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David Canevet, Marc Sallé, Guanxin Zhang, Deqing Zhang, Daoben Zhu. Tetrathiafulvalene (TTF) derivatives: key building-blocks for switchable processes. *Chemical Communications*, 2009, 17, pp.2245-2269. 10.1039/b818607n . hal-03345108

HAL Id: hal-03345108

<https://univ-angers.hal.science/hal-03345108>

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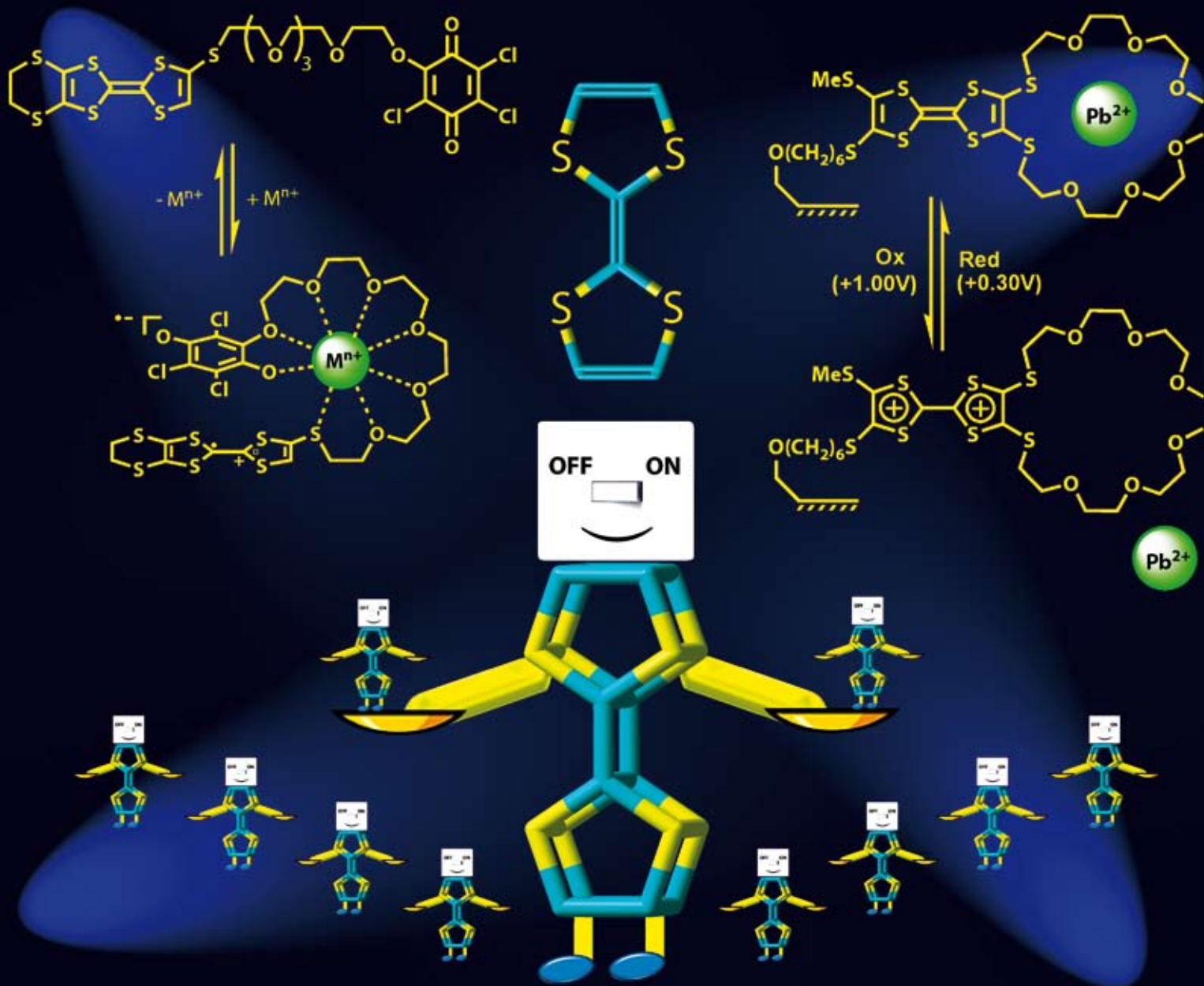
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ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 17 | 7 May 2009 | Pages 2225–2412



ISSN 1359-7345

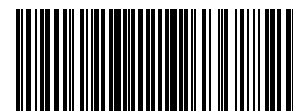
FEATURE ARTICLE

Marc Sallé, Deqing Zhang *et al.*
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FEATURE ARTICLE

Zhenglong Yang, Yunfeng Lu
and Zhenzhong Yang
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1359-7345(2009)17;1-#

Tetrathiafulvalene (TTF) derivatives: key building-blocks for switchable processes

David Canevet,^a Marc Sallé,^{*a} Guanxin Zhang,^b Deqing Zhang^{*b} and Daoben Zhu^b

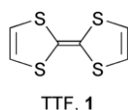
Received (in Cambridge, UK) 20th October 2008, Accepted 8th January 2009

First published as an Advance Article on the web 19th March 2009

DOI: 10.1039/b818607n

Besides a traditional use for the development of organic conducting materials, the tetrathiafulvalene (TTF) unit and its derivatives have recently appeared as key constituents for new applications, exploiting remarkable redox properties: a high π -donating ability and occurrence of three stable redox states. Indeed, in very recent years, an impressive variety of switchable TTF-based molecular and supramolecular (multifunctional) architectures have been designed and synthesized. In this feature article, we discuss recent developments of TTF-based molecular and supramolecular systems in this respect, including molecular sensors, redox-fluorescent switches, multi-input systems for logic gates, electrochemically-driven conformational controls, molecular clips and tweezers, and redox-controlled gelation processes.

1. Introduction



Tetrathiafulvalene (TTF, **1**) is rare among organic compounds in that it is characterized by a relatively simple structure yet is associated with a broad range of applications.^{1–5} This π -electron donor, synthesised nearly forty years ago,^{6,7} has received a

tremendous attention over the years. This attention was stimulated early on by the discovery of high electrical conductivity for the corresponding oxidized salt with chloride as counter anion,⁸ as well as metallic conducting behavior for the charge-transfer complex tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF-TCNQ).^{9,10} Since then, considerable efforts have been devoted to the synthesis^{11,12} of TTF derivatives and to preparing the corresponding electrically conducting salts; this has led *inter alia* to the production of the first superconducting organic materials. Also, this unit has known important developments as a key component for molecular materials presenting various physical properties, such as magnetic, NLO¹³ or photovoltaic¹⁴ properties for example. Several reviews^{1–5,11,15} have addressed recent advances related to these topics of material chemistry, which therefore will not be covered by this Feature article. Instead a particular attention will be paid to the growing use of this unit in the field of molecular switches.

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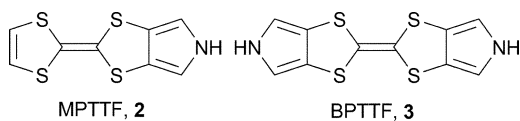
David Canevet and Marc Sallé

David Canevet was born in Angers (France) in 1984. He obtained his Master Degree from the University of Angers in Molecular Engineering and Nanotechnologies in 2006 working on TTF–perylene dyads under the supervision of Prof. Pierrick Hudhomme. Since, he has been a PhD student in Organic Chemistry in Prof. Marc Sallé's team. His research interests mainly concern switching processes in assemblies incorporating TTF units.

Prof. Marc Sallé was born in Toulon (France) in 1963. He studied chemistry at the Ecole Nationale Supérieure de Chimie de Rennes (ENSCR) and at the University of Paris VI. He received his PhD degree in Organic Chemistry from the University of Angers in 1991 under the supervision of Professor Alain Gorgues. For this work he was awarded the Dina Surdin prize of year 1992. After a postdoctoral stay with Professor

M. R. Bryce at the University of Durham (UK), he became Maître de Conférences at the University of Angers, where he was promoted to Professor in 1998. He has been a junior member of the Institut Universitaire de France (IUF) (2003–2008). His research interests concern organic chemistry of molecular materials and supramolecular chemistry associated with electroactive molecular receptors.

The TTF system has received a renewed interest in recent years. This has been due in part to advances in synthetic methods that have resulted in a myriad of new TTF derivatives becoming available for use as “molecular building blocks”. This, in turn, has opened the door to an incredible variety of new functions and applications. Among these are the so-called “molecular switches”, where the redox properties of TTF are exploited to produce systems whose structure and function can be varied through an external stimulus. For instance, recent years have borne witness to the increasing use of TTF in the preparation of interlocked compounds,^{16,17} such as rotaxanes and catenanes. These systems are of particular importance as prototypical molecular machines and molecular-level devices. In this context, the development in Odense of monopyrrolo-tetrathiafulvalene (MPTTF, **2**)¹⁸ and bispyrrolo-tetrathiafulvalene (BPTTF, **3**),^{18,19} corresponds to a synthetic breakthrough that has permitted a very significant step forward in the construction of conformationally switchable [2]rotaxanes^{18,20–24} and [2]catenanes.^{18,25} This has led to considerable promising results in the specific field of mechanical bonds and interlocked systems which will not be covered by this Feature article.



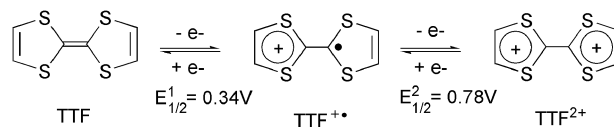
Besides electrochemically-driven molecular motions in interlocked systems, various kinds of TTF-based switchable systems have emerged recently. As detailed below, these take advantage of the unique combination of structure (planar) and



Deqing Zhang

Prof. Deqing Zhang studied chemistry in Beijing Normal University from 1983 to 1987. He then joined in the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) as a graduate student and obtained his MS. in Organic Chemistry in 1990. He conducted research on electron donor–acceptor cyclophanes at the Max-Planck Institute for Medical Research in Heidelberg (Germany) under the supervision of Prof. Dr H. A. Staab, and received

*his Doctor degree (DR. RER. NAT.) from Ruprecht-Karls University Heidelberg in 1996. He is now a research Professor in ICCAS. His research interests include development of external stimuli-responsive molecular systems for molecular switches, logic gates and chemical/bio-sensors. He also shows interests in design and synthesis of organic functional materials and organic nano-assemblies. He has published more than 130 papers in refereed journals. He serves as editorial advisory board member of several scientific journals including *Adv. Funct. Mater.*, *Langmuir* and *Dyes and Pigments*.*



Scheme 1 TTF: A redox active species characterized by three readily accessible and stable redox states (vs. Ag/AgCl in acetonitrile).

conjugation provided by the TTF skeleton. The ability of TTF to support switchable processes comes from:

1 - TTF **1** and its derivatives are electroactive and, as strong π -donors, their redox potentials are sensitive to their environment. As a result, redox responsive ligands and sensors can be constructed that include TTF within the framework.

2 - TTF **1** is a non-aromatic 14 π -electron molecule and can be easily and reversibly oxidized to TTF \bullet^+ and TTF $^{2+}$. These cationic species possess aromatic character according to the Hückel rule, with one and two 6 π -electron 1,3-dithiolium cations, respectively. Therefore, TTF **1**, besides being a small planar system presenting a high propensity for stacking processes, meets three important electrochemical criteria for switchable processes (Scheme 1): (i) **1** can be easily oxidized (low $E^1_{1/2}$ and $E^2_{1/2}$ values); (ii) two successive one-electron oxidation steps may be carried out either chemically or electrochemically and, importantly, with full control over the oxidized species that are produced. Specifically, the electron donating ability of TTF system can be tuned; (iii) both oxidation steps are reversible, which accounts for the good stability of both charged species TTF \bullet^+ and TTF $^{2+}$; this point is of course critical when aiming for switchable systems.

