trade-off in the efficiency of the NLO transparency is overcome.

The charge-transfer nature of this band, which is a prerequisite for the attainment of high β values,[197, 198] has been studied by quantum-chemical methods. Figure 13 depicts the molecular orbital topologies calculated by using the PM3 semiempirical method for the HOMO and LUMO orbitals of compound **174c**. This topology is representative of

Table 2. UV/Vis absorption [nm] and $\mu\beta$ values [10^{-48} esu] of selected TTF-containing NLO materials.

				λ_{max}[a]	$\mu\beta$[b]	$\mu\beta_0$[b]	Ref.
171	A = CHO		$n = 1$	486	80	35	[192]
172	A = 		**a**: $n = 1$	636	470	190	[192]
			b: $n = 2$	628	630	320	[193]
173	A = 		**a**: $n = 1$	512	135	135	[194]
			b: $n = 2$	500	270	180	
			c: $n = 3$	500	315	205	
174	A = 		**a**: $n = 0$	798	–	–	[196]
			b: $n = 1$	726	700	259	
			c: $n = 2$	690	1350	570	
175	A = 	R = H, X = O	**a**: $n = 0$	641	80	39	[195]
			b: $n = 1$	597	190	104	
176		R = CH$_3$, X = O	**a**: $n = 0$	650	142	67	
			b: $n = 1$	609	290	154	
177		R = CH$_3$-CH$_2$, X = S	**a**: $n = 0$	716	480	180	
			b: $n = 1$	661	760	347	
			c: $n = 2$	646	960	455	

[a] Recorded in CH_2Cl_2. [b] Measured by the EFISH technique at 1907 nm; R = H, SCH_3, or $\overset{\frown}{RR} = S(CH_2)_2S$.

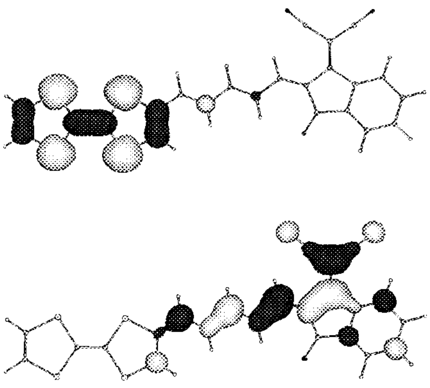


Figure 13. Molecular orbitals (PM3) of **174c**.

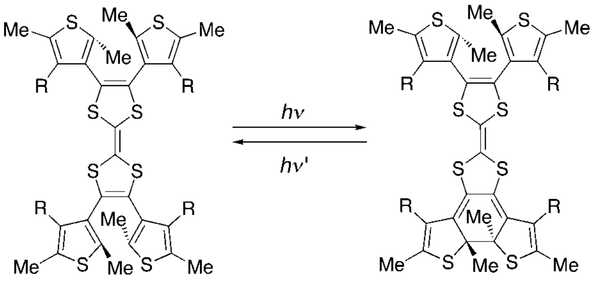
that calculated for the other TTF-containing NLO materials. It can be seen how the HOMO is mainly located on the TTF unit while the LUMO extends along the acceptor moiety and the ethylenic spacer. The different location of these orbitals indicate the charge-transfer character of the HOMO–LUMO transition and shows the HOMO–LUMO overlap necessary for obtaining good NLO responses.[197]

With these promising results in hand, better $\mu\beta$ values may be expected for TTF-containing materials in which more polarizable spacers and stronger acceptor units are included. In addition, TTF-based NLO chromophores display good thermal stabilities which make them potential candidates for incorporation in poled polymers.

The NLO behavior of TTF derivatives seems not to be limited to second-order effects. In 1999, Nakano et al.[199] reported that the radical cation of TTF provides unique third-order optical nonlinearity, that is, a large negative γ value (second hyperpolarizability) according to a structure–property correlation rule developed by their research group.[200] The sign of γ is important in quantum optics:[201] the positive values cause the self-focusing effect of an incident beam, while the negative one causes the self-defocusing effects. Thus, since systems with negative values of γ are in general rare and are also expected to be candidates for fundamental systems of "controllable NLO materials", the finding that the radical cation of TTF exhibits large negative values of γ paves the way for further studies on this specific property. Furthermore, as the radical cation of TTF is present in the segregated stacks of several electrically conducting charge-transfer complexes in combination with acceptor counterparts, this type of material may constitute a new possibility for multiproperty systems combining high electrical conductivity and unique third-order nonlinearity ($\gamma < 0$).

3.5.2. TTF Derivatives as Photochromic Materials

Organic photochromic compounds that allow reversible modulation of a given electronic property, such as conjugation, by an external trigger, such as light, are attractive for different applications[202] including optical information storage systems.[203] One important class of these compounds are those bearing the diarylethene moiety because of their fatigue resistance and thermally irreversible reactivity.[204] Compounds of this type undergo a reversible electrocyclic interconversion (Scheme 8) between a colorless, unconjugated open state (o) and a colored, conjugated state (c) on irradiation.



178o: R = CH_3 **178c**: R = CH_3
179o: R = H **179c**: R = H

Scheme 8. Photochemical interconversion of compounds **178** and **179** between their open (o) and closed (c) forms.

Uchida et al. have recently synthesized 4,4′,5,5′-tetrakis(2,4,5-trimethyl-3-thienyl)tetrathiafulvalene (**178**) and 4,4′,5,5′-tetrakis-(2,5-dimethyl-3-thienyl)tetrathia-fulvalene (**179**) bearing the dithienylethene units.[205] Upon irradiation with UV light, the colorless solution of **178** changed to yellow. The yellow color was bleached by irradiation with visible light ($\lambda > 450$ nm). In contrast to **178** which underwent reversible photochromic reactions, the related analogue **179** did not show any color change by irradiation with UV light. This remarkably different behavior has been accounted for by the lack of steric repulsion which takes place between the methyl groups in **178** and results in an inactive photochromic conformation.

Interestingly, light-triggered electrochemistry of **178** was examined by cyclic voltammetry and revealed that this TTF derivative undergoes a direct electron-transfer reaction with the electrode on irradiation with UV light, whereas irradiation with visible light decreased the Faradaic current. Therefore, an electrochemical switching function was also observed to accompany the photochromism. This first example of photochromism in TTF derivatives paves the way for the very appealing field of multiproperty materials and, therefore, more effort should be paid to this type of TTF-based photochromic system.

3.5.3. Photovoltaic Applications of TTF-Containing Fullerenes

The design and synthesis of organic molecules with two chromophores, namely an electroactive donor and an acceptor fragment connected through a spacer, that display charge separation is an important topic in chemistry since they can be used as artificial photosynthetic systems to transform sunlight into chemical energy.[206]

During the last few years fullerenes, and particularly [60]fullerene, have been shown to have unique photophysical properties that are promising features for the preparation of photovoltaic devices.[207] Thus, one of the most outstanding properties of [60]fullerene in electron-transfer processes is that it accelerates the photoinduced charge separation and retards the charge recombination in the absence of light.[208] These findings suggest that C_{60} and its derivatives are promising candidates for the preparation of artificial photosynthetic systems and photovoltaic devices, which constitutes one of the most realistic and outstanding applications of fullerenes.

Since the preparation of C_{60} on a multigram scale in 1990[209] a huge amount of work has been devoted to the chemistry of C_{60} and it is already well-established. Therefore, during the last few years many C_{60}-donor systems have been prepared in the search for electron-transfer properties. We have recently reviewed this topic and a wide variety of C_{60}-based intermolecular as well as intramolecular complexes have been synthesized.[210]

It is worth mentioning that most of the donor molecules used in the preparation of C_{60}-σ-donor systems have an aromatic character in the ground state which is partially or totally lost upon oxidation to form the radical cation species.[210] In contrast, TTF and its derivatives are nonaromatic molecules which upon oxidation form the 1,3-dithiolium cation which possesses aromatic character (Scheme 1). This gain of aromaticity in forming the radical cation and dication species of TTF in the oxidation process is an important improvement for increasing the stabilization of the charge-separated state (Figure 14).

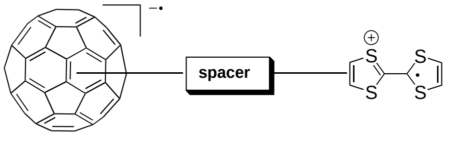
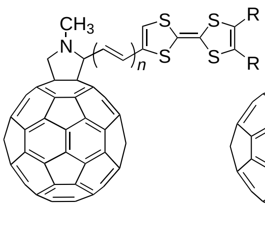
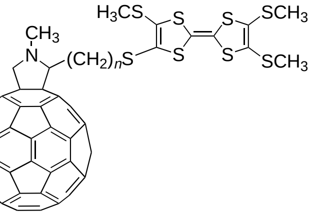


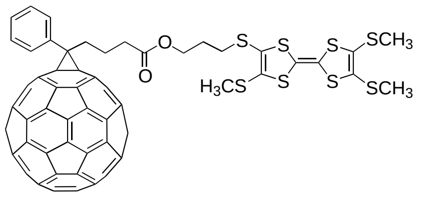
Figure 14. Approach for the design of molecules showing remarkably long-lived CS states: the TTF unit gains aromaticity upon oxidation.

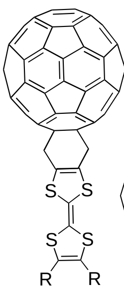
The first C_{60}-TTF dyad (**180**) was simultaneously and independently reported by Prato et al.[211] and Martín et al.[212] in 1996. Since then, other C_{60}-TTF derivatives, such as **181**,[213] **182**,[214] **183**,[215] **184**,[216] **185**,[217] and **186**,[218] have been published in the search of photoinduced electron-transfer processes.

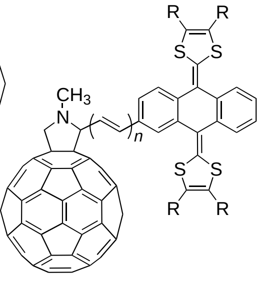
The C_{60}-TTF dyad **183** was prepared by a Diels–Alder cycloaddition of the *o*-quinodimethane analogue of TTF to C_{60}.[215] These systems undergo a rapid quenching of the triplet excited states, as observed by nanosecond-resolved flash photolysis, to generate transient charge-separated open-shell species with lifetimes typically around 75 μs.[219] These lifetimes are, however, far away from those measured for dyads such as **180** and **185**–**187**.