3 - When TTF and its derivatives are linked to electron acceptors to form the corresponding D–A dyads/triads, intramolecular charge transfer/photoinduced electron transfer may occur. Performing redox reactions on TTF moieties, it is possible to switch on/off these intramolecular charge/electron transfer processes within these assemblies. Accordingly, the spectral properties of D–A dyads/triads containing TTF subunits may be reversibly modulated.

4 - The successive transformation of TTF into TTF \bullet^+ and TTF $^{2+}$ can potentially modulate intramolecular interactions in molecules or supramolecules containing two or more TTF moieties. Consequently the global conformation of the system may be switched by varying the oxidation states of the constituent TTF moieties.

5 - TTF and its derivatives tend to self-assemble into nanostructures through π – π and S \cdots S interactions. Again, it is possible to modulate these self-assembly characteristics and the nature of the resulting structures by varying the oxidation state of the associated TTF moieties.

In general, by adjusting the π -donor ability of TTF derivatives and taking advantage of the three redox-states that can be produced from this subunit, it has proved possible to develop an incredible variety of switchable molecular and supramolecular (multifunctional) architectures. In addition to reviewing representative examples of these novel structures, concepts that we would like to highlight in this Feature article include various topics, such as molecular sensors, redox-fluorescent switches, multi-input systems for logic gates, electrochemically

driven conformational controls, molecular clips and tweezers, and redox-controlled gelation processes, among others. Special emphasis is given to very recent results; not discussed is the tremendous body of work devoted to optimizing the solid-state properties of TTF-based materials,¹¹ or the synthetic¹² efforts displayed to produce the associated TTF derivatives.

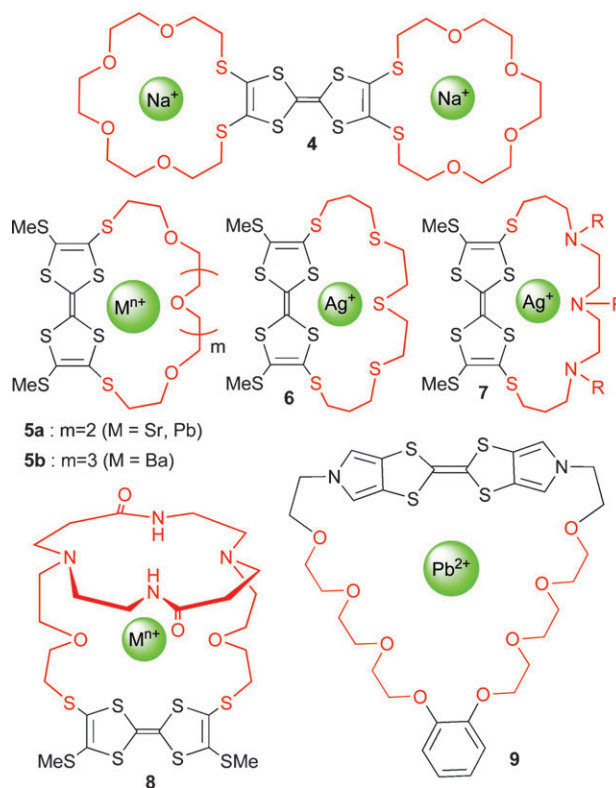
2. Tetrathiafulvalene-based receptors

Considering the well-defined redox and electron-donating properties of TTF, it is not surprising that this subunit has been exploited extensively for the construction of electron-rich receptors, including redox-responsive and/or -switchable ligands. In this context, a broad range of redox-active receptors have been constructed by associating a binding unit to the electroactive TTF framework. Basically, the corresponding molecular hosts are designed to complex neutral or ionic guests, and to undergo a change in their redox or/and their optical properties upon guest binding. While the design of such systems is constrained by the need to include both binding and redox subunits, as well as efficient through-space or through-bond communication between both subunits, as a general rule, this has proven to be a very rich approach to sensor development. Beyond simply sensing, this paradigm may allow for a modulation of the host-guest binding constant with, at the limit, full control over the binding behavior with regard to a given guest. One way to classify receptors and sensors of this type is in terms of the character of the guest (charged or neutral).

2.1. TTF-based redox-responsive (-switchable) ligands for cationic guests

Redox-sensors for cationic guests^{26–28} such as metal cations, constitute a well-developed family. Binding a cation in a cavity close to a TTF core leads to an alteration of the π -donating ability of this key redox-active unit. This behavior is ascribed to the inductive effect exerted by the bound-cation, and is generally easily monitored by cyclic voltammetry (CV) with typically a positive shift in the first redox potential ($E_{1/2}^1$) of the TTF subunit being seen. Using the Nernst equation, the value of $\Delta E_{1/2}^1$ can be directly correlated to the K^0/K^+ ratio, where K^0 and K^+ correspond to the binding constants at the neutral (TTF⁰) and monocationic (TTF^{•+}) states. Therefore, observation of a high $\Delta E_{1/2}^1$ value is characteristic of a strong difference in the binding abilities of the neutral and oxidized receptor. Much of the interest in using the TTF framework compared to other redox-active units such as ferrocene for instance, relies on its ability to be oxidized according to two successive reversible one-electron processes to produce a cation-radical (TTF^{•+}) and a dicationic (TTF²⁺) species, respectively. In the limit, the electrostatic repulsive interactions occurring between the doubly charged TTF²⁺ unit and a bound cationic guest will cause expulsion of the guest (typically a metal cation) outside the binding cavity ($K^{2+} = 0$). Altogether, the value of $\Delta E_{1/2}^1$ provides insights into the differences in binding ability displayed by the neutral and the monocharged receptor, a lack of variation in $E_{1/2}^2$ provides an indication that the putative cationic guest is being expelled from the cavity.

A major pioneering contribution to this field was achieved in Odense under impulsion of J. Becher and led, in particular to the synthesis of annelated-TTF derivatives such as **4**



Scheme 2 Examples of crown-annelated TTFs responsive-ligands.

(Scheme 2).^{29,30} Importantly, although receptors of this family were found to bind alkaline cations well, the redox signature of the binding event proved to be only moderate, with a low $\Delta E_{1/2}^1$ value being recorded and only in the presence of a very large excess of the metal cation in question (>250 equiv.). Such behavior results presumably from a lack of electronic communication between the binding site and the central $S_2C=CS_2$ core of the TTF unit, where the charge density is mainly located.

Other receptors which, like **4**, incorporate a crown-ether unit fused on two vicinal positions of TTF, have been described,³¹ and also present moderate electrochemical responses to metal binding ($\Delta E_{1/2}^1 < 25$ mV) whereas complexation does occur. Such observations underscore the importance of the molecular design and the crucial role of the connection in between the binding site and TTF redox-active readout element. A breakthrough in the synthesis of TTF derivatives, which has already permitted access to a myriad of new redox-active systems, is the methodology developed by Becher and co-workers, which relies on selective thiolate protection/deprotection sequences, using bromopropionitrile and cesium hydroxide monohydrate, respectively.³²

This methodology provides in particular an efficient entry to bis-substituted TTF derivatives, such as **5–7**, that were synthesized in Angers and which present a binding unit lying along the long axis of the TTF skeleton. Crown-ether TTFs **5**^{33,34} and their sulfur analogue **6**³⁵ exhibit high affinity for many targeted cations (typical K^0 values 10^3 – 10^4 M⁻¹ in $CH_3CN-CH_2Cl_2$) when the TTF subunit is in its neutral form, as shown by ¹H NMR, UV-vis and/or by MS titration studies. It is worth noting that in these cases, a clear electrochemical recognition behavior could be observed in the presence of stoichiometric (1 : 1) quantities of added metallic cations. In

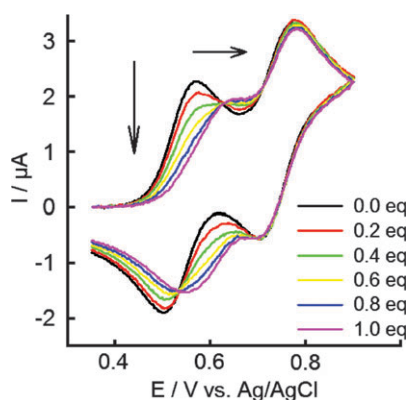


Fig. 1 Cyclic voltammograms of **5b** recorded in the presence of increasing quantities of $\text{Ba}(\text{ClO}_4)_2$; $[\mathbf{5b}] = 10^{-3} \text{ mol L}^{-1}$ in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1 : 1), Bu_4NPF_6 (0.1 mol L^{-1}), 293 K, 100 mV s^{-1} .

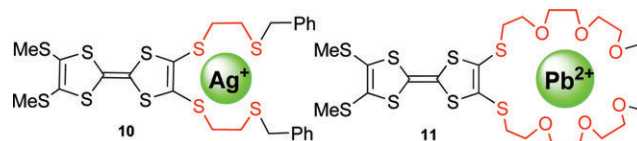
addition, significant positive shifts in the first redox potential could be observed (e.g. $\Delta E_{1/2}^1 = 45\text{--}100 \text{ mV}$ for **5** or **6**) (Fig. 1). This different behavior of **5** and **6**, which is related to type **1** receptors, is assigned to a greater relative spatial proximity for the bound cation and the zone of higher charge density (located on the central $\text{S}_2\text{C}=\text{CS}_2$ motif as noted above).³⁶ Metal ion selectivity could be demonstrated, depending on the size (**5a** vs. **5b**) or on the hard/soft nature of interaction sites (**5a** vs. **6**).³⁵ For instance, whereas the crown-ether systems **5a** and **5b** demonstrate good affinity for group II metal ions (Sr^{2+} and Ba^{2+} , respectively), receptor **6** involving S-atoms binds preferentially the relatively soft cation, Ag^+ as well as does **7** with N-atoms.³⁷ Interestingly, in all cases, no variation in the second redox potential ($E_{1/2}^2$) is observed upon introduction of the cation in the electrolytic solution. This is ascribed to the expulsion of the metal ion at this potential.

Based on the same design principle, the dioxocyclam unit, known to possess effective cation complexation properties, was introduced along the long axis of TTF (compound **8**).³⁸ Although silver cation complexation was inferred from FAB mass spectrometric analyses, no electrochemical signature of the binding was observed with this receptor.

Actually, compounds **5–8** exist as mixtures of two *Z/E* isomers relative to the TTF skeleton. Even if in some cases the geometric isomers can be separated, oxidation to $\text{TTF}^{\bullet+}$ or TTF^{2+} results in a rotation around the central $\text{S}_2\text{C}=\text{CS}_2$ bond, and subsequent reduction to the neutral state necessarily leads to a mixture of isomers. These systems also potentially isomerize under slightly acidic conditions subsequently to protonation of the central electron-rich $\text{S}_2\text{C}=\text{CS}_2$ double bond.

It has been shown by ^1H NMR studies that only the *Z*-isomer in **5–8** is capable of metal binding, and therefore systems devoid of *Z/E* isomerization are of interest. This is accomplished with compound **9**,³⁹ constructed around the bis(pyrrolo)TTF skeleton,¹⁸ combining the desirable electrochemical properties of the TTF subunit while avoiding issues associated with isomerism. In this case, a very high affinity for Pb^{2+} ($\log K^0 = 6.2$ in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$, 1 : 1), along with a remarkable electrochemical signature were found ($\Delta E_{1/2}^1 = +140 \text{ mV}$).