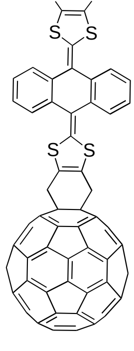

180: R = H, SCH_3, $(SCH_2)_2$
n = 0-2

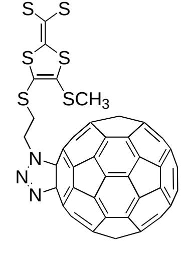

181: n = 3, 10

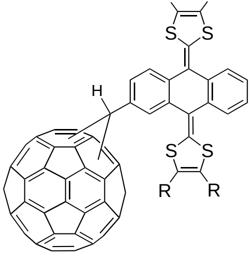

182


183: R = H, CH_3, SCH_3, CO_2CH_3


184: R = H, SCH_3 or R R = $S(CH_2)_2S$
n = 0, 1


185: R = H, SCH_3


186


187 [5,6] and [6,6]

The nature and length of the spacer linking the two electroactive moieties have a profound impact on the rate and efficiency of intramolecular electron-transfer processes.[220] Thus, we have prepared dyads (**180**) in which the TTF donor unit is attached to the C_{60} core through a single σ bond and one ($n = 1$) or two ($n = 2$) vinyl spacers. We have recently reported the photophysics of the TTF-containing dyads **180**[221] and **186**.[218] Absorption of light by these dyads leads to the formation of the excited singlet state of fullerene, which undergoes an intramolecular electron transfer to form the charge-separated (CS) state (Figure 14). Evidence for the electron transfer comes from steady-state and time-resolved photolysis.[221, 222] It is worth mentioning that an increase in the stabilization of the CS state takes place by gaining aromaticity upon oxidation of the TTF moiety.

Charge recombination proceeds mainly through formation of the triplet excited state of fullerene as a result of the strong second-order vibronic spin–orbit coupling induced by the presence of the sulfur atoms of the TTF unit. This charge-recombination behavior forming a fullerene triplet excited state is different to most of the previously reported C_{60}-based dyads that bear donor moieties other than TTF (Figure 15).[221]

The lifetimes of the charge-separated states in all these C_{60}-TTF dyads are in the range of 1–2 ns, which is similar to that found in other C_{60}-based tetraphenylporphyrin dyads (ca. 0.5 ns) endowed with similar spacers.[223]

More recently, we have found that C_{60}-based dyads bearing a π-extended TTF fragment (**187**) that forms very stable cationic species upon oxidation exhibit a CS state with a highly remarkable stability, being improved by about two orders of magnitude relative to other C_{60}-TTF dyads.[224]

Systems **188**[225] and **189**[226] are other more complex electroactive systems involving C_{60} and TTF moieties. These

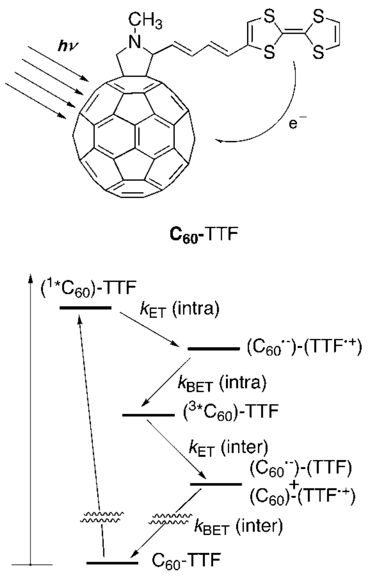
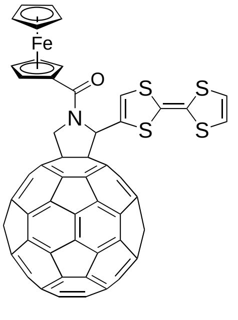
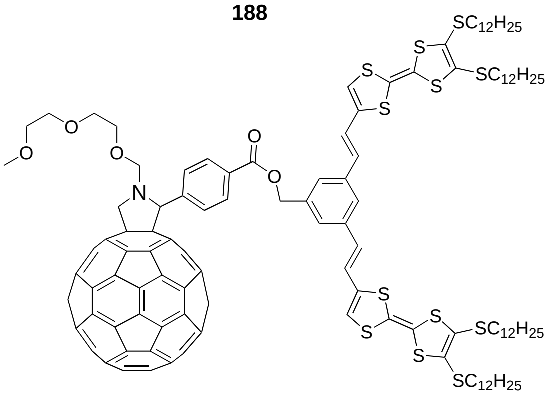


Figure 15. Deactivation process of the singlet excited state of fullerene in C_{60}-TTF dyads.



188



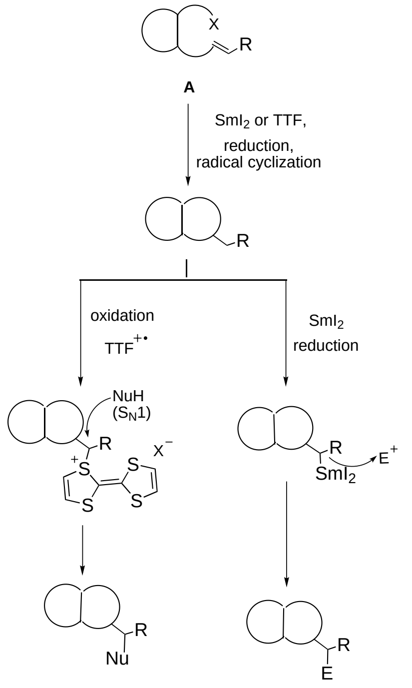
189

have been recently prepared in the search for a range of redox centers which could stabilize the formed CS state. Work is currently in progress to determine this behavior.

These findings suggest that C_{60}-TTF dyads are promising candidates for the preparation of devices for the conversion of solar energy. The search for novel photovoltaic devices and artificial photosynthetic systems is currently a major task in chemistry and the photophysical properties shown by dyads involving TTF and π-extended TTFs are among the most outstanding found for these purposes. In fact, we are currently working on the preparation of photovoltaic cells using TTF derivatives as donor moieties in C_{60}-based dyads.

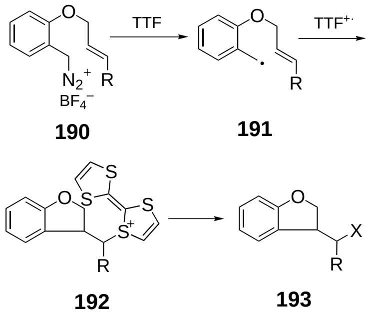
3.6. Tetrathiafulvalene as a Catalyst for Radical–Polar Crossover Reactions

In spite of the extensive studies on the chemistry of TTF as a precursor of new conductors and semiconductors, it has been litle exploited in synthesis. Given that it is an excellent donor, Murphy and co-workers anticipated that it could be used as a single-electron-donating catalyst in new sequential reactions.[227] Tietze and Beifuss[228] reviewed the advantages of using sequential reactions in organic synthesis in 1993 and, more recently, Skrydstrup has studied new examples of these types of reactions that rely on single-electron-donating agents to provide an effective means to synthesize a series of polycyclic compounds.[229] In contrast to the traditional radical/polar reactions induced by SmI_2,[230] Murphy and co-workers have shown that radical cyclizations promoted by TTF may be terminated by S_N1-type nucleophilic substitution at the new exocyclic center (Scheme 9). Single-electron reduction of a suitable substrate **A** by TTF and subsequent radical cyclization in analogy to the SmI_2-promoted reactions yields a carbon radical which can be oxidized by combination with the TTF radical cation. While the carbon radical is further reduced by a second SmI_2 molecule in the SmI_2-mediated reactions, a sulfonium ion is formed in the TTF-mediated reaction sequence. Substitution at the sulfonium ion containing a carbon center by external nucleophiles (for example, solvents such as H_2O, MeOH, CH_3CN) were found to follow S_N1-type kinetics.



Scheme 9. Comparison of the SmI_2-induced radical/polar reaction with the radical route involving a TTF-mediated cyclization, which can proceed through a S_N1-type nucleopilic substitution to form an exocyclic center.

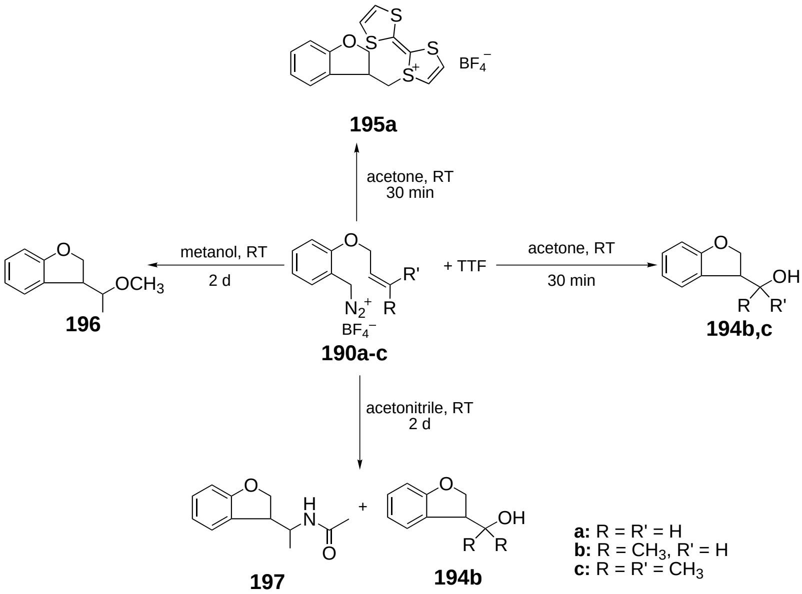
These reactions have so far been mostly applied to aryldiazonium salts and therefore are restricted to cyclizations of aryl radicals. In the original paper of Murphy and co-workers[227a] they reported how aryldiazonium salts (**190**) could be converted into aryl radicals (**191**) which then underwent a further cyclization. The alkyl radicals produced then underwent C–S bond formation with the tetrathiafulvalene radical cation. Such salts underwent a rapid unimolecular substitution in moist acetone, methanol, or acetonitrile to afford alcohols, ethers, and amides, respectively (Scheme 10, **193**). Solvolysis was so retarded for TTF salts **192**[231] (where R = H) that it was not observed under the reaction conditions.