The first example of TTF-based receptors involving an acyclic binding site was described by Bryce and co-workers (compound **10**) (Scheme 3).⁴⁰ Interest in this family of



Scheme 3 TTF-based receptors involving acyclic binding sites.

compounds relies on a more straightforward synthetic approach (no need for high-dilution conditions), but also on higher solubility and greater conformational flexibility than for crown-systems. Compound **10** shows a good selectivity for Ag^+ in agreement with the HSAB theory ($\log K^0 = 3$, CH_3CN), and a $\Delta E_{1/2}^1$ value of $+40 \text{ mV}$.

The TTF-based podand **11**,^{41,42} which shows a good affinity for Pb^{2+} ($\log K^0 = 5.0$, $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1 : 1)), was also described by the Angers group. In this case, a strong association was inferred from a ^1H NMR spectroscopic titration study (Fig. 2), from which a K^0 value could be extracted and the 1 : 1 stoichiometry of the corresponding lead(II) complex confirmed. In addition, introduction of lead(II) to an electrolytic solution of **11** was found to be accompanied by very remarkable CV behavior (Fig. 3). Specifically, progressive addition of $\text{Pb}(\text{ClO}_4)_2$ not only led to an anodic shift in the potentials, but also to the appearance of a new redox system ($E_{1/2}^1 = E_{1/2}^1 + 120 \text{ mV}$) corresponding to the **11**- Pb^{2+} (1 : 1) complex; this latter grew in at the expense of the signal for the free ligand **11**. Interestingly, the $E_{1/2}^2$ values remains constant, a finding that once again is interpreted in terms of cation expulsion taking place in this oxidized form.

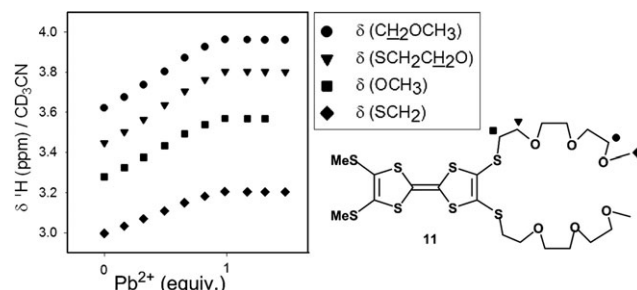


Fig. 2 ^1H NMR titration curve for **11** in presence of $\text{Pb}(\text{ClO}_4)_2$ (ref. 42. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

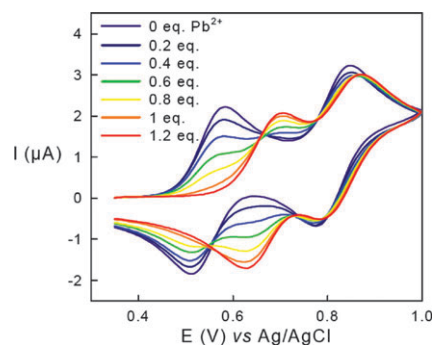
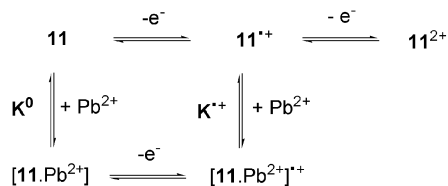


Fig. 3 CV behavior of **11** in the presence of increasing amounts of $\text{Pb}(\text{ClO}_4)_2$; $[\mathbf{11}] = 10^{-3} \text{ mol L}^{-1}$ in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1 : 1), Bu_4NClO_4 (0.1 mol L^{-1}), 293 K, 100 mV s^{-1} (reproduced from ref. 41. Copyright 2004, American Chemical Society).

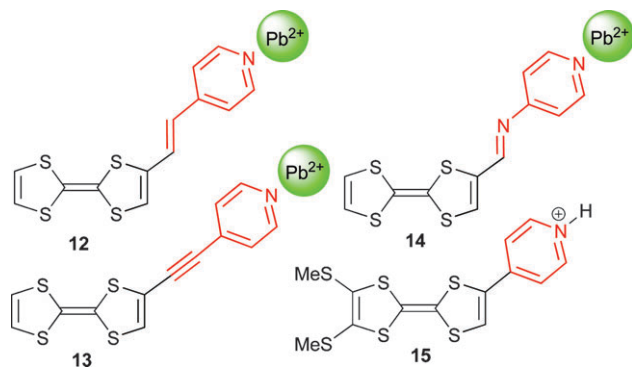


Scheme 4 Square scheme for the electrochemical titration of **11** with $\text{Pb}(\text{ClO}_4)_2$.

On the basis of the square scheme presented (Scheme 4) and the use of a CV simulation program, the binding constants for the different redox states of TTF could be evaluated as $\log K^0 = 5.5$, $\log K^{+} = 3.3$ and $\log K^{2+} = 0$, respectively. Such behavior can be exploited in the design of devices able to electrochemically control metal binding *via* external adjustments in the redox state of the constituent TTF subunits (*vide infra*).

Many efforts have been engaged for several years in the preparation of hybrid organic–inorganic architectures involving a TTF moiety and a transition metal cation. The aim of these studies relies on multifunctional materials designed to allow interactions in the solid state, between mobile π -electrons of organic conducting TTF layers and localized electron spins of a paramagnetic transition metal ion.^{43,44}

In the quest for such hybrid organic–inorganic materials, a considerable variety of TTF-pyridine derivatives have been described in the recent years. Such solid-state studies are far beyond the subject of this article and moreover have been reviewed during the submission process of the present article.⁴⁵ Nevertheless we wish to focus on those examples of TTF–pyridines which behave as chemical sensors in solution. The TTF–pyridine ligand **12** (Scheme 5) corresponds to a donating–accepting chromophore (D– π -A) described by Andreu *et al.* few years ago,⁴⁶ and for which sensing properties for Pb^{2+} were demonstrated by Wu and co-workers.⁴⁷ Derivatives **13**⁴⁸ and **14**,⁴⁹ involving alternative conjugated acetylenic and imine linkers, respectively, were described very recently. The recognition behavior of systems **12–14** for lead(II) are very similar, which illustrates the efficiency of the associated linkers in the conjugation process. The sensing ability of these TTF-based systems clearly follows a different mechanism than the classical one supported by electrostatic interactions, and described above for TTF-based receptors such as **4–11**. Indeed, chemosensors **12–14** exhibit a dual responsive behavior to metal binding, with both colorimetric and electrochemical detection being possible in the case of lead(II).



Scheme 5 Some recent TTF-pyridines with switchable ICT properties.



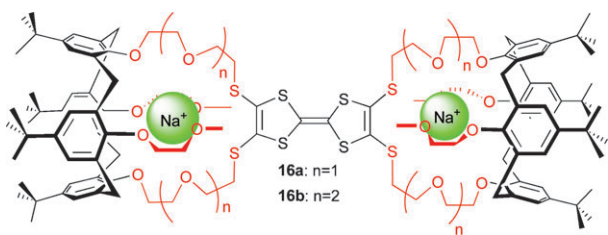
Fig. 4 Color evolution seen upon the introduction of an excess of metal cation to a solution of **14** (5×10^{-4} mol L^{-1}) in CH_2Cl_2 – CH_3CN .

In practical terms, one of the key features of receptors **12–14** is that the yellow–orange color of the free ligands changes to deep purple–deep blue upon addition of lead(II) (Fig. 4). These changes result from a strong modification of the intramolecular charge transfer (ICT), which takes place from the HOMO of the donating part (TTF) to the accepting pyridyl moiety upon metal coordination. An additional feature of these systems comes from the novel nature of the electrochemical recognition. This recognition is manifest by a positive shift in the TTF redox potentials as the case of TTF-based receptors **4–11**. However, in the case of **12–14** this shift is based on a through-bond interaction rather than on a through-space electrostatic interaction between the bound cation and the TTF moiety.

Efforts devoted to grafting a pyridyl unit directly to a TTF moiety have also been reported. Here, the goal was to increase the interaction between a bound cation and the redox-active TTF “read out” element. The TTF–pyridine derivative **15** has been studied in this context.⁵⁰ The authors were able to show that ICT in this donating–accepting molecule could be tuned *via* metal ion coordination. Protonation of the pyridine moiety was also used to convert this heterocyclic substituent into a strong accepting pyridinium unit. The effect of protonation is remarkable on the spectroscopic features (*e.g.*, $\Delta\lambda_{\text{max}} = +136$ nm), but also on $\Delta E_{1/2}^1$, which was found to be positively shifted by +80 mV. A continuous addition of *p*-toluenesulfonic acid from 0 to 1 equivalent (relative to **15**) was found to produce a similar evolution in the CV as did the progressive addition of a metallic cation guest (*cf.* Fig. 3). In addition, the value for the second redox potential ($E_{1/2}^2$) was found to remain constant, a finding that is reminiscent of an oxidation-coupled proton dissociation process.

Modulating the guest binding properties as a function of the TTF redox state, requires first a high binding constant (K^0) for the neutral state. From this point of view, the calix[4]arene moiety has been extensively used in the literature as a suitable platform for generating three-dimensional binding cavities capable of complexing various guests with high affinity. In this context, we have synthesized TTF-based receptors **16a,b** (Scheme 6) and studied their metal ion binding ability.^{51,52}

The cone structure of both calixarene platforms **16a** and **16b** promotes the construction of two 3D pockets, and these cryptand-like architectures are reminiscent of geometries encountered in the case of bibrachial lariat ethers (BiBLE). Binding studies performed with these receptors revealed a good affinity for sodium cation. Further, the resulting disodium complex could be characterized in the solid-state. A slight increase in the $E_{1/2}^1$ value ($\Delta(E_{1/2}^1) = +30$ mV) could



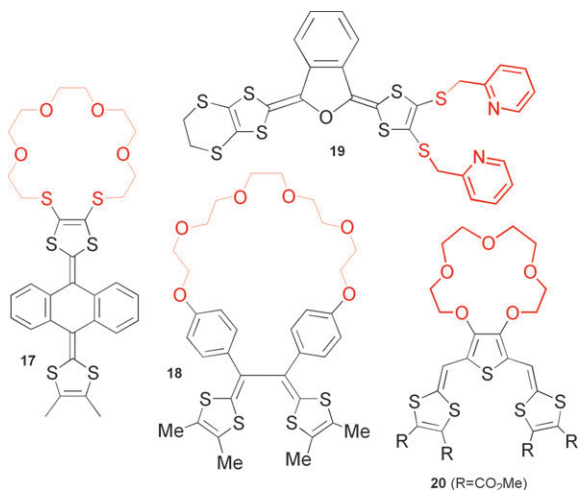
Scheme 6 Bis(calixcrown)tetrathiafulvalene receptors.

be observed upon addition of NaClO_4 (up to 2 equivalents). Such a moderate increase in the $\Delta(E_{1/2}^1)$ value is thought to reflect poor electronic communication between the redox-active TTF subunits and the bound sodium cations.

In addition to efforts devoted to the introduction of new binding subunits (podands, coronands, cryptands, ...), some structural variations have been carried out recently on the redox-active TTF part itself. Much of this effort has centered around extensions of the conjugated π -system. Illustrative examples are shown in Scheme 7.

One family is based on compound **17**,⁵³ and related polyether derivatives described recently.⁵⁴ Three additional examples have appeared in the very recent literature, namely a crown ether vinyllogous TTF receptor **18**⁵⁵ whose cation binding ability is accompanied by a tuning of intramolecular movements (*vide infra*), and two extended TTF-based receptor **19**⁵⁶ and **20**⁵⁷ that contain, respectively, a furano-quinonoid or a thienylene spacer between the 1,3-dithiol-2-ylidene rings.

Considering the specific voltammetric features of the redox units involved in those systems, it is possible to anticipate the electrochemical recognition behaviour of the corresponding receptors. Actually, three different kinds of voltammetric recognition behavior are found for **17**, **19** and **20**. Indeed, Group I and II cations are efficiently detected by **20** (Na^+ or Ba^{2+} : $\Delta(E_{1/2}^1) = +90$ mV; $\Delta(E_{1/2}^2) = 0$). The behavior in this case matches a square scheme very similar to that for the parent TTF derivatives **4–11**, from which it is inferred that expulsion of the metal ion takes place at the doubly oxidized stage ($E_{1/2}^2$). This behavior is assigned to the localization of the positive charge on the median thiophene ring upon oxidation of the extended-TTF



Scheme 7 Metal cation receptors involving a π -extended TTF unit.

skeleton. This is favored by the presence of O-atoms on the 3,4-positions of the thiophene spacer, *i.e.* near the binding cavity. On the other hand, compound **17** involves an anthracenyl-based extended-TTF unit (*ex*TTF),^{53,54} whose electrochemical behavior is clearly distinct from that of TTF; this species is oxidized following a single two-electron oxidation to generate the dication exTTF^{2+} . A good affinity of **17** for Na^+ and Ag^+ could also be demonstrated, with a remarkable electrochemical response to metal complexation being observed. This latter is manifest by a positive displacement of the two-electron oxidation wave (*ca.* $\Delta E_{\text{ox}} = +80$ mV). This observation is worth noting, since this compound appears significantly more sensitive to metal binding than its non-extended analogue **4**. This is rationalized in terms of a single two-electron oxidation process, which in the case of *ex*TTF **17** is accompanied by a conformational change (rotation around the Ar–CS₂ bond). Both positive charges are consequently localized on the peripheral dithiolyldene moieties, *i.e.* in close proximity to the binding site, making the system primed for an effective voltammetric response.

Finally, a third kind of electrochemical feature is observed with **19**. In this case, various M(II) cations could be recognized through pyridyl coordination. In particular, introduction of Pb^{2+} , Pd^{2+} , Ni^{2+} is accompanied by a remarkable four-wave behavior (Fig. 5), with both redox waves considerably positively shifted (*ca.* $\Delta(E_{1/2}^1) = +150$ mV; $\Delta(E_{1/2}^2) = +140$ mV). Such original behavior illustrates the high stability of the complex even at the dicationic stage. This is presumably a consequence of the increased charge delocalization and the lowered coulombic repulsion generated upon oxidation of such a conjugated system.

Considering practical aspects of chemical sensors and devices, a critical next step involves immobilizing the functional active group (receptor) on a solid surface, in particular to allow an easier separation between the host and the guest substrate. For this to work, the recognition process under interfacial conditions must mirror that seen in homogeneous solution. A very convenient and straightforward way to reach modified surfaces involves the preparation of self-assembled monolayers (SAMs). In the case of TTF-based receptors, pioneering efforts in this area were carried out by the groups of Bryce⁵⁸ and Echegoyen.^{59,60} These efforts, which have already been reviewed,^{1,2,4} were largely focused on crown-annulated TTF-systems analogous to

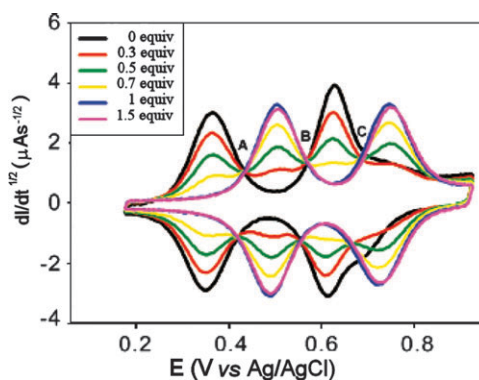


Fig. 5 Deconvoluted CV of **19** in presence of increasing amounts of $\text{Pd}(\text{ClO}_4)_2$; $[\mathbf{19}] = 10^{-3}$ mol L^{-1} in CH_2Cl_2 – CH_3CN (1 : 1), Bu_4NPF_6 (0.1 mol L^{-1}), 293 K, 100 mV s^{-1} (reproduced from ref. 56. Copyright 2007, American Chemical Society).

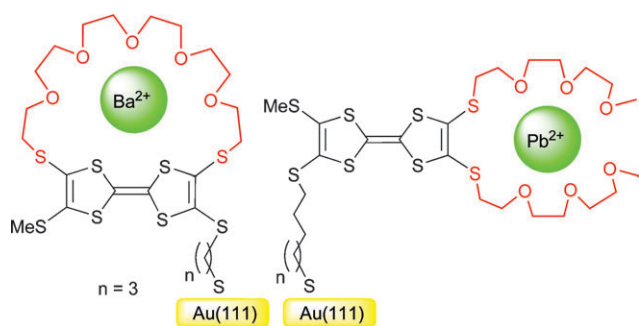


Fig. 6 SAMs of TTF-based receptors **5b** and **11**.

compound **4** (various crown sizes), which were then adsorbed on gold electrodes *via* alkyl chains terminated by thiol⁵⁸ or 1,2-dithiolane⁵⁹ anchoring groups. More recently the Angers group has prepared SAMs from receptors **5b** and **11** substituted with alkythiol grafting sites (Fig. 6); these were designed to achieve recognition of the Ba^{2+} and Pb^{2+} cations, respectively (*vide supra*). The corresponding monolayers demonstrated sufficient stability on the gold substrate as well as good sensing abilities for these two cations; this was manifested by a positive shift of the first oxidation wave ($\Delta E^{\text{ox}}_1 = +40$ mV and $+60$ mV for **5b** and **11** with Ba^{2+} and Pb^{2+} , respectively).

An alternative, and seemingly original strategy was used to immobilize the crown-annelated TTF system **5b** onto a platinum surface. This route uses the propensity of dendrimeric molecules persubstituted on their periphery with electroactive units, to electrodeposit on Pt. Dendrimers bearing up to 96 TTF units have been built.⁶¹ Successive scans of the potentials between the neutral (TTF^0) and the dicationic (TTF^{2+}) states, resulted in a progressive electrodeposition of the dendrimer.

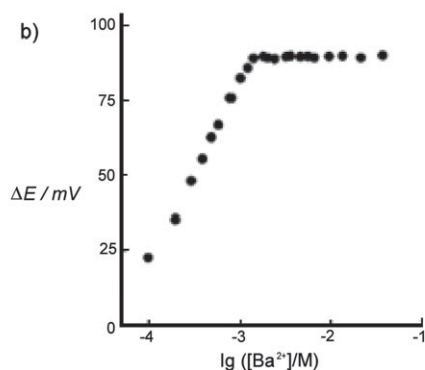
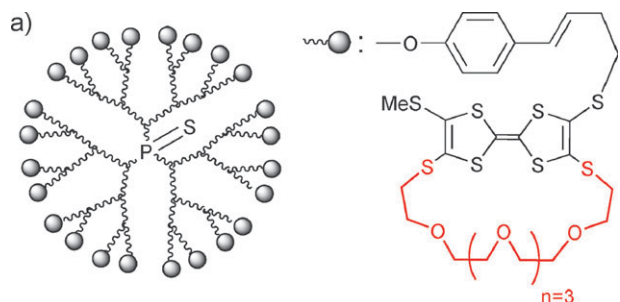


Fig. 7 (a) A dendrimer persubstituted with a redox-responsive ligand; (b) plot of $\Delta E (= E_{\text{pa1}}([\text{Ba}^{2+}] = 0) - E_{\text{pa1}}([\text{Ba}^{2+}] \neq 0))$ vs. $\log([\text{Ba}^{2+}])$ for dendrimer modified Pt electrodes (ref. 61). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

The resulting modified electrodes demonstrated a nice electrochemical response to Ba^{2+} in a $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1 : 1) solution (Bu_4NPF_6 0.1 M) (Fig. 7).

In addition to their utility for cation detection as noted above, TTF-based redox systems, such as **11**, are able to tune the binding/expulsion process for a given cation. This feature is based on a simple control of the applied potential and hence the redox state of the TTF unit. This feature is considered useful in applications involving metal cation rich solutions, *e.g.* environmental problems, where the ability to effect cation binding or release is deemed advantageous. Nevertheless, for this method to be broadly applicable and permit metal complexation at a functionally useful scale, it is necessary to produce thick films on the conducting surface, with high surface coverage. A suitable solution to this latter problem involves the preparation of substituted electroconducting films. Some have been prepared from the redox-active receptor **5b** attached to a poly(ethylenedioxythiophene) (PEDOT) or to a polypyrrole skeleton.⁶² The corresponding modified surfaces were found to show moderate recognition properties for Ba^{2+} . Very interestingly, a Pt surface similarly modified by a conducting PEDOT polymer poly(**11**) bearing pendant receptor units derived from **11**, demonstrated remarkable voltammetric recognition behavior for the Pb^{2+} cation (Fig. 8).⁴¹ It is of interest to note that the CV behavior is very similar to that shown in Fig. 3 (taking into account changes between diffusion conditions (**11** in an electrolytic solution), and a

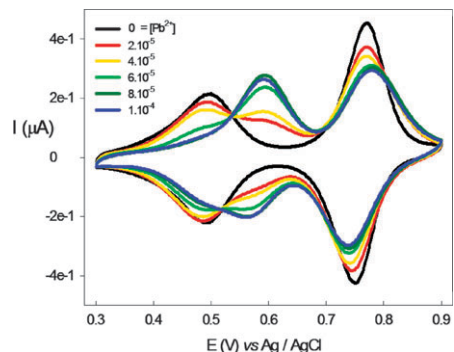
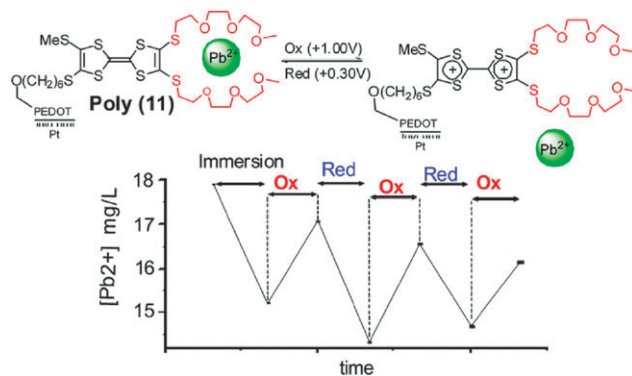


Fig. 8 CV response of poly(**11**) seen upon the addition of increasing quantities of Pb^{2+} (reproduced from ref. 41. Copyright 2004, American Chemical Society).



Scheme 8 An electrochemically triggered metal-cation "sponge"; evolution of $[\text{Pb}^{2+}]$ upon surface electrode polarization (reproduced from ref. 41. Copyright 2004, American Chemical Society).

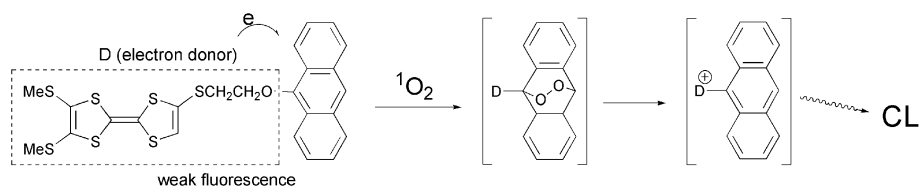
redox-species immobilized onto an electrode (poly(**11**)); this is a first indication that the key complexation–expulsion behavior is comparable in homogeneous solution and in the films. The concentration of Pb^{2+} in solution could also be followed by atomic absorption and EQCM analyses, and these methods were thus used to demonstrate Pb^{2+} complexation within poly(**11**) for neutral TTF, and expulsion upon oxidation to TTF^{2+} (Fig. 8 and Scheme 8).