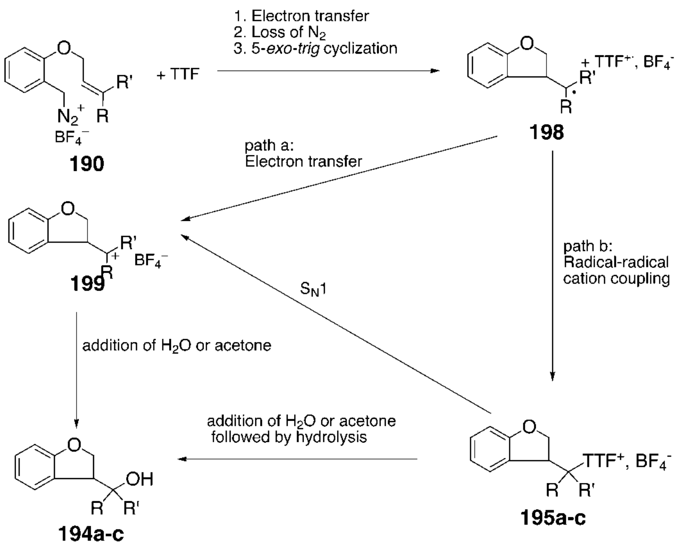
X = OH, OCH$_3$, NHAc

Scheme 10. Reaction of aryldiazonium salts **190** to form the radical intermediate **191** and subsequent reaction with the TTF radical cation.

The 2-allyloxybenzenediazonium salts **190b,c** react with TTF in acetone at room temperature to furnish the alcohols **194b,c**. The arenediazonium salt **190b** reacts with TTF in methanol to give the methyl ether **196**, and in acetonitrile to give the amide **197**. The diazonium salt **190a** reacts with TTF in acetone to give the sulfonium salt **195a** as a mixture of two diastereoisomers. It was not possible to effect conversion of this compound into the alcohol **194a** (Scheme 11).[232]



Scheme 11. Reactions of the 2-allyloxybenzodiazonium salts **190a–c**.

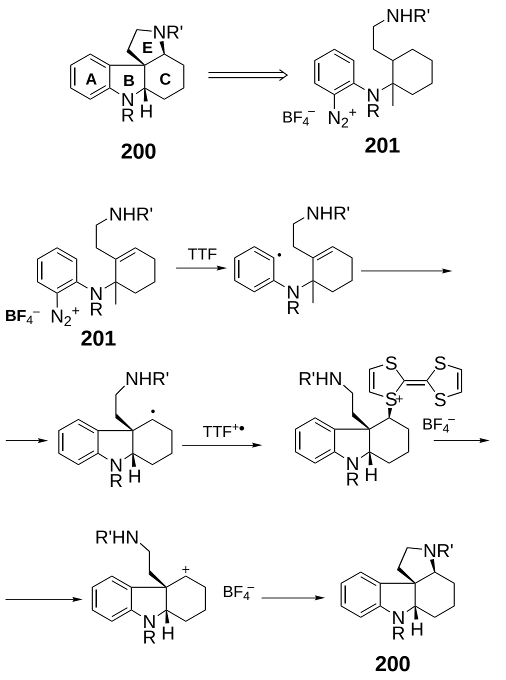


Scheme 12. Reaction mechanism for the conversion of the 2-allyloxybenzodiazonium salts **190a** by Murphy and co-workers.[232]

Although different mechanisms have been proposed for these reactions,[233] the most likely mechanism is that proposed by Murphy and co-workers[232] which is outlined in Scheme 12. The reaction starts with a single-electron transfer (SET) followed by nitrogen expulsion and 5-*exo*-trig cyclization to afford the intermediate alkyl radical **198** and the tetrathiafulvalenium radical cation. The reaction can follow two alternative pathways: in path a, the oxidation occurs by SET to another molecule of the diazonium salt or, less likely to the TTF radical cation. The observed alcohols can then be formed upon reaction of the so-formed carbocation **199** with residual moisture in the acetone. In path b, the alkyl radical and the TTF radical cation couples to give the intermediate salt **195**, which upon substitution would yield alcohols **194**.

As the stereocontrolled construction of complex polycyclic systems is a challenging goal in synthetic organic chemistry, Murphy and co-workers explored whether these TTF-mediated radical–polar crossover reactions could afford a direct, novel, and stereoselective route to alkaloids[234] by using intramolecular nucleophiles.[235] Many members of the *Aspidosperma* alkaloids (aspidospermidine and strychnine) contain the ABCE tetracyclic substructure **200** which features defined stereochemistry at three contiguous centers. Murphy and co-workers proposed that the diazonium salt **201** should afford **200** with complete stereoselectivity (Scheme 13). Thus, by using this synthetic strategy, a family of tetracyclic synthetic precursors of complex alkaloids have been synthesized[234a–c] and, in 1999, a novel route to (±)-aspidospermidine was reported as the first application of the TTF-mediated radical–polar crossover reactions to total synthesis.[234d]

In a recent study by Bashir and Murphy on the role of neighboring group participation in the TTF-mediated radical–polar crossover reactions, secondary alkyl radicals have been trapped for the first time, thus confirming the proposed mechanism. In addition, it has also been observed that groups other than arenes can participate in the solvolysis, thus extending the scope of the radical–polar crossover reaction.[236]



Scheme 13. Stereospecific synthesis of the tetracyclic ABCE substructure **200** from the diazonium salt **201**.[234a–c]

4. Summary and Outlook

The first two decades after the first synthesis of tetrathiafulvalene (TTF) in 1970 have witnessed an impressive development of TTF chemistry in the search for improved electrically conducting materials. However, during the 1990s a renewed interest was devoted to the use of the TTF molecule as a new building block able to exhibit other different nonconventional properties. In this review on the new concepts in TTF chemistry, we have classified the latest advances in this field in three structurally different levels, namely at the molecular level, the macromolecular level, and the supramolecular level.

Although the chemistry of TTF can be considered well-established at the molecular level, important advances in the synthesis of the parent TTF molecule in multigram quantities and, particularly, on the discovery of the cyanomethyl protecting group for the selective protection/deprotection chemistry of thiolate groups have occurred.

In regard to the development of new TTF derivatives in the search of electrically conducting materials, some alternatives to the study of single crystals have been used to grow layers of charge-transfer complexes, such as the formation of LB films or chemical vapor (CV) deposition. Preparation of mesogenic derivatives in which the TTF molecule is linked to a mesogenic liquid crystalline center has also been used as an alternative to form ordered arrays of TTF units. Although these strategies are not comparable to the single crystals in terms of conductivity, they present better opportunities for incorporation into optoelectronic devices for practical applications.

At the macromolecular level, a systematic study of molecules containing TTF units has been undertaken and molecules running from dimers, trimers, and oligomers to polymers have been prepared. In addition, dendrimers comprised of TTF or TTF and acceptors have been prepared, thus forming giant molecules that show only electron-donor or amphoteric redox behavior. These dendrimeric materials offer the possibility of combining the control over the number and localization of TTF units with well-behaved solubility features, thus integrating the redox properties of TTF with the film-formation and processability of polymers. In the same way, cyclodextrins have also been used as platforms to carry TTF units.

The incorporation of TTF into polymeric matrices is well documented from several years ago. However, there is no control over the orientation of the TTF groups relative to one another as a consequence of the great number of different conformations of the polymer. Therefore, during the last few years, efforts have been directed towards the reduction of the conformational freedom by using ladder-type polymers containing TTF as part of the main chain. When doped, these polymers showed reasonable electrical conductivity values.

In recent years, interest has mainly focused on the association of TTF-based conductors with linear π-conjugated structures since better processability and conductivity are expected. In these materials two parallel charge-transport mechanisms might be possible: through intrastack interactions of the TTF units and the polaron/bipolaron conduction in the π-conjugated chain.

Although multi-TTF macromolecules can not compete with other typical conducting polymers, they can be envisaged as promising electroactive systems for multiple applications which deserve to be studied in more depth.

At the supramolecular level, different types of intermolecular interactions have been used to build novel supramolecular assemblies. Thus, incorporation of TTF units into calix[4]arenes, the use of crystal engineering, and gel formation have been used successfully to achieve ordered arrays of TTF-containing molecules. However, one of the most challenging projects in the field of molecular optoelectronics involves the assembly of monolayers (SAM) of electroactive molecular systems on solid supports. Some TTF-containing SAMs have been reported which are almost indefinitely stable and which can be used to prepare thin-film sensors.

During the last decade, the study of TTF derivatives has undergone an explosive growth of activity in the search for nonconventional applications. Thus, macrocycles and supramolecular systems endowed with TTF units have allowed the preparation of chemical sensors, molecular shuttles, and new molecular switches.

The intriguing concept of molecular switches has recently attracted great interest from a variety of perspectives.[237] In this regard, TTF-based NLO chromophores can act as a molecular-scale switch. The preparation of materials exhibiting electronic/photonic properties that can be switched by stimulating changes at the molecular and/or macroscopic levels still represents a challenge in TTF chemistry.

To achieve a switching effect, the D-π-A molecules must be stable in two states that show very different NLO properties. Complete reversibility and a high speed of response are also important for practical applications.[238] Tetrathiafulvalene fulfills the above requirements as a result of its unique redox properties. Consequently, TTF-based D-π-A systems are suited for redox-switching NLO responses since changes in the β values will occur upon oxidation of the TTF moiety.

The switching of NLO responses which utilize redox reactions as stimuli is currently a less-well studied strategy for the molecular engineering of switchable NLO materials in which TTF deserves to be explored in depth.

Although important advances have been carried out in the search for magnetic properties and a number of organic ferromagnets have been recently reported, the transition temperatures exhibited are still extremely low. The versatility of organic chemistry to tailor desired materials properties represents an advantage over the traditional inorganic materials. However, to raise the transition temperature for applications in devices is far from reality at the moment.

Pico- and nanosecond-resolved transient absorption measurements of dyads comprised of TTF and C_{60} have shown rapid transformations of the initially formed singlet excited fullerene states into the charge-separated (CS) radical pairs. The lifetime (several hundreds of nanoseconds) of the CS radical pair has been accounted for by the gain of aromaticity, which occurs upon oxidation of the TTF moiety. This feature is an important property of TTF which makes it a very attractive candidate for the development of further devices for electron/energy storage. In this regard, a large effort is currently being devoted to the study of multichromophoric redox systems which resemble the primary photosynthetic process. The TTF molecule, and particularly the π-extended derivatives, fulfill most of the requirements necessary to improve some of the artificial photosynthetic systems prepared so far.

In summary, tetrathiafulvalene (TTF) is a molecule with unique electronic properties that challenges the creativity and inventiveness of chemists in areas such as organic chemistry, polymer and materials chemistry, and supramolecular chemistry. The knowledge obtained during its thirty years of existence paves the way for the development of the outstanding properties that TTF derivatives display. Thus, TTF faces the new century as one of the target molecules to be exploited in depth.

We thank the DGES of Spain (Project PB98-0818) for financial support. The authors thank the scientists who have participated in the development of this chemistry whose names are cited in the references, and particularly to the research groups of Zaragoza (Prof. J. Garín), Valencia (Prof. E. Ortí), and Notre Dame (Prof. D. M. Guldi) for their fruitful collaborations.