2.2 TTF-based redox responsive ligands for anionic or neutral guests (including clips, tweezers and other poly-TTF receptors)

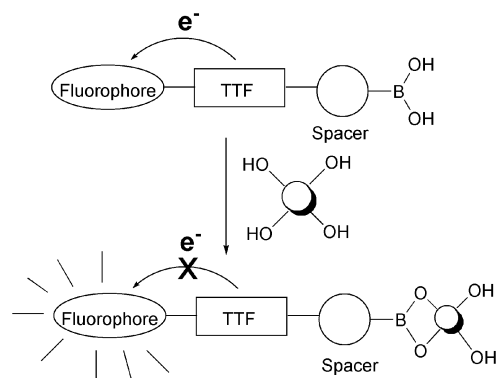
Anion receptors are the subject of intense current interest, and TTF probes have emerged recently on the forefront of this field. A more challenging, but often chemically related problem, involves the recognition of neutral molecules. Here too TTF-based systems have an important role to play. For instance, reliable detection methods for singlet oxygen ($^1\text{O}_2$) are still rare, whereas both high selectivity and sensitivity have been obtained with anthracenyl-TTF derivatives **21a**⁶³ and **21b**,⁶⁴ synthesized in Beijing and used as chemiluminescent traps. Indeed the association of the strong electron donor TTF and the reactive luminophore anthracene (which is specific for $^1\text{O}_2$), results in an optimized trapping reactivity as well as in an efficient photoinduced electron transfer (PET), which serves to limit the fluorescence. In addition to their strong sensitivity, the high selectivity of these systems for $^1\text{O}_2$ is demonstrated by a strong chemiluminescence, which is not observed with other reactive oxygen species (ROS) such as H_2O_2 , OCl^- , $\bullet\text{OH}$, or O_2^- . A three-steps chemiluminescence mechanism is proposed in Scheme 9. It is based on an initial trapping of $^1\text{O}_2$ by the anthracene unit; this presumably leads to an unstable endoperoxide, whose decomposition not only promotes excitation of the anthracene core and light emission through radiative deactivation, but also oxidation of the π -donating TTF unit. Interestingly, similar results could be obtained in alcoholic–water solutions using the hydrophilic derivative **21c**.⁶⁵



Detection of saccharides constitutes an additional challenge that could be overcome by associating TTF to anthracene and boronic acid units, as in receptors **22a**⁶⁶ and **22b**.⁶⁷ The fluorescence of the anthracene unit in these compounds is very weak due to a photoinduced electron transfer process from the TTF to the

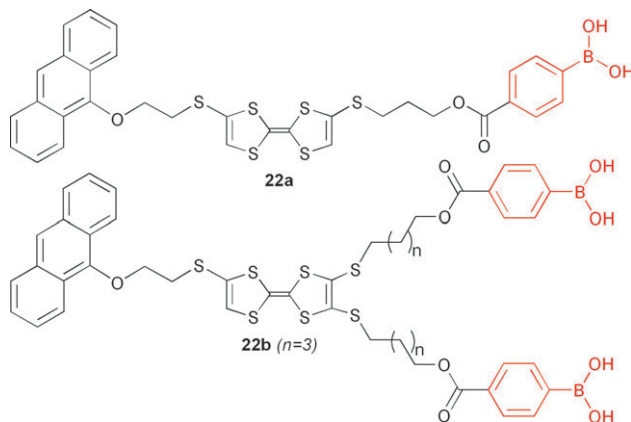


Scheme 9 Possible mechanism for the strong chemiluminescence from the reaction **21a** and $^1\text{O}_2$ (reproduced from ref. 63. Copyright 2004, American Chemical Society).

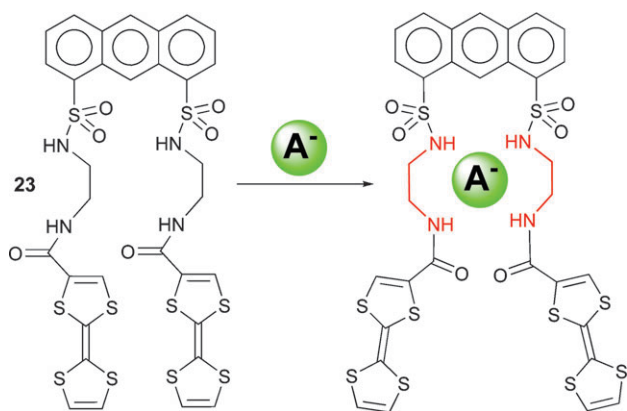


Scheme 10 Fluorescence detection mechanism of saccharides by TTF-based sensors.

anthracene subunits. When saccharides are bound with the boronic acid group(s) of **22a** and **22b**, their fluorescence intensities are enhanced. A high selectivity and sensitivity toward D-fructose was seen in the case of the monoboronic acid derivative **22a**, whereas D-glucose was more easily detected with the diboronic acid derivative **22b**. The observed phenomenon can be explained as follows (Scheme 10): upon reaction with saccharides, the boronic acid group is converted to the boronate form which is a stronger Lewis acid (stronger electron acceptor) compared with the corresponding boronic acid group. Therefore, PET between the TTF and the boronate takes place at the expense of PET between TTF and anthracene units. As a result, the fluorescence of **22a** and **22b** increases upon reaction with saccharides.

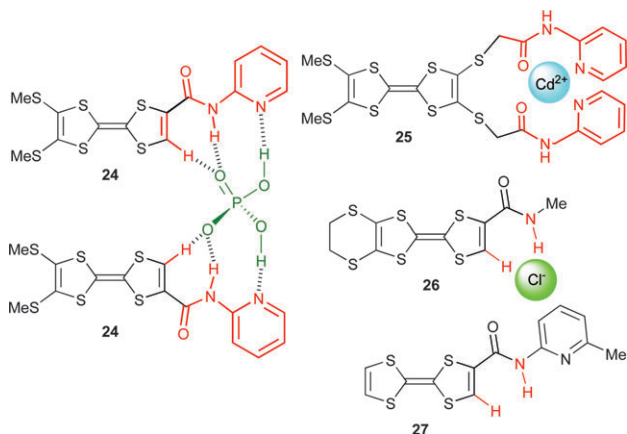


As for cation recognition (*vide supra*), the electroactive TTF core can be used to contribute to the anion recognition process, at least to a certain extent. The anion acceptor **23** is based on an anthracene disulfonamide derivative incorporating two TTF units.⁶⁸ As previously mentioned, a PET can usually occur in



Scheme 11 A dual optical-electrochemical anion receptor.

anthracene–TTF dyads. In the case of **23**, the distance between the anthracene and TTF units can be modulated through anion binding in the intermediate NH pocket (Scheme 11). In particular, **23** shows a high sensitivity and selectivity toward fluoride ion, which is characterized by a strong enhancement of the anthracene fluorescence. An additional feature of this system relies in its redox-active character, which can also be studied by CV in order to probe the binding efficiency. No evidence of fluoride binding could be observed by CV. Nevertheless, introduction of H_2PO_4^- to an electrolytic solution of **23** was found to give rise to a remarkable electrochemical response, which is accompanied by a negative shift of the first redox-potential ($\Delta E^{1/2}_1 = -172$ mV). Therefore, receptor **23** constitutes a dual signaling optical-electrochemical receptor for anions. Similar electrochemical behavior was observed in the case of the TTF derivative **24**.⁶⁹ This compound, which encompasses H-bond donating and accepting sites (*i.e.* secondary amide groups and pyridyl units, respectively), also exhibits remarkable selectivity for H_2PO_4^- over a wide range of anions (Scheme 12). A 2 : 1 stoichiometry between **24** and H_2PO_4^- was inferred from ^1H NMR spectroscopic studies (Job's method), as well as by computational modeling. The corresponding electrochemical titrations revealed that the complex is easier to oxidize than the free ligand, a finding that is explained in terms of a delocalization of the negative charge over the TTF framework. This explanation is confirmed by computing calculations, which indicate that the negative charge brought by the anionic

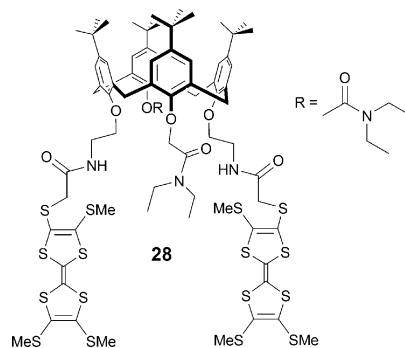


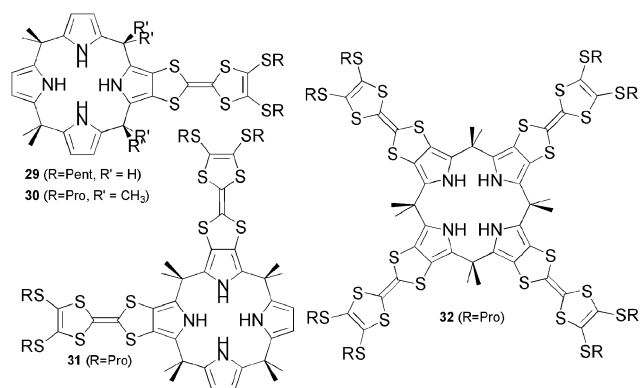
Scheme 12 TTF–amide(II)–pyridyl assemblies: molecular engineering for anion or cation complexation.

substrate, leads to a significant increased value for the HOMO of the anion-bound form relative to the free ligand.

At this stage it is interesting to note that a fine tuning of the molecular design, which is made relatively easy by the chemical versatility of the TTF platform, can give rise to complexation of either anionic or cationic guests. Indeed, in a very recent report⁷⁰ it was noted that compound **25**, which is similar to **24** in that a TTF core is associated with secondary amide functionalities and pyridyl groups, shows a high affinity for $\text{M}(\text{II})$ transition metal cations. In the particular case of Cd^{2+} , this recognition ability is manifested in terms of a remarkable four-wave voltammetric response associated, which reflects the strong stability of the metal complex in both oxidized states of TTF. This behavior is ascribed to the peculiar rigid spatial arrangement observed in the X-ray structure, where the metal appears locked in a strongly rigid environment and centered over the redox unit.

Adjusting the strength, number and orientation of hydrogen bonding interactions between host–guest complexes is another target of considerable current interest within the supramolecular chemistry community. In particular, electrochemical oxidation of a redox-active host, such as TTF, may profoundly influence the donor/acceptor hydrogen bonding ability within an overall host–guest assembly. This can lead to major changes in the strength of the intermolecular interactions. Interesting examples within this general context, are the amide TTF derivatives **26** and **27**. These systems were described, respectively, by Batail, Fourmigué *et al.*⁷¹ and by Cooke *et al.*⁷² These researchers were able to show that such compounds may exhibit an efficient hydrogen bond tweezer effect for guests, in which both N–H and C–H hydrogen bond donors are involved in a cooperative way. This effect has been demonstrated in solution (NMR spectroscopy, CV) and in the solid state, at least in the case of **26** in the presence of Cl^- ,⁷¹ or $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ ⁷³ anions. It appears in this case that upon oxidation of the TTF unit, an activation of the N–H and C–H hydrogen bond donor ability occurs. Anion binding by secondary amide sites acting in a cooperative manner has also been observed in the case of receptors built up using the calix[4]arene platform. The calixarene derivative **28** shows a good affinity for H_2PO_4^- with a cone structure that then becomes rigidified upon anion binding.^{74,75} This conclusion was supported by ^1H NMR spectroscopic data, as well as from the electrochemical response, wherein a negative shift in the first redox potential is observed upon introduction of H_2PO_4^- .





Scheme 13 TTF-calix[4]pyrrole derivatives.

The calix[4]pyrrole core, which bears some structural analogy to calixarenes, has been extensively studied in recent years in the field of anion receptors.^{76,77} Based on this skeleton, the team of Sessler and Jeppesen *et al.* have produced an elegant series of TTF-calix[4]pyrroles assemblies **29–32** (Scheme 13). A very remarkable feature of these systems is their halide anion sensing ability. The four central NH protons plays a critical role in establishing a high affinity for halide anions in organic media. This anion binding process may be followed by ¹H NMR spectroscopy, with titrations revealing the binding process very clearly.⁷⁸ Actually, receptor **29** shows affinities for X[−] anions that are among the highest seen for non-strapped calix[4]pyrrole systems^{77,79} (*e.g.*, $K = 2.1 \times 10^6 \text{ M}^{-1}$ for F[−] in an acetonitrile-*d*₆ containing 0.5% *v/v* D₂O). A clear advantage of this system compared to other simple calix[4]pyrrole derivative, is the presence of a redox-active TTF probe. This allows binding events to be followed by electrochemistry. Specifically, a negative displacement in the first oxidation potential is seen when a stoichiometric amount of Br[−] or Cl[−] is introduced (*ca.* $\Delta E_1 = -40 \text{ mV}$). This behavior is ascribed to the effect the negative charge of the halide substrate bound within the (N–H)₄ · X[−] binding network has on the redox active TTF center. The synthetic methodology has been adapted to new TTF oligopyrroles based on the more stable *meso*-octamethylcalix[4]pyrrole platform, involving one (**30**), two (**31**) or four (**32**) monopyrrolo-TTF units.⁸⁰

Again, a strong affinity is found for halide anions, which was shown by both ¹H NMR and isothermal titration calorimetry (ITC). As a general rule, higher binding constants, but reduced selectivities, were observed as the number of TTF units on the periphery increased. In the event, remarkable electrochemical recognition behavior was observed in the case of **30** treated with Cl[−] ($\Delta E_1 = -145 \text{ mV}$). X-Ray diffraction studies on single crystals of **30** and **32** revealed that these systems adopt a 1,3-alternate conformations in the solid state in the absence of anions. This conformational preference has been nicely exploited in the case of **32**. Here, recognition studies established that this system can act as a receptor for electron-deficient neutral guests.⁸¹ Indeed, as shown by X-ray structural and accompanying solution-state binding analyses, two electron-poor aromatic molecules (*e.g.*, the explosive 1,3,5-trinitrobenzene, TNB) can be “sandwiched” in between each pair of electron-rich TTF units defined by the overall “double clamshell” 1,3-alternate conformation (Fig. 9). Such a binding mode gives rise to a 1 : 2 charge-transfer complex, allowing the

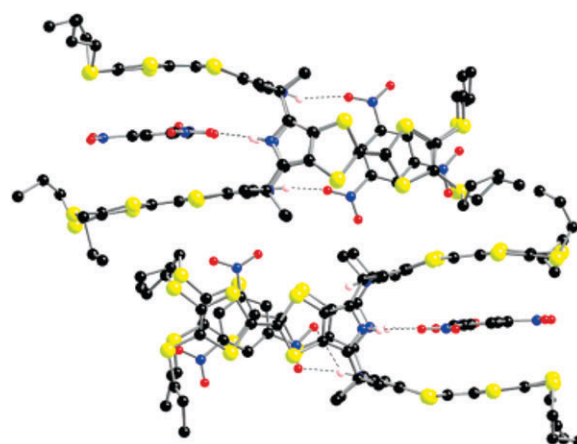
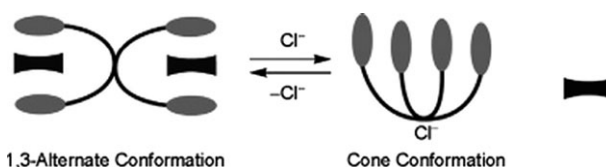
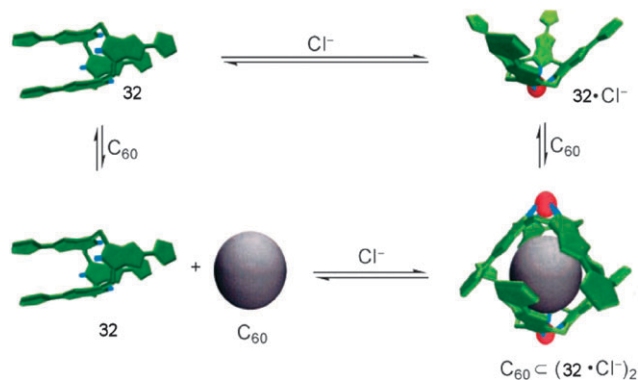


Fig. 9 The “double clamshell” 1 : 2 complex (**32**·(1,3,5-trinitrobenzene)₂). Reproduced from ref. 81. Copyright 2004, American Chemical Society.

recognition process to be monitored spectroscopically or even visualized by the naked eye. The strong affinity of **32** for Cl[−] was used to switch the equilibrium from the 1,3-alternate conformation to the cone conformation *via* the introduction of chloride anion (Scheme 14). This addition and the associated conformational change leads to a remarkable color change from green (reflecting the CT band between electron-deficient guest and TTF) to yellow (disappearance of this CT band). A remarkable step further⁸² was achieved by using this same anion-triggered 1,3-alternate-to-cone conformational switching to produce a 2 : 2 : 1 ensemble containing C₆₀ (Scheme 15). The resulting complex consists of two chloride anion-stabilized “bowls” with an overall electron-rich cavity well suited for the encapsulation of the electron-deficient, fullerene guest. No fullerene binding by **32** is observed in the absence of Cl[−], supporting the notion that only



Scheme 14 Dynamic behavior of receptor **32** in presence of an electron-poor planar guest (distorted rectangle) and chloride anion (reproduced from ref. 81. Copyright 2004, American Chemical Society).



Scheme 15 Mechanistic scheme for the proposed complex formation between **32** and C₆₀ in the presence of chloride ions (ref. 82. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

the chloride-induced cone conformation **32**·Cl[−] can encapsulate C₆₀. As in the case of TNB, the anion-triggered binding of C₆₀ could be readily monitored through color changes. In addition, and as expected given the proposed interaction between the electron-rich TTF binding cavity and the C₆₀ guest, fullerene encapsulation is accompanied by a significant negative shift of the first reduction potential of C₆₀ (−74 mV).

Given the stronger affinity displayed by the 1,3-alternate conformation of **32** for planar electron-deficient guests, as well the preference of the cone complex **32**·Cl[−] for C₆₀, the same groups also described very recently an additional facet of this system.⁸³ Specifically, they studied the competitive binding of a bifunctional guest **33** and noted a switchable binding behavior.

Guest **33** was designed to contain an electron-poor fluorene-based skeleton directly tethered to a fullerene moiety. (Scheme 16).

Here again, a differential binding process was used to generate a dynamic system that could be easily monitored by following the change in color of organic solutions containing the species in question. The initial report detailing this system has now been complemented by an exhaustive study⁸⁴ that was just recently published. Using ITC and NMR spectroscopies, these authors demonstrated the existence of a complex between **32**·Cl[−] and the tetrabutylammonium cation that is formed with a significant binding constant ($K_1 = 7.4 \times 10^3 \text{ M}^{-1}$ in CDCl₃). Thus, it seems reasonable to foresee that a real competition

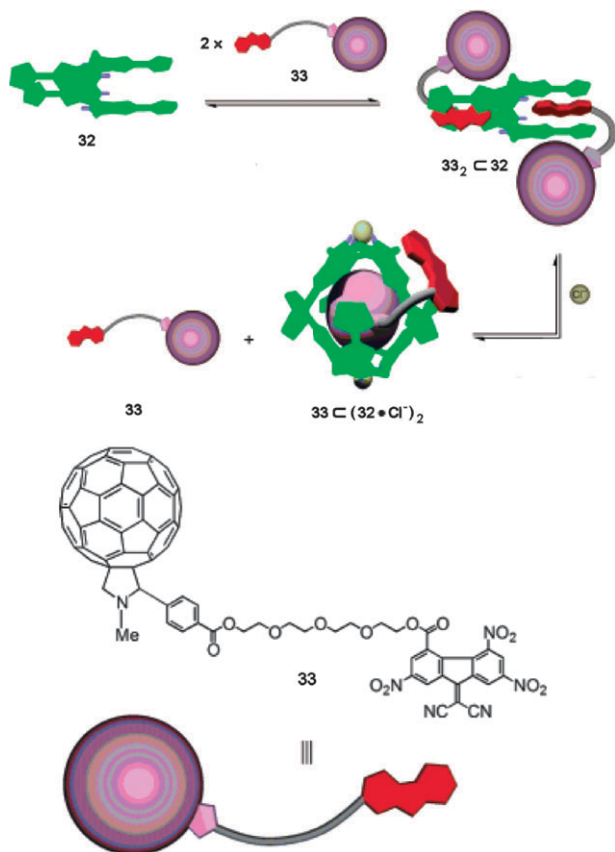
exists between this equilibrium and the one involving a **32**·Cl[−] unit and a C₆₀ fullerene substrate ($K_2 = 2.3 \times 10^3 \text{ M}^{-1}$), and to anticipate a very high affinity between **32**·Cl[−] and C₆₀ if the presence of TBA cation inside the cavity could be avoided. By adding successively a solution of tetrabutylammonium chloride and then one containing sodium tetraphenylborate (to precipitate sodium chloride), this team was able to demonstrate further the versatility of the TTF–calixpyrrole skeleton. In these experiments, NMR spectroscopic analyses confirmed that various signals revert back to their initial positions; this is as would be expected after sodium chloride precipitation since the loss of this anion should trigger a return to the original 1,3-alternate shape. These additions and associated precipitations could be repeated, demonstrating the very good reversibility of such a sequence. The recognition properties of **32** and **32**·Cl[−] could also be followed by monitoring the fluorescence emission quenching of various electron deficient fluorophores. For instance, complexation between a planar electrodeficient guest and **32** leads to a decrease in the fluorescence of the added fluorophore (which acts as an acceptor), while the C₆₀ emission is reduced when encapsulated within two **32**·Cl[−] cavities.

The synthesis of a calix[2]pyrrole[2]thiophene derivative incorporating two tetrathiafulvalene units has also been recently described,⁸⁵ along with its X-ray crystal structure. In analogy to what was observed in the case of **32**, the 1,3-alternate conformation is observed in the absence of an anion, with the resulting cavity proving capable of accommodating the electron-poor guest TCNQ.