Received: December 20, 1999
Revised: September 7, 2000 [A377]

---

[1] F. Wudl, G. M. Smith, E. J. Hufnagel, *J. Chem. Soc. Chem. Commun.* **1970**, 1453.

[2] J. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.

[3] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, A. J. Heeger, *Solid State Commun.* **1973**, *12*, 1125.

[4] A. Andrieux, C. Duroure, D. Jérome, K. Bechgaard, *J. Phys. Lett.* **1979**, *40*, 381.

[5] D. Jérome, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.* **1980**, *41*, L195.

[6] M. R. Bryce, *Chem. Soc. Rev.* **1991**, *20*, 355.

[7] V. Khodorkovsky, J. Y. Becker in *Organic Conductors* (Ed.: J.-P. Farges), Marcel Dekker, New York, **1994**, Chap. 3.

[8] M. R. Bryce, *J. Mater. Chem.* **1995**, *5*, 1481

[9] a) G. Schukat, A. M. Richter, E. Fanghänel, *Sulfur Rep.* **1987**, *7*, 155; b) G. Schukat, E. Fanghänel, *Sulfur Rep.* **1993**, *14*, 245; c) G. Schukat, E. Fanghänel, *Sulfur Rep.* **1996**, *18*, 1.

[10] J. Garín, *Adv. Heterocycl. Chem.* **1995**, *62*, 249.

[11] K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mørk, G. J. Kristensen, J. Becher, *Synthesis* **1996**, 407.

[12] T. Otsubo, Y. Aso, K. Takimiya, *Adv. Mater.* **1996**, *8*, 203.

[13] M. Adam, K. Müllen, *Adv. Mater.* **1994**, *6*, 439.

[14] J. Becher, J. Lau, P. Mørk in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, pp. 198–233.

[15] M. R. Bryce, W. Davenport, L. M. Goldenberg, C. Wang, *Chem. Commun.* **1998**, 945.

[16] T. Jørgensen, T. K. Hansen, J. Becher, *Chem. Soc. Rev.* **1994**, 41.

[17] K. B. Simonsen, J. Becher, *Synlett* **1997**, 1211.

[18] M. B. Nielsen, J. Becher, *Liebigs Ann.* **1997**, *2177*.

[19] E. Coronado, C. J. Gómez-García, *Chem. Rev.* **1998**, *98*, 273.

[20] J. Roncali, *J. Mater. Chem.* **1997**, *7*, 2307.

[21] P. Day, M. Kurmoo, *J. Mater. Chem.* **1997**, *8*, 1291.

[22] M. R. Bryce, *Adv. Mater.* **1999**, *11*, 11.

[23] M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153.

[24] M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589.

[25] a) C. Katan, *J. Phys. Chem. A* **1999**, *103*, 1407; b) I. Hargittai, J. Brunvoll, M. Kolonits, V. Khodorkovsky, *J. Mol. Struct.* **1994**, *317*, 273.

[26] A. J. Moore, M. R. Bryce, *Synthesis* **1997**, 407.

[27] For a review on the chemistry of DMIT, see N. Svenstrup, J. Becher, *Synthesis* **1995**, 215.

[28] J.-I. Yamada, H. Nishikawa, K. Kikuchi, *J. Mater. Chem.* **1999**, *9*, 617 and references therein.

[29] For recent examples of π-extended TTF derivatives, see a) A. J. Moore, M. R. Bryce, P. J. Skabara, A. S. Batsanov, L. M. Goldenberg, J. A. K. Howard, *J. Chem. Soc. Perkin Trans.* **1997**, 3443; b) S. González, N. Martín, L. Sánchez, J. L. Segura, C. Seoane, I. Fonseca, F. H. Cano, J. Sedó, J. Vidal-Gancedo, C. Rovira, *J. Org. Chem.* **1999**, *64*, 3498; c) S. Akoudad, P. Frère, N. Mercier, J. Roncali, *J. Org. Chem.* **1999**, *64*, 4267; d) T. Finn, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *Chem. Commun.* **1999**, 1835; e) C. A. Cristensen, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, J. O. Jeppesen, J. Becher, *Chem. Commun.* **1999**, 2433.

[30] For recent examples of TTF dimers, see a) S. González, N. Martín, J. L. Segura, C. Seoane, *Tetrahedron Lett.* **1998**, *39*, 3051; b) M. Formigué, C. Mézière, E. Canadell, D. Zitoun, K. Bechgaard, P. Auban-Senzier, *Adv. Mater.* **1999**, *11*, 766; c) M. Iyoda, K. Hara, C. R. V. Rao, Y. Kuwatani, K. Takimiya, A. Morikami, Y. Aso, T. Otsubo, *Tetrahedron Lett.* **1999**, *40*, 5729; d) K. Ueda, Y. Kamata, T. Kominami, M. Iwamatsu, T. Sugimoto, *Chem. Lett.* **1999**, 987; e) J.-I. Yamada, M. Watanabe, H Anzai, H. Nishikawa, I. Ikemoto, K. Kikuchi, *Angew. Chem.* **1999**, *111*, 841; *Angew. Chem. Int. Ed.* **1999**, *38*, 810; f) N. Gautier, N. Mercier, A. Riou, A. Gorgues, P. Hudhomme, *Tetrahedron Lett.* **1999**, *40*, 5997; g) D. E. John, A. J. Moore, M. R. Bryce, A. S. Batsanov, M. A. Leech, J. A. K. Howard, *J. Mater. Chem.* **2000**, *10*, 1273.

[31] P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863.

[32] H. Kato, T. Kobayashi, *Adv. Mater.* **1993**, *5*, 750.

[33] P. Maslak, *Adv. Mater.* **1994**, *6*, 405.

[34] a) E. Nishikawa, H. Tatemitsu, Y. Sakata, S. Misumi, *Chem. Lett.* **1986**, 2131; b) H. Tatemitsu, E. Nishikawa, Y. Sakata, S. Misumi, *Synth. Met.* **1987**, *19*, 565.

[35] K. Ueda, M. Yamanoha, T. Sugimoto, H. Fujita, A. Ugawa, K. Yakushi, K. Kano, *Chem. Lett.* **1997**, 461.

[36] R. Gómez, J. L. Segura, N. Martín, *Org. Lett.* **2000**, *2*, 1585.

[37] D. Lorcy, R. Carlier, A. Robert, A. Tallec, P. Le Maguerès, L. Ouahab, *J. Org. Chem.* **1995**, *60*, 2443.

[38] a) Y. Yamashita, M. Tomura, M. B. Zaman, K. Imaeda, *Chem. Commun.* **1998**, 1657; b) C. Rimbaud, P. Le Margures, L. Ouahab, D. Lorcy, A. Robert, *Acta Crystallogr. Sect. C* **1998**, *54*, 679.

[39] a) M. R. Bryce, A. J. Moore, *Synth. Met.* **1988**, *25*, 203; b) M. R. Bryce, A. J. Moore, *Synth. Met.* **1988**, *27*, B557; c) M. R. Bryce, A. J. Moore, *Pure Appl. Chem* **1990**, *62*, 473.

[40] a) N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, *J. Org. Chem.* **1998**, *63*, 1268; b) N. Martín, L. Sánchez, C. Seoane, C. Fernández, *Synth. Met.* **1996**, *78*, 137.

[41] N. Martín, I. Pérez, L. Sánchez, C. Seoane, *J. Org. Chem.* **1997**, *62*, 870.

[42] C. Boulle, O. Desmars, N. Gautier, P. Hudhomme, M. Cariou, A. Gorgues, *Chem. Commun.* **1998**, 2196.

[43] I. Pérez, S.-G. Liu, N. Martín, L. Echegoyen, *J. Org. Chem.* **2000**, *65*, 3796.

[44] a) Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda, H. Inokuchi, *Adv. Mater.* **1994**, *6*, 295; b) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi, *Chem. Lett.* **1991**, 1213; c) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi, M. Sano, *J. Org. Chem.* **1992**, *57*, 5517.

[45] a) Y. Yamashita, S. Tanaka, K. Imaeda, *Synth. Met.* **1995**, *71*, 1965; b) K. Imaeda, Y. Yamashita, S. Tanaka, H. Inokuchi, *Synth. Met.* **1995**, *73*, 107.

[46] Y. Yamashita, M. Tomura, K. Imaeda, *Chem. Commun.* **1996**, 2021.

[47] M. R. Bryce, M. C. Petty, *Nature* **1995**, *374*, 771.

[48] For a recent and extensive review on conducting LB films, see T. Nakamura in *Handbook of Organic Conductive Molecules and Polymers*, *Vol. 1* (Ed.: H. S. Nalwa), Wiley, **1997**, pp. 727–780.

[49] J. Caro, S. Garelik, A. Figueras, *Chem. Vap. Deposition* **1996**, *2*, 251.

[50] J. Caro, J. Fraxedas, A. Figueras, *Chem. Vap. Deposition* **1997**, *3*, 263.

[51] a) U. T. Mueller-Westerhoff, A. Nazzal, R. J. Cox, A.-M. Giroud, *J. Chem. Soc. Chem. Commun.* **1980**, 497; b) A. Babeau, N. H. Tinh, H. Gasparoux, C. Polycarpe, E. Torreilles, L. Giral, *Mol. Cryst. Liq. Cryst.* **1982**, *72*, 171; c) N. B. Chanh, M. Cotrait, J. Gautlier, Y. Haget, N. H. Tinh, C. Polycarpe, E. Torreilles, *Mol. Cryst. Liq. Cryst.* **1983**, *101*, 129; d) C. Polycarpe, E. Torreilles, L. Giral, A. Babeau, N. H. Tinh, H. Gasparoux, *J. Heterocycl. Chem.* **1984**, *21*, 1741; e) G. Saito, *Pure Appl. Chem* **1987**, *59*, 999; f) A. J. Seed, K. J. Toyne, J. W. Goodby, *Abstr. Pap. 58 Proc. 15th Int. Liq. Cryst. Conf.* (Budapest, Hungary) **1994**; g) M. A. Fox, H.-L. Pan, *J. Org. Chem.* **1994**, *59*, 6519.

[52] a) R. Andreu, J. Barberá, J. Garín, J. Orduna, J. L. Serrano, T. Sierra, P. Leriche, M. Sallé, A. Riou, M. Jubault, A. Gorgues, *Synth. Met.* **1997**, *86*, 1869; b) R. Andreu, J. Barberá, J. Garín, J. Orduna, J. L. Serrano, T. Sierra, P. Leriche, M. Sallé, A. Riou, M. Jubault, A. Gorgues, *J. Mater. Chem.* **1998**, *8*, 881.