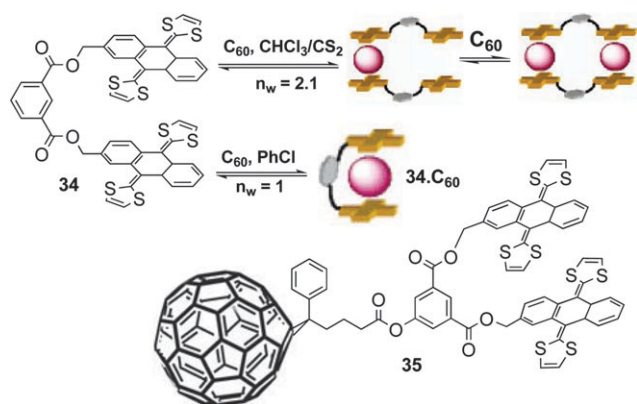
As far as C₆₀ binding is concerned, electron-rich receptors, such as those based on TTF derivatives, appear attractive as underscored by the success enjoyed with receptor **32**. An interesting alternative illustration of this concept is embodied in receptors involving extended TTF skeletons. In particular, the *ex*TTF skeleton which has been extensively used for the preparation of donor–acceptor dyads, has been applied very recently for fullerene recognition. For instance, the group of N. Martín has reported the tweezer-like system **34**,⁸⁶ which contains two large and concave aromatic surfaces (*ex*TTF). This system was designed to provide favorable van der Waals and π – π interactions with fullerenes (Scheme 17), and indeed, it exhibits a good binding ability for C₆₀ ($K \approx 3 \times 10^3 \text{ M}^{-1}$ in chlorobenzene). Depending on the solvent, the resulting 1 : 1 complex appears either as one fullerene sandwiched between two *ex*TTF units (chlorobenzene) or to exist as a supramolecular tetramer (CHCl₃–CS₂).

In a similar manner—*i.e.*, exploiting complementarity in the electronics and shape characteristics of a convex receptor capable of accepting C₆₀ and the concave electron donating features of a *ex*TTF tweezer—the same group has described the synthesis of a redox-amphoteric supramolecular polymer.⁸⁷ In this case, the monomer **35** was found to self-assemble nicely through non-covalent interactions to produce a linear head-to-tail macromolecule; this arrangement prevents C₆₀ aggregation and provides a promising new entry into D–A devices.

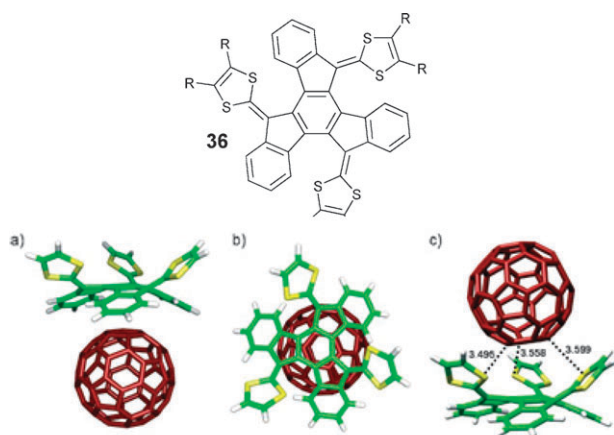
An alternative concave *ex*TTF-inspired structure was also reported by N. Martín *et al.* in the form of compound **36** (Scheme 18).⁸⁸ This extended unit is built around the truxene platform, and exhibits a moderate donating character. The association constant corresponding to the interaction between **36** and C₆₀ or C₇₀ was investigated using ¹H NMR



Scheme 16 Mechanistic scheme of the proposed complexation events involving receptor **32** and guests **33**, as observed in the absence and presence of chloride anions (reproduced from ref. 83. Copyright 2008, American Chemical Society).



Scheme 17 *ex*TTF-based tweezers **34** and **35**; compound **34** shows solvent-dependent fullerene complexation behavior (reproduced from ref. 86. Copyright 2006, American Chemical Society).



Scheme 18 Truxene-TTF derivative **36** and the calculated structure of the corresponding C_{60} complex (ref. 88. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

spectroscopic titrations, and revealed binding constants of $1.2 \times 10^3 \text{ M}^{-1}$ and $8.0 \times 10^3 \text{ M}^{-1}$, respectively, in $\text{CDCl}_3\text{-CS}_2$. During the writing process of this feature, this promising concave-convex complementarity approach has been reviewed by the group of Madrid.⁸⁹

3. Redox-controlled molecular motions

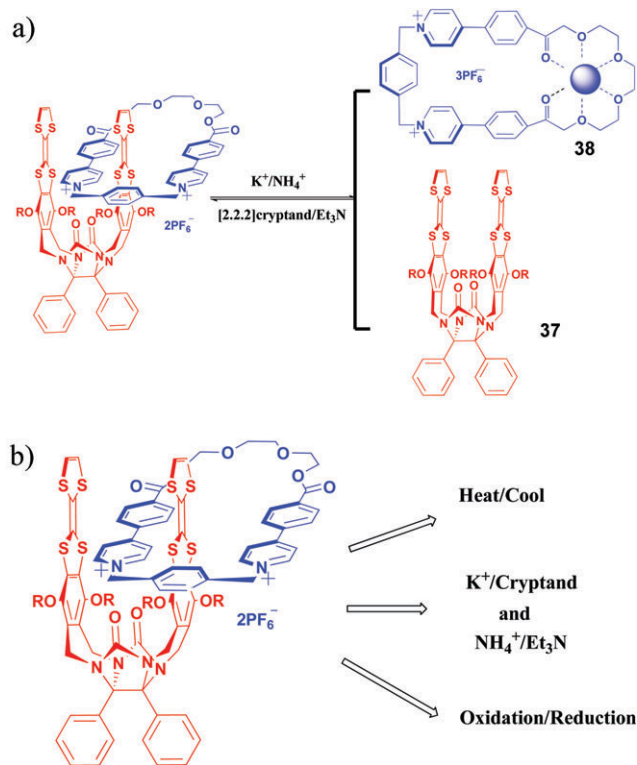
3.1 TTF-based molecular clips and tweezers

Receptors in which the shape of the binding cavity can be controlled by an external stimulus are of evident interest, for example in connection with the capture/transport/release of a given guest. They relate directly to the ongoing challenge of controlling motions at the molecular level, a topic that is of great current interest, especially as regard the creation of molecular devices and machines. From this point of view, the TTF moiety has appeared as an efficient actuator unit for the design of various molecular architectures involving redox-controlled movements.

An elegant example has been recently designed by Chiu *et al.* with TTF-based molecular clip **37**^{90,91} built on the glycoluril-based platform, and presenting two TTF units which are positioned face to face at a suitable interplanar distance to allow

inclusion of guest species. This molecular clip was found to form complexes with 4,4'-bipyridinium, due to charge-transfer interactions and C-H...O bonding. Macrocycles with 4,4'-bipyridinium motifs, such as **38**, can form the macrocycle/molecular-clip complex as shown in Scheme 19. The threaded and unthreaded states can be distinguished by their absorption spectra that correspond to different colors that are observable to the naked eye. Interestingly, the movement between the threaded and unthreaded states can be manipulated by four different sets of external stimuli— $\text{K}^+/[2.2.2]\text{cryptand}$, $\text{NH}_4^+/\text{Et}_3\text{N}$ and (*p*-BrPh)₃NSbCl₆/Zn pairs, and heating/cooling—as illustrated in Scheme 19; either recognition of K^+ or NH_4^+ , oxidation of the TTF moieties, or heating the solution can lead to dissociation of the macrocycle/molecular-clip complex. Moreover, the absorption spectral variation in response to these stimuli mimics the function of a three-input NOR logic gate.

Another example, namely the series of conjugated TTF derivatives **39–41**, has been developed by Lorcy and co-workers. The basic system involves a vinylogous TTF (TTFV) framework that is non-planar in its neutral state because of the steric hindrance generated by the R (=Ar) substituents. Conversely, the oxidized species become planar with the R groups perpendicular to the conjugated vinylogous TTF system. This structural change (stretching) is fast, reversible, and is observed at easily attainable oxidation potentials (Scheme 20). Compound **41**,⁹² shows that the two coordinating picoline units strongly bind Zn^{2+} in a cooperative manner; this prevents the molecular motion (stretching) from taking place upon oxidation. Therefore,

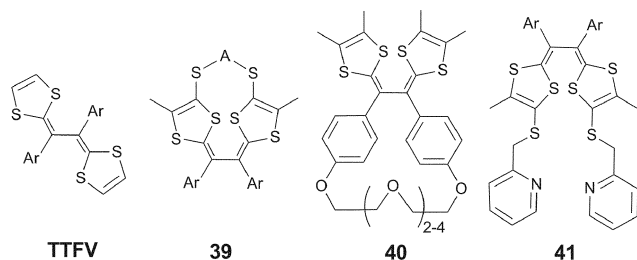


Scheme 19 (a) Example of a complexation-dissociation process between clip **37** and ring **38**; (b) four different sets of external stimuli have been put for tuning the process *via* relative stabilization of the threaded and unthreaded states.



Scheme 20 Vinyllogous TTFs undergoing redox-controlled molecular movements: (a) the parent system TTFV; (b) a stretching movement in **40**. Reproduced from ref. 55. Copyright 2007, American Chemical Society.

by adjusting the location, the length and the nature of the linker on the periphery of the TTFV subunit, systems were produced whose stretching or clipping movements could be triggered by electron transfer (**39**),⁹³ and which were seen to respond electrochemically to the presence of a cation (lead(II) in the case of **40**).⁵⁵

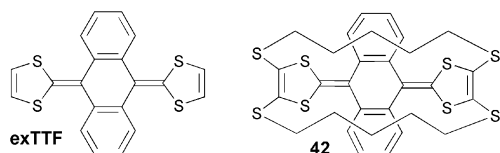


Another illustration of the richness of the TTFV scaffold in setting up redox-control of conformational changes was proposed by Bryce and co-workers. It involves a related system bearing a 9-thioxanthene modulus as one of the Ar substituents.⁹⁴ Such systems can be considered as conjugated TTF derivatives whose conformation evolves upon oxidation.

From this point of view, they bear analogy to *ex*TTF derivatives that incorporate a central *p*-quinodimethane spacer. The latter skeleton is well known to undergo a remarkable conformational change that is accompanied by a single two-electron oxidation step. This stands in contrast to the parent TTF, which is known to be oxidized according to two successive one-electron processes. This knowledge has permitted significant control over the redox and conformational properties of *ex*TTF derivatives as has been proposed recently for the bridged analogue **42** (Scheme 21).⁹⁵ Oxidation of this compound (and other related cyclophanes) occurs in two reversible, one-electron oxidation waves. These systems thus mimic what is seen with TTF; presumably, this reflects the fact that the corresponding oxidized species cannot escape from the folded geometry enforced by the framework (and hence exist as well at the neutral state).