[53] S. Frenzel, S. Arndt, R. M. Gregorious, K. Müllen, *J. Mater. Chem.* **1995**, *5*, 1529.

[54] M. J. Cook, G. Cooke, A. Jafari-Fini, *Chem. Commun.* **1996**, 1925.

[55] R. A. Bissell, N. Boden, R. J. Bushby, C. W. G. Fishwick, E. Holland, B. Movaghar, G. Ungar, *Chem. Commun.* **1998**, 113.

[56] D. E. John, A. S. Batsanov, M. R. Bryce, J. A. K. Howard, *Synthesis* **2000**, *6*, 824.

[57] K. Takimiya, Y. Shibata, K. Imamura, A. Kashihara, Y. Aso, T. Otsubo, F. Ogura, *Tetrahedron Lett.* **1995**, *36*, 5045.

[58] a) J. Tanabe, T. Kudo, M. Okamoto, Y. Kawada, G. Ono, A. Izuoka, T. Sugawara, *Chem. Lett.* **1995**, 579; b) K. Takimiya, Y. Aso, T. Otsubo, *Synth. Met.* **1997**, *86*, 1891; c) K. Takimiya, K. Imamura, Y. Shibata, Y. Aso, F. Ogura, T. Otsubo, *J. Org. Chem.* **1997**, *62*, 5567; d) M. B. Nielsen, N. Thorup, J. Becher, *J. Chem. Soc. Perkin Trans. 1*, **1998**, 1305.

[59] K. Takimiya, A. Oharuda, A. Morikami, Y. Aso, T. Otsubo, *Angew. Chem.* **1998**, *110*, 640; *Angew. Chem. Int. Ed.* **1998**, *37*, 619.

[60] K. B. Simonsen, N. Thorup, J. Becher, *Synthesis* **1997**, 1399.

[61] J. Lau, P. Blanchard, A. Riou, M. Jubault, M. P. Cava, J. Becher, *J. Org. Chem.* **1997**, *62*, 4936.

[62] S. Yunoki, K. Takimiya, Y. Aso, T. Otsubo, *Tetrahedron Lett.* **1997**, *38*, 3017.

[63] M. B. Nielsen, Z.-T. Li, J. Becher, *J. Mater. Chem.* **1997**, *7*, 1175.

[64] a) P. Blanchard, N. Svenstrup, J. Becher, *Chem. Commun.* **1996**, 615; b) P. Blanchard, N. Svenstrup, J. Rault-Berthelot, A. Riou, J. Becher, *Eur. J. Org. Chem.* **1998**, 1743.

[65] M. R. Bryce, G. J. Marshallsay, A. J. Moore, *J. Org. Chem.* **1992**, *57*, 4859.

[66] M. Formigué, P. Batail, *J. Chem. Soc. Chem. Commun.* **1991**, 1370.

[67] a) J. Lau, S. Becher, *Synthesis* **1997**, 1015; b) T. Akutagawa, Y. Abe, T. Hasegawa, T. Nakamura, T. Inabe, K.-I. Sugiura, Y. Sakata, C. A. Christensen, J. Lau, J. Becher, *J. Mater. Chem.* **1999**, *9*, 2737.

[68] K. Sako, M. Kusakabe, T. Watanabe, H. Tatemitsu, *Synth. Met.* **1995**, *71*, 1949.

[69] H. Nishikawa, S. Kawauchi, Y. Misaki, T. Yamabe, *Chem. Lett.* **1996**, 43.

[70] M. Adam, E. Fanghänel, K. Müllen, Y.-J. Shen, R. Wegner, *Synth. Met.* **1994**, *66*, 275.

[71] D. Solooki, T. C. Parker, S. I. Khan, Y. Rubin, *Tetrahedron Lett.* **1998**, *39*, 1327.

[72] a) M. Iyoda, M. Fukuda, M. Yoshida, S. Sasaki, *Chem. Lett.* **1994**, 2369; b) M. Iyoda, M. Fukuda, S. Sasaki, M. Yoshida, *Synth. Met.* **1995**, *70*, 1171.

[73] a) M. Formigué, I. Johannsen, K. Boubekeur, C. Nelson, P. Batail *J. Am. Chem. Soc.* **1993**, *115*, 3752; b) A. González, J. L. Segura, N. Martín, *Tetrahedron Lett.* **2000**, *41*, 3083.

[74] J. Lau, O. Simonsen, J. Becher, *Synthesis* **1995**, 521.

[75] M. A. Blower, M. R. Bryce, W. Devonport, *Adv. Mater.* **1996**, *8*, 63.

[76] C. Wang, M. R. Bryce, A. S. Batsanov, C. F. Stanley, A. Beeby, J. A. K. Howard, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1671.

[77] C. Wang, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **1997**, *3*, 1679.

[78] C. A. Christensen, M. R. Bryce, A. S. Batsanov, J. Becher, *Chem. Commun.* **2000**, 331.

[79] M. Iyoda, K. Hara, Y. Kuwatani, S. Nagase, *Org. Lett.* **2000**, *2*, 2217

[80] A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665.

[81] a) O. A. Matthews, A. N. Shipway, J. F. Stoddart, *Prog. Polym. Sci.* **1998**, *23*, 1; b) for a review on redox-active dendrimers, see M. R. Bryce, W. Davonport in *Advances in Dendritic Macromolecules*, *Vol. 3* (Ed.: G. R. Newcome), JAI Press, London, **1996**, p. 115.

[82] M. R. Bryce, W. Devonport, A. J. Moore, *Angew. Chem.* **1994**, *106*, 1862; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1761.

[83] a) M. R. Bryce, W. Devonport, *Synth. Met.* **1996**, *76*, 305; b) W. Devonport, M. R. Bryce, G. J. Marshallsay, A. J. Moore, L. M. Goldenberg, *J. Mater. Chem.* **1998**, *8*, 1361.

[84] C. A. Christensen, L. M. Goldenberg, M. R. Bryce, J. Becher, *Chem. Commun.* **1998**, 509.

[85] C. Wang, M. R. Bryce, A. S. Batsanov, L. M. Goldenberg, J. A. K. Howard, *J. Mater. Chem.* **1997**, *7*, 1189.

[86] M. R. Bryce, P. de Miguel, W. Devonport, *Chem. Commun.* **1998**, 2565.

[87] a) N. Martín, J. L. Segura, C. Seoane, *J. Mater. Chem.* **1997**, *7*, 1661; b) V. Kampar, O. Neilands, *Russ. Chem. Rev.* **1986**, *55*, 334; c) S. Hünig *J. Mater. Chem.* **1995**, *5*, 1469.

[88] Y. Le Bras, M. Sallé, P. Leriche, C. Mingotaud, P. Richomme, J. Møller, *J. Mater. Chem.* **1997**, *7*, 2393.

[89] For a compilation of former TTF-polymers see ref. [9].

[90] G. Scherowsky, J. Weiland, *Chem. Ber.* **1974**, *107*, 3155.

[91] J. Röhrig, K. Müllen, *J. Org. Chem.* **1992**, *57*, 2374.

[92] R. L. Meline, I. T. Kim, J. Chen, S. Basak, R. L. Elsenbaumer, *Polym. Prepr.* **1998**, *39*, 341.

[93] L. Huchet, S. Akoudad, E. Levillain, J. Roncali, A. Emge, P. Bäuerle, *J. Phys. Chem. B* **1998**, *102*, 7776.

[94] J. H. Perlstein, *Angew. Chem.* **1977**, *89*, 534; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 519.

[95] a) J. L. Brédas, B. Thémans, J. M. André, R. R. Chance, R. Silbey, *Synth. Met.* **1984**, *9*, 265; b) A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, *Rev. Mod. Phys.* **1988**, *781*, 60.

[96] M. R. Bryce, A. D. Chissel, J. Gopal, P. Kathirgamanathan, D. Parker, *Synth. Met.* **1991**, *39*, 397.

[97] C. Thobie-Gautier, A. Gorgues, M. Jubault, J. Roncali, *Macromolecules* **1993**, *6*, 4094.

[98] a) A. Charlton, A. E. Underhill, G. Williams, M. Kalaji, P. J. Murphy, D. E. Hibbs, M. B. Hursthouse, K. M. Abdul Malik, *Chem. Commun.* **1996**, 2423; b) A. Charlton, A. E. Underhill, G. Williams, M. Kalaji, P. J. Murphy, K. M. Abdul Malik, K. M. Hursthouse, *J. Org. Chem.* **1997**, *62*, 3098.

[99] a) P. J. Skabara, K. Müllen, *Synth. Met.* **1997**, *84*, 345; b) P. J. Skabara, I. M. Serebryakov, D. M. Roberts, I. F. Perepichka, S. J. Coles, M. B.

Hursthouse, *J. Org. Chem.* **1999**, *64*, 6418; c) P. J. Skabara, D. M. Roberts, I. M. Serebryakov, C. Pozo-Gonzalo, *Chem. Commun.* **2000**, 1005.

[100] F. B. Kaufman, A. H. Shroeder, E. M. Engler, S. R. Kramer, J. Q. Chambers, *J. Am. Chem. Soc.* **1980**, *102*, 483.

[101] J. Roncali, *Chem. Rev.* **1997**, *97*, 173.

[102] L. Huchet, S. Akoudad, J. Roncali, *Adv. Mater.* **1998**, *10*, 541.

[103] T. Yamamoto, T. Shimizu, *J. Mater. Chem.* **1997**, *7*, 1967.

[104] a) T. Yamamoto, *Progr. Polym. Sci.* **1992**, *17*, 1153; b) T. Yamamoto, K. Sugiyama, T. Kushida, T. Inoue, T. Kanbara, *J. Am. Chem. Soc.* **1996**, *118*, 3930.

[105] a) T. Yamamoto, W. Yamada, M. Tagaki, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, *Macromolecules* **1994**, *27*, 6620; b) K. Sanechika, T. Yamamoto, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 752.

[106] S. Booth, E. N. K. Wallace, K. Shingal, P. N. Bartlett, J. D. Kilburn, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1467.

[107] X. Marguerettaz, G. Redmond, S. N. Rao, D. Fitzmaurice, *Chem. Eur. J.* **1996**, *2*, 420.

[108] J.-M. Lehn, *Angew. Chem.* **1988**, 100, 91; Angew. *Chem. Int. Ed. Engl.* **1988**, *27*, 89.

[109] D. N. Reinhoudt, J. F. Stoddart, R. Ungaro, *Chem. Eur. J.* **1998**, *4*, 1349.

[110] S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384.

[111] C. V. K. Sharma, G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.

[112] G. R. Desiraju, *The Crystal as a Supramolecular Entity*, Wiley, Chichester, **1995**.

[113] D. O. Cowan, A. Kini in *The Chemistry of Organic Selenium and Tellurium*, *Vol. 2* (Ed.: S. Patai), Wiley, New York, **1987**, Chap. 12.

[114] a) D. Jérome, *Science* **1991**, *252*, 1509; b) J. M. Wiiliams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W. K. Kwok, M. H. Whangbo, J. E. Schirber, *Science* **1991**, *252*, 1501; c) H. Mori, *Int. J. Mod. Phys. A* **1994**, *8*, 1; d) J. A. Schlueter, J. M. Williams, U. Geiser, J. D. Dudek, S. A. Sirchio, M. E. Kelly, J. S. Gregar, W. K. Kwok, J. A. Fendrich, J. E. Schirber, W. R. Bayless, D. Naumann, T. Roy, *J. Chem. Soc. Chem. Commun.* **1995**, 1311; e) Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka, *Angew. Chem.* **1995**, *107*, 1340; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1222, and references therein; f) J. J. Novoa, M. C. Rovira, C. Rovira, J. Veciana, J. Tarrés, *Adv. Mater.* **1995**, *7*, 233; g) M. C. Rovira, J. J. Novoa, J. Tarrés, C. Rovira, J. Veciana, S. Yang, D. O. Cowan, E. Canadell, *Adv. Mater.* **1995**, *7*, 1023; h) M. Sallé, M. Jubault, A. Gorgues, K. Boubekeur, M. Formigué, P. Batail, E. Canadell, *Chem. Mater.* **1993**, *5*, 1196; i) M. Sallé, A. Gorgues, M. Jubault, K. Boubekeur, P. Batail, R. Carlier, *Bull. Soc. Chim. Fr.* **1996**, *133*, 417; j) P. Hudhomme, P. Blanchard, M. Sallé, S. Le Moustarder, A. Riou, M. Jubault, A. Gorgues, G. Duguay, *Angew. Chem.* **1997**, *109*, 896; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 878; k) C. Durand, P. Hudhomme, G. Duguay, M. Jubault, A. Gorgues, *Chem. Commun.* **1998**, 361; l) E. Ojima, H. Fujiwara, H. Kobayashi, *Adv. Mater.* **1999**, *11*, 758.

[115] a) R. Ketcham, A. B. Hörnfeldt, S. Gronowitz, *J. Org. Chem.* **1984**, *49*, 1117; b) C. Wang, A. Ellern, J. Y. Becker, J. Bernstein, *Adv. Mater.* **1995**, *7*, 644; c) T. Jigami, K. Takimiya, T. Otsubo, Y. Aso, *J. Org. Chem.* **1998**, *63*, 8865.

[116] a) J. Y. Becker, J. Bernstein, S. Bittner, J. A. R. P. Sarma, L. Shahal, *Tetrahedron Lett.* **1988**, *29*, 6277; b) J. Y. Becker, J. Bernstein, M. Dayan, L. Shahal, *J. Chem. Soc. Chem. Commun.* **1992**, 1048; c) J. Y. Becker, J. Bernstein, M. Dayan, A. Ellern, L. Shahal, *Adv. Mater.* **1994**, *6*, 758; d) C. Wang, A. Ellern, J. Y. Becker, J. Bernstein, *Tetrahedron Lett.* **1994**, *35*, 8489; e) C. Wang, A. Ellern, V. Khodorkovski, J. Y. Becker, J. Bernstein, *J. Chem. Soc. Chem. Commun.* **1994**, 2115.

[117] a) J. Y. Becker, J. Bernstein, S. Bittner, L. Shahal, S. S. Shaik, *J. Chem. Soc. Chem. Commun.* **1991**, 92; b) B. W. Knight, S. T. Purrington, R. D. Beremen, P. Singh, *Synthesis* **1994**, 460; c) C. Wang, A. Ellern, V. Khodorkowsky, J. Bernstein, J. Y. Becker, *J. Chem. Soc. Chem. Commun.* **1994**, 983; d) T. Imakubo, H. Sawa, R. Kato, *Synth. Met.* **1997**, *86*, 1883; e) Y. Kuwatani, E. Ogura, H. Nishikawa, I. Ikemoto, M. Iyoda, *Chem. Lett.* **1997**, 817; f) R. Andreu, M. J. Blesa, J. Garín, A. López, J. Orduna, M. Savirón, *Synth. Met.* **1997**, *86*, 1897.

[118] a) P. Blanchard, K. Boubekeur, M. Sallé, G. Duguay, M. Jubault, A. Gorgues, J. D. Martin, E. Canadell, P. Auban-Senzier, D. Jérome, P. Batail, *Adv. Mater.* **1992**, *4*, 579; b) C, Guillot, P. Hudhomme, P. Blanchard, A. Gorgues, M. Jubault, G. Duguay, *Tetrahedron Lett.* **1995**, *36*, 1645.

[119] a) J. M. Fabre, J. Garín, S. Uriel, *Tetrahedron Lett.* **1991**, *32*, 6407; b) J. M. Fabre, J. Garín, S. Uriel, *Tetrahedron* **1992**, *48*, 3983; c) A. S. Batsanov, M. R. Bryce, G. Cooke, A. S. Dhindsa, J. N. Heaton, J. A. K. Howaed, A. J. Moore, M. C. Petty, *Chem. Mater.* **1994**, *6*, 1419; d) A. J. Moore, M. R. Bryce, A. S. Batsanov, C. W. Lehamnn, J. A. K. Howard, *Synth. Met.* **1997**, *86*, 1901; e) K. Heuzé, M. Formigué, P. Batail, *J. Mater. Chem.* **1999**, *9*, 2373; f) K. Heuzé, M. Formigué, P. Batail, E. Canadell, P. Auban-Senzier, *Chem. Eur. J.* **1999**, *5*, 2971.

[120] J.-B. Regnouf-de-Vains, M. Sallé, R. Lamartine, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2461.

[121] H. M. Yamamoto, J.-I. Yamaura, R. Kato, *J. Am. Chem. Soc.* **1998**, *120*, 5905.

[122] *Langmuir–Blodgett Films* (Ed.: G. Roberts), Plenum, New York, **1990**.

[123] M. Jørgensen, K. Bechgaard, T. Bjørnholm, P. Sommer-Larsen, L. G. Hansen, K. Schaumburg, *J. Org. Chem.* **1994**, *59*, 5877.

[124] For a recent review on gelators, see P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133.

[125] a) G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behhera, G. H. Escamilla, M. J. Saunders, *Angew. Chem.* **1992**, *104*, 901; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 917; b) G. R. Newkome, G. R. Baker, S. Arai, M. J. Saunders, P. S. Russo, K. J. Theriot, C. N. Moorefield, L. E. Rogers, J. E. Miller, T. R. Lieux, M. E. Murray, B. Phillips, L. Pascal, *J. Am. Chem. Soc.* **1990**, *112*, 8458.

[126] I. Willner, B. Willner, *J. Mater. Chem.* **1998**, *8*, 2543.

[127] I. Fujihara, H. Nakai, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1999**, 737.

[128] a) Q. Cheng, A. Brajter-Toth, *Anal. Chem.* **1992**, *64*, 1998; b) Y. Wang, A. E. Kaifer, *J. Phys. Chem. B* **1998**, 9922; c) R. Blonder, I. Willner, A. F. Buckmann, *J. Am. Chem. Soc.* **1998**, *120*, 9335.

[129] a) H. Liu, S. Liu, L. Echegoyen, *Chem. Commun.* **1999**, 1493; b) S.-G. Liu, H. Liu, K. Bandyopadhyay, Z. Gao, L. Echegoyen, *J. Org. Chem.* **2000**, *65*, 3292.

[130] a) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Marenco, J. Yarwood, M. J. Joyce, S. N. Port, *Adv. Mater.* **1998**, *10*, 395; b) WO 98/58246, **1998** [*Chem. Abstr.* **1999**, *130*, 75509j].

[131] J. M. Williams, J. R. Ferraro, P. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo, *Organic Superconductors (Including Fullerenes): Synthesis*, *Structure*, *Properties*, *and Theory*, Prentice-Hall, Englewood, **1992**.

[132] *Organic Conductors. Fundamentals and applications* (Ed.: J.-P. Farges), Marcel Dekker, New York, **1994**.

[133] J. Becher, Z.-T. Li, P. Blanchard, N. Svenstrup, J. Lau, M. B. Nielsen, P. Leriche, *Pure Appl. Chem.* **1997**, *69*, 465.

[134] L. M. Goldenberg, M. R. Bryce, M. C. Petty, *J. Mater. Chem.* **1999**, *9*, 1957.

[135] J. Ippen, C. Tao-Pen, D. Schweitzer, H. A. Staab, *Angew. Chem.* **1980**, *92*, 51; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 67.

[136] K. Takimiya, Y. Aso, F. Ogura, T. Otsubo, *Chem. Lett.* **1995**, 735.

[137] a) A. Bertho-Thoraval, A. Robert, A. Souizi, K. Boubekeur, P. Batail, *J. Chem. Soc. Chem. Commun.* **1991**, 843; b) K. Matsuo, K. Takimiya, Y. Aso, T. Otsubo, F. Ogura, *Chem. Lett.* **1995**, 523.

[138] F. Le Derf, M. Sallé, N. Mercier, J. Becher, P. Richomme, A. Gorgues, J. Orduna, J. Garín, *Eur. J. Org. Chem.* **1998**, 1861.

[139] F. Le Derf, M. Mazari, N. Mercier, E. Levillain, P. Richomme, J. Becher, J. Garín, J. Orduna, A. Gorgues, M. Sallé, *Chem. Commun.* **1999**, 1417.

[140] K. B. Simonsen, N. Svenstrup, J. Lau, N. Thorup, J. Becher, *Angew. Chem.* **1999**, *111*, 1515; *Angew. Chem. Int. Ed.* **1999**, *38*, 1417.

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

[142] R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, S. J. Langford, S. Menzer, L. Prodi, J. F. Stoddart, M. Venturi, D. J. Williams *Angew. Chem.* **1996**, *108*, 1056; Angew. *Chem. Int. Ed. Engl.* **1996**, *35*, 978, and references therein.

[143] a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *Angew. Chem Int. Ed Engl.* **1996**, *35*, 1154; c) F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1643.

[144] G. A. Breault, C. A. Hunter, P. C. Mayers, *Tetrahedron* **1999**, *55*, 5265.

[145] M.-J. Blanco, M. C. Jiménez, J.-C. Chambron, V. Heitz, M. Linke, J.-P. Sauvage, *Chem. Soc. Rev.* **1999**, *28*, 293.

[146] D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1991**, 1584.

[147] W. Devonport, M. A. Blower, M. R. Bryce, L. M. Goldenberg, *J. Org. Chem.* **1997**, *62*, 885.

[148] V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405.

[149] A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart, *J. Am. Chem. Soc.* **1997**, *119*, 2679.

[150] a) P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Mattersteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 3951; b) V. Balzani, A. Credi, G. Mattersteig, O. A. Mathews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2000**, *65*, 1924.

[151] C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, J. R. Heath, *Science* **1999**, *285*, 391.

[152] R. F. Service, *Science* **1999**, *285*, 314.

[153] L. Ouahab, *Coord. Chem. Rev.* **1998**, *180*, 1501.

[154] M. Clemente-León, E. Coronado, P. Delhaes, J. R. Galán-Mascarós, C. J. Gómez-García, C. Mingotaud in *Supramolecular Engineering of Synthetic Metallic Materials: NATO ASI Ser. C*, *Vol. 518* (Eds.: J. Veciana, C. Rovira, D. Amabilino), Kluwer, Dordrecht, **1999**, pp. 291–313.

[155] *Molecular Magnetism: From Molecular Assemblies to the Devices: NATO ASI Ser. E*, *Vol. 321* (Eds.: E. Coronado, P. Delhaès, D. Gatteschi, J. S. Miller), Kluwer, Dordrecht, **1996**.

[156] M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse, P. Guionneau, *J. Am. Chem. Soc.* **1995**, *117*, 12209.

[157] P. Cassoux, H. Kobayashi in ref. [154], pp. 313–327.

[158] P. Day, M. Kurmoo, T. Mallah, I. R. Marsden, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseau, J. Gaultier, G. Bravic, L. Ducasse, *J. Am. Chem. Soc.* **1992**, *114*, 10722.

[159] a) C. J. Gómez-García, C. Giménez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Ouahab, L. Ducasse, C. Sourisseau, P. Delhaes, *Inorg. Chem.* **1995**, *34*, 4139; b) E. Coronado, L. R. Falvello, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, V. N. Lauhkin, A. Pérez-Benítez, C. Rovira, J. Veciana, *Adv. Mater.* **1997**, *9*, 984; c) E. Coronado, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, S. Triki, *J. Am. Chem. Soc.* **1998**, *120*, 4671; d) E. Ribera, C. Rovira, J. Veciana, J. Tarrés, E. Canadell, R. Rousseau, E. Molins, M. Mas, J.-P. Schoeffel, J.-P. Pouget, J. Morgado, R. T. Henriques, M. Almeida, *Chem. Eur. J.* **1999**, *5*, 2025; e) N. Yoneyama, A. Miyazaki, T. Enoki, G. Saito, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 639; f) E. Ojima, H. Fujiwara, K. Kato, H. Kobayashi, H. Tanaka, A. Kobayashi, M. Tokumoto, P. Cassoux, *J. Am. Chem. Soc.* **1999**, *121*, 5581; g) C. Rovira in ref. [154], pp. 377–392; h) P. Delhaes, L. Ducasse in ref. [154], pp. 473–502.

[160] C. Rovira, *Chem. Eur.J.* **2000**, *6*, 1723. Spin ladders are defined as low-dimensional magnetic quantum systems that consist of a finite number of strongly magnetically coupled chains of spins that are at the crossroad between one and two dimensions.

[161] C. Kollmar, O. Kahn, *Acc. Chem. Res.* **1993**, *26*, 259.

[162] M. Kinoshita in *Organic Conductive Molecules and Polymers*, *Vol. 1* (Ed.: H. S. Nalwa), Wiley, Chichester, **1997**, pp. 781–800.

[163] a) J. S. Miller, A. J. Epstein, *Angew. Chem.* **1994**, *106*, 399; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385; b) J. S. Miller, A. J. Epstein, *Chem. Eng. News* **1995**, *73*, 30.

[164] a) R. Wood, *Understanding Magnetism*, Tab Books, Blue Ridge Summit, **1988**, Chap. 2; b) D. C. Mattis, *The Theory of Magnetism*, Springer, New York, **1981**, Chap. 1; c) A. L. Robinson, *Science* **1984**, *223*, 920; d) K. H. J. Buschow, *Mater. Sci. Rep.* **1986**, *1*, 1; e) M. Cohen in *Advancing Materials Research* (Eds.: P. A. Psaras, H. D. Langford), National Academy Press, Washington, **1987**, p. 91; f) J. J. Croat, J. F. Herbst, *MRS Bull.* **1988**, *13*, 37; g) R. M. White, *Science* **1985**, *229*, 4807; h) W. E. Wallace, *J. Less Common Met.* **1984**, *100*, 85; i) P. Chaudhari, M. Flemings, *Materials Science and Engineerings for the 1990s*, National Academy Press, Washington, **1989**, p. 94.

[165] a) J. Veciana in ref. [155], pp. 425–448; b) "Organic Magnetic Materials: Intramolecular Magnetic Interactions": J. Veciana in *Proc. 4th Escuela Nacional de Materiales Moleculares* (Eds.: N. Martín, T. Torres), San Lorenzo de El Escorial, **1999**.

[166] a) M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, Y. Maruyama, *Chem. Lett.* **1991**, 1225; b) R. Chiarelli, M. A. Novak, A. Rassat, J. L. Tholence, *Nature* **1993**, *363*, 147; c) T. Nogami, T. Ishida, H. Tsuboi, H. Yoshikawa, H. Yamamoto, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, M. Ishikawa, *Chem. Lett.* **1995**, 635; d) T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, M. Ishikawa, *J. Chem. Soc. Chem. Commun.* **1994**, 1723; e) J. Cirujeda, M. Mas, E. Molins, F. L. Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, J. Veciana, *J. Chem. Soc. Chem. Commun.* **1995**, 709; f) K. Mukai, K. Konishi, K. Nedachi, K. Takeda, *J. Magn. Mater.* **1995**, *140–144*, 1449; g) A. Caneschi, F. Ferraro, D. Gatteschi, A. Lirzin, M. A. Novak, E. Rentschler, R. Sessoli, *Adv. Mater.* **1995**, *7*, 476.

[167] a) K. Yamaguchi, H. Nishimoto, T. Fueno, T. Nogami, Y. Shirota, *Chem. Phys. Lett.* **1990**, *166*, 408; b) K. Yamaguchi, M. Okumura, T. Fueno, K. Nakasuji, *Synth. Met.* **1991**, *41*, 3631.

[168] a) R. Kumai, M. M. Matsushita, A. Izuoka, T. Sugawara, *J. Am. Chem. Soc.* **1994**, *116*, 4523; b) R. Kumai, H. Sakurai, A. Izuoka, T. Sugawara, *Mol. Cryst. Liq. Cryst.* **1996**, *279*, 133; c) H. Sakurai, R. Kumai, A. Izuoka, T. Sugawara, *Chem. Lett.* **1996**, 879.

[169] a) J. Nakazaki, M. M. Matsushita, A. Izuoka, T. Sugawara, *Tetrahedron Lett.* **1999**, *40*, 5027; b) H. Fujiwara, H. Kobayashi, *Chem. Commun.* **1999**, 2417.

[170] T. Sugimoto, S. Yamaga, M. Nakai, H. Nakatsuji, J. Yamauchi, H. Fujita, H. Fukutome, A. Ikawa, H. Mizouchi, Y. Kai, N. Kanehisa, *Adv. Mater.* **1993**, *5*, 741.

[171] M. Iyoda, S. Sasaki, M. Miura, M. Fukuda, J. Yamauchi, *Tetrahedron Lett.* **1999**, *40*, 2807.

[172] a) H. Mizouchi, A. Ikawa, H. Fukutome, *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 127; b) H. Mizouchi, A. Ikawa, H. Fukutome, *J. Am. Chem. Soc.* **1995**, *117*, 3260.

[173] a) R. D. McCullough, J. A. Belot, *Chem. Mater.* **1994**, *6*, 1396; b) R. D. McCullough, J. A. Belot, A. L. Rheingold, G. P. A. Yap, *J. Am. Chem. Soc.* **1995**, *117*, 9913.

[174] a) O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, J. Sletten, *J. Am. Chem. Soc.* **1988**, *110*, 782; b) O. Kahn, *Struct. Bonding* **1987**, *68*, 89.

[175] J. B. Torrance, *Acc. Chem. Res.* **1979**, *12*, 79.

[176] a) K. Ueda, M. Goto, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto, H. Fujita, *Synth. Met.* **1997**, *85*, 1679; b) K. Ueda, M. Goto, M. Iwamatsu, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto, H. Fujita, *J. Mater. Chem.* **1998**, *8*, 2195.

[177] A. Aviram, M. Ratner, *Chem. Phys. Lett.* **1974**, *9*, 2271.

[178] R. Hoffmann, *Acc. Chem. Res.* **1971**, *4*, 1.

[179] a) C. A. Panetta, N. E. Heimer, C. L. Hussey, R. M. Metzger, *Synlett* **1991**, 301; b) R. M. Metzger, C. A. Panetta, *New J. Chem.* **1991**, *15*, 209; c) H. Nadizadeh, D. L. Mattern, J. Singleton, X.-L. Wu, R. M. Metzger, *Chem. Mater.* **1994**, *6*, 268; d) A. C. Brady, B. Hodder, A. S. Martin, J. R. Sambles, C. P. Ewels, R. Jones, P. R. Briddon, A. M. Musa, C. A. Panetta, D. L. Mattern, *J. Mater. Chem.* **1999**, *9*, 2271.

[180] For a recent review article on unimolecular rectifiers, see R. M. Metzger, *J. Mater. Chem.* **1999**, *9*, 2027, and references therein.

[181] R. M. Metzger, *Acc. Chem. Res.* **1999**, *32*, 950.

[182] R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Villaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, *119*, 10455.

[183] R. M. Metzger, H. Tabibana, X. Wu, U. Höpfner, B. Chen, M. V. Lakshmikantham, M. P. Cava, *Synth. Met.* **1997**, *85*, 1359.

[184] S. Scheib, M. P. Cava, J. W. Baldwin, R. M. Metzger, *J. Org. Chem.* **1998**, *63*, 1198.

[185] P. de Miguel, M. R. Bryce, L. M. Goldenberg, A. Beeby, V. Khodorkovsky, L. Shapiro, A. Niemz, A. O. Cuello, V. Rotello, *J. Mater. Chem.* **1998**, *8*, 71.

[186] J. L. Segura, N. Martín, C. Seoane, M. Hanack *Tetrahedron Lett.* **1996**, *37*, 2503.

[187] M. González, B. Illescas, N. Martín, J. L. Segura, C. Seoane, M. Hanack, *Tetrahedron* **1998**, *54*, 2853.

[188] E. Tsiperman, T. Regev, J. Y. Becker, J. Bernstein, A. Ellern, V. Khodorkovsky, A. Shames, L. Shapiro, *Chem. Commun.* **1999**, 1125.

[189] L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fitfield, G. Phelan, C. Kinkaid, J. Amend, A. Jen, *J. Mater. Chem.* **1999**, *9*, 1905.

[190] a) P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effect in Molecules and Polymers*, Wiley, New York, **1991**; b) D. S. Chemla in *Nonlinear Optical Properties of Organic Materials and Crystals* (Ed.: J. Zyss), Academic Press, New York, **1987**; c) S. R. Marder, B. Kippelen, A. K.-Y. Jen, N. Peyghambarian, *Nature* **1997**, *388*, 845.

[191] a) J. J. Wolff, R. Wortmann, *J. Prakt. Chem.* **1998**, *340*, 99; b) T. J. Marks, M. A. Ratner, *Angew. Chem.* **1995**, *107*, 167; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155; c) R. G. Denning, *J. Mater. Chem.* **1995**, *5*, 365.

[192] a) A. I. de Lucas, N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, *Tetrahedron* **1998**, *54*, 4655; b) R. Andreu, A. I. de Lucas, J. Garín, N. Martín, J. Orduna, L. Sánchez, C. Seoane, *Synth. Met.* **1997**, *86*, 1817.

[193] M. González, N. Martín, J. L. Segura, J. Garín, J. Orduna, *Tetrahedron Lett.* **1998**, *39*, 3269.

[194] M. R. Bryce, A. Green, A. J. Moore, M. González, N. Martín, J. L. Segura, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, *Eur. J. Chem.* **2001**, in press.

[195] J. Garín, J. Orduna, J. I. Rupérez, R. Alcalá, B. Villacampa, C. Sánchez, N. Martín, J. L. Segura, M. González, *Tetrahedron Lett.* **1998**, *39*, 3577.

[196] M. González, N. Martín, J. L. Segura, C. Seoane, J. Garín, J. Orduna, R. Alcalá, C. Sánchez, B. Villacampa *Tetrahedron Lett.* **1999**, *40*, 8599.

[197] D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195.

[198] a) J. L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446; b) J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664.

[199] M. Nakano, S. Yamada, K. Yamaguchi, *J. Phys. Chem.* **1999**, *103*, 3103.

[200] a) M. Nakano, K. Yamaguchi, *Chem. Phys. Lett.* **1993**, *206*, 285; b) M. Nakano, S. Kiribayashi, S. Yamada, L. Shigemoto, K. Yamaguchi, *Chem. Phys. Lett.* **1996**, *262*, 66.

[201] Y. R. Shen, *The Principles of Nonlinear Optics*, Academic Press, New York, **1984**.

[202] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**, Chap. 8; b) J. M. Lehn, *Angew. Chem.* **1990**, *102*, 1347; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304.

[203] a) M. Irie, *Mol. Cryst. Liq. Cryst.* **1993**, *227*, 263; b) B. L. Feringa, W. F. Jager, B. de Lange, *Tetrahedron* **1993**, *49*, 8267; c) J. Whittal in *Photochromism*, *Molecules and Systems* (Eds.: H. Durr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**, p. 467.

[204] a) S. H. Kawai, S. L. Gilat, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1994**, 1011; b) S. H. Kawai, S. L. Gilat, R. Ponsinet, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275; c) M. Irie, M. Mohri, *J. Org. Chem.* **1998**, *53*, 803; d) S. Nakamura, M. Irie, *J. Org. Chem.* **1988**, *53*, 6136; e) A. Fernández-Acebes, J.-M. Lehn, *Adv. Mater.* **1999**, *11*, 910.

[205] K. Uchida, G. Masuda, Y. Aoi, K. Nakayama, M. Irie, *Chem. Lett.* **1999**, 1071.

[206] a) W. Rettig, *Angew. Chem.* **1986**, *98*, 969; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 971; b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163; c) H. Kurreck, M. Huber, *Angew. Chem.* **1995**, *107*, 929; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849.

[207] C. S. Foote, *Top. Curr. Chem.* **1994**, *169*, 347; b) D. M. Guldi, M. Prato, *Acc. Chem. Res.* **2000**, *33*, 695.

[208] P. A. Liddell, J. P. Sunida, A. N. McPherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, D. Gust, *Photochem. Photobiol.* **1994**, *60*, 537.

[209] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354.

[210] N. Martín, L. Sánchez, B. Illescas, I. Pérez, *Chem. Rev.* **1998**, *98*, 2527.

[211] M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandoná, G. Farnia, *Tetrahedron* **1996**, *52*, 5221.

[212] N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, *Tetrahedron Lett.* **1996**, *37*, 5979.

[213] K. B. Simonsen, V. V. Konovalov, T. A. Konovalova, T. Kawai, M. P. Cava, L. D. Kispert, R. M. Metzger, J. Becher, *J. Chem. Soc. Perkin Trans 2* **1999**, 657.

[214] S. Ravaine, P. Delhaès, P. Leriche, M. Sallé, *Synth. Met.* **1997**, *87*, 93.

[215] a) P. Hudhomme, C. Boullé, J. M. Rabreau, M. Cariou, M. Jubault, A. Gorgues, *Synth. Met.* **1998**, *94*, 73; b) C. Boullé, J. M. Rabreau, P. Hudhomme, M. Cariou, M. Jubault, A. Gorgues, J. Orduna, J. Garín, *Tetrahedron Lett.* **1997**, *38*, 3909; c) J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell, C. Rovira, *Chem. Commun.* **1997**, 659.

[216] a) N. Martín, L. Sánchez, I. Pérez, C. Seoane, *J. Org. Chem.* **1997**, *62*, 5690; b) M. A. Herranz, N. Martín, L. Sánchez, C. Seoane,D. M. Guldi, *J. Organomet. Chem.* **2000**, *599*, 2.

[217] M. A. Herranz, N. Martín, *Org. Lett.* **1999**, *1*, 2005.

[218] D. M. Guldi, S. González, N. Martín, A. Antón, J. Garín, J. Orduna, *J. Org. Chem.* **2000**, *65*, 1978.

[219] J. Llacay, J. Veciana, J. Vidal-Gancedo, J. L. Bourdelande, R. González-Moreno, C. Rovira, *J. Org. Chem.* **1998**, *63*, 5201.

[220] a) V. Balzani *Supramolecular Photochemistry*, Reidel, Dordrecht, **1987**; b) D. Gust, T. A. Moore in *Photoinduced Electron Transfer* (Ed.: J. Mattay), Springer, Berlin, **1991**; c) F. L. Carter *Molecular Electronic Devices*, Marcel Dekker, New York, **1987**.

[221] N. Martín, L. Sánchez, M. A. Herranz, D. M. Guldi *J. Phys. Chem. A* **2000**, *104*, 4648.

[222] N. Martín, L. Sánchez, B. Illescas, S. González, M. A. Herranz, D. M. Guldi, *Carbon* **2000**, *38*, 1577.

[223] a) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537; H. Imahori, Y. Sakata *Eur. J. Org. Chem.* **1999**, 2445.

[224] N. Martín, L. Sánchez, D. M. Guldi, *Chem. Commun.* **2000**, 113.

[225] M. A. Herranz, B. Illescas, N. Martín, C. Luo, D. M. Guldi, *J. Org. Chem.* **2000**, *65*, 5728.

[226] J. L. Segura, E. M. Priego, N. Martín, *Tetrahedron Lett.* **2000**, *41*, 7737.

[227] a) C. Lampard, J. A. Murphy, N. Lewis, *J. Chem. Soc. Chem. Commun.* **1993**, 295; b) C. Lampard, J. A. Murphy, F. Rasheed, N. Lewis, M. B. Hursthouse, D. E. Hibbs, *Tetrahedron Lett.* **1994**, *35*, 8675; c) M. E. Begley, J. A. Murphy, S. J. Roome, *Tetrahedron Lett.* **1994**, *35*, 8679; d) J. A. Murphy, S. J. Roome, *J. Chem. Soc. Perkin Trans 1* **1995**, 1349.

[228] L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; Angew. *Chem. Int. Ed. Engl.* **1993**, *32*, 131.

[229] T. Skrydstrup, *Angew. Chem.* **1997**, *109*, 355; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 345.

[230] a) G. A. Molander, L. S. Harring, *J. Org. Chem.* **1990**, *55*, 6171; b) D. P. Curran, T. L. Fevig, M. L. Totleben, *Synlett* **1990**, 773; c) G. A. Molander, J. A. McKie, *J. Org. Chem.* **1995**, *60*, 872; d) G. A. Molander, C. R. Harris, *J. Am. Chem. Soc.* **1995**, *117*, 3705; e) G. A. Molander, C. R. Harris, *J. Am. Chem. Soc.* **1996**, *118*, 4059.

[231] O. Callaghan, X. Franck, J. A. Murphy, *Chem. Commun.* **1997**, 1923.

[232] R. J. Fletcher, C. Lampard, J. A. Murphy, N. Lewis, *J. Chem. Soc. Perkin Trans 1* **1995**, 623.

[233] N. Bashir, O. Callaghan, J. A. Murphy, T. Ravishanker, S. J. Roome, *Tetrahedron Lett.* **1997**, *38*, 6255.

[234] a) R. J. Fletcher, D. E. Hibbs, M. Hursthouse, C. Lampard, J. A. Murphy, S. J. Roome, *Chem. Commun.* **1996**, 739; b) M. Kizil, C. Lampard, J. A. Murphy, *Tetrahedron Lett.* **1996**, *37*, 2511; c) R. Fletcher, M. Kizil, C. Lampard, J. A. Murphy, S. J. Roome, *J. Chem. Soc. Perkin Trans 1*, **1998**, 2341; d) O. Callaghan, C. Lampard, A. R. Kennedy, J. A. Murphy, *Tetrahedron Lett.* **1999**, *40*, 161.

[235] J. A. Murphy, F. Rasheed, S. J. Roome, N. Lewis, *Chem. Commun.* **1996**, 737.

[236] N. Bashir, J. A. Murphy, *Chem. Commun.* **2000**, 627.

[237] M. D. Ward, *Chem. Soc. Rev.* **1995**, *24*, 121.

[238] B. J. Coe, *Chem. Eur. J.* **1999**, *5*, 2464.