3.2 TTF-cavitand, -carcerand and -calixarene derivatives

Other nice examples of redox control over conformation are provided by various derivatives of resorcin[4]arene-based

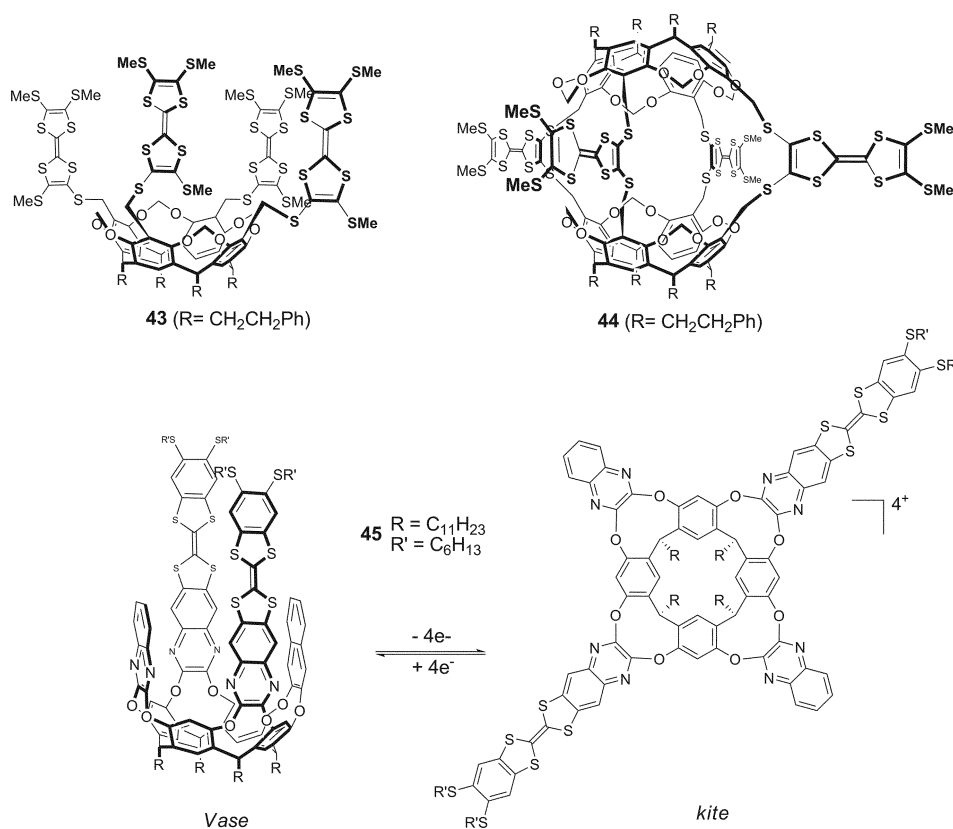


Scheme 21 The chemical structure of **42** (an analogue of *ex*TTF) which undergoes redox-controlled molecular movements.

cavitands. The first results in this area were obtained by Kaifer and co-workers as illustrated by the synthesis of TTF-appended cavitand **43** and the related hemicarcerand **44** (Scheme 22).⁹⁶ These systems present the usual two successive clearly defined redox waves of TTF derivatives. This behavior corresponds to TTF units that behave independently and which are not interacting electronically.

Alternatively, several resorcin[4]arene-based cavitands are known to be switched reversibly from a closed *vase* form to a *kite* conformer, depending on the solvent or temperature. Therefore, decorating this platform with TTF redox units was expected to allow the closing/opening process of the bowl-shaped cavity to be triggered *via* TTF oxidation. Such a redox process would allow a change from a *vase* to a *kite* form. In this context, the TTF-cavitand **45**⁹⁷ was synthesized by Diederich, Echegoyen and co-workers. This system is characterized by a cyclic voltammogram with two redox waves corresponding to TTF. A critical point, when considering conformational aspects in multi-TTFs systems, lies on the shape of the first redox wave ($E_{1/2}^1$): If broader than the second one ($E_{1/2}^2$), it means that the two TTF subunits are interacting (*i.e.* are in close intramolecular proximity) during the first redox process. This observation results from the stabilization of the first formed radical cation by the π -electrons of the neighboring TTF moiety, leading to a reduction of the first one-electron oxidation step. Consequently, the second one-electron oxidation becomes more difficult; this is a result of the proximity of the initially generated radical cation, and this explains the broadening of the corresponding electrochemical response. On the contrary, the second redox wave of **45** is narrower and corresponds to a two-electron oxidation to the bis(dication); here, the TTF units behave independently, *i.e.*, are located at a larger distance because of the electrostatic repulsive interactions. This behavior corresponds, therefore, to an electrochemical manifestation of the conformational change between the *vase* and *kite* forms depending on the redox state of TTF units.

The calix[4]arene unit constitutes, beside resorcin[4]arene, a strongly developed polyaromatic three-dimensional scaffold. Interest in this system reflects in part its easy and selective functionalization. It also permits a defined spatial organization of the pendant substituents. Using this scaffold, some of us have prepared derivative **46**,⁹⁸ which contains two TTF moieties on two 1,3-distal aromatic rings corresponding to the lower rim of the calixarene scaffold. A tetracarbonyl binding cavity, which is known to exhibit a strong affinity for alkaline cations, is generated through two ester and two amide groups. This cavity is appropriate for Na^+ complexation, as shown by X-ray diffraction studies (Fig. 10). These latter reveal that the metal cation is octa-coordinated by oxygen atoms. A CV titration, corresponding to the progressive addition of Na^+ , revealed peculiar behavior. The expected positive potential shift of the first redox potential of TTF ($E_{1/2}^1$) was observed, but was found to undergo a transformation from a broad to a thinner redox wave. Such a change in the shape of the voltammogram before and after the addition of the sodium cation is characteristic of a conformational change taking place concurrently with complexation. This change is thought to reflect an evolution from a conformationally flexible



Scheme 22 TTF-cavitands and -carcerands and redox-triggered conformational changes.

situation wherein the TTF units can interact at $E^{1/2}$ upon formation of dimeric oxidized species $[(\text{TTF})_2]^{+\bullet}$ and $(\text{TTF}^{\bullet+})_2$, to a conformation wherein rigidity is gained upon sodium complexation. This latter situation compels the TTF units to interact resulting in independent redox behavior. This system thus provides an example of redox-triggered molecular movement involving an additional input through metal cation binding.

Of course, such redox-controlled motions can be expected from alternative multi-TTFs systems, derived from other

scaffolds. This has indeed proved to be the case with various recent bis-TTF^{99–101} and tris-TTF¹⁰² derivatives.

4. Interplay between redox and other switchable properties in TTF derivatives

4.1 Tuning the intramolecular charge-transfer in TTF-quinone (and tetracyano-*p*-quinodimethane analogues) D-A compounds

A number of electron donor (D)-acceptor (A) dyads including the tetrathiafulvalene (TTF) unit or derivatives as the electron donating part have been reported. For instance TTF-C₆₀ dyads have been extensively studied in the recent years in particular in the quest for new efficient molecular solar energy conversion materials. Some recent reviews^{14,103} have been dedicated to this family, which therefore will not be detailed in this article. Other accepting units have been covalently associated to TTF, such as TCNQ (tetracyano-*p*-quinodimethane)^{104,105} or quinone moieties and are characterized by an intramolecular charge-transfer.¹⁰⁶ It is also the case with ruthenium(III) complexes of tetrathiafulvalene-fused dipyrrophenazine (TTF-dppz).^{107,108} Discussion about CT properties in D-A TTF-based systems is far beyond the content of this feature; still, addressing the specific aspect of the reversible control of the charge-transfer process in D-A systems, thanks to an external stimulus, open interesting perspectives for molecular electronics. In particular, it remains a challenge to tune the HOMO-LUMO gap. The dyad **47** associating a TTF skeleton to a tetracyano-anthraquinodimethane unit has recently been designed with this aim.¹⁰⁹ Originality of this structure relies on the occurrence

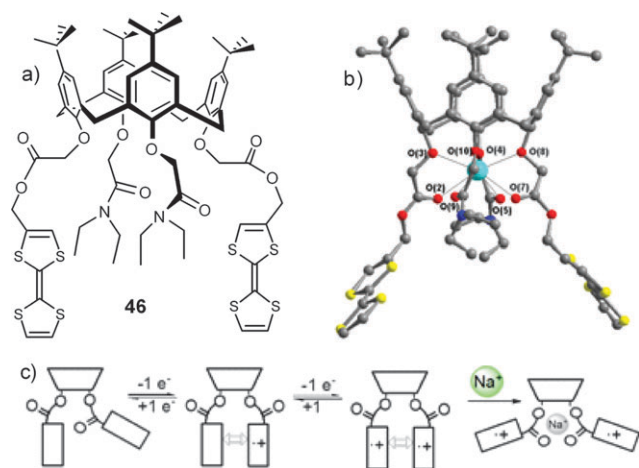
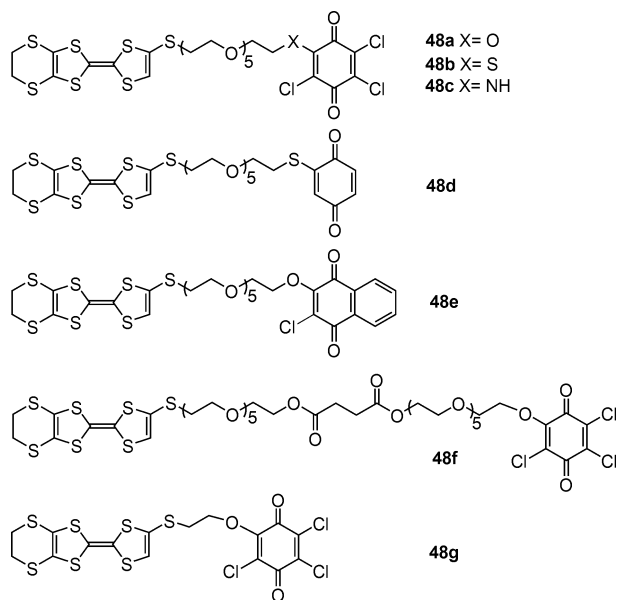
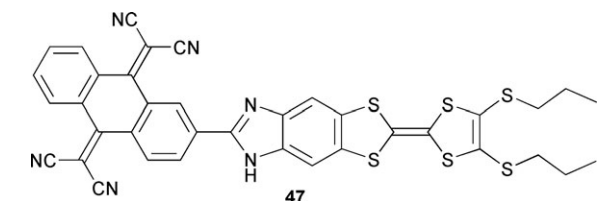


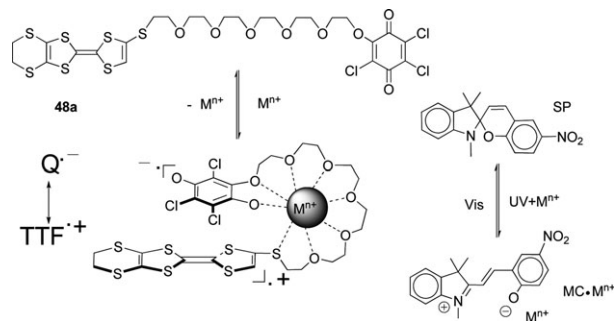
Fig. 10 (a) A calix[4]arene-TTF derivative involving redox- or Na⁺ binding-triggered conformational changes; (b) X-ray structure; (c) a cartoon featuring molecular movements.

of an imidazole ring in-between both redox counter parts, which provides a unique opportunity to tune the HOMO-LUMO gap as a function of pH.



Some of us recently reported TTF-quinone dyads **48a-f** with coordinating glycol chains as linkers.^{110,111} Conformation of such flexible dyads may be modulated through coordination with suitable metal ions, resulting in a shortening of the through-space distance between the TTF and quinone units, and giving rise to a control over the corresponding charge-transfer interactions. Both absorption and ESR spectral studies confirm that electron transfer takes place between TTF and quinone units of these dyads, in the presence of $\text{Pb}^{2+}/\text{Sc}^{3+}/\text{Zn}^{2+}$ ions. A control experiment with dyad **48g** in which the TTF and quinone units are connected by a simple $\text{S-CH}_2\text{-CH}_2\text{-O}$ fragment indicates that the synergic coordinations of the glycol chain and the oxygen atoms of the radical anion of quinone play an important role in promoting the electron transfer within dyads **48a-f** (Scheme 23).

Based on the synergic coordination model (Scheme 23), it is anticipated that it is possible to modulate the thermal electron transfer processes within these dyads through competitive binding of metal ions by other ligands. The open form (merocyanine, MC) of spiropyran can coordinate with metal ions ($\text{MC}\cdot\text{M}^{n+}$), while the spiropyran (SP) does not show this property; moreover, metal ion can be released from $\text{MC}\cdot\text{M}^{n+}$ after visible light irradiation and concomitantly MC is transformed into SP.^{110,111} By taking advantage of this feature of spiropyran, reversible modulation of intramolecular electron transfer processes within dyads **48a** and **48f** facilitated by



Scheme 23 Proposed mechanism for the metal ion-promoted intramolecular electron transfer and the photomodulation in the presence of spiropyran.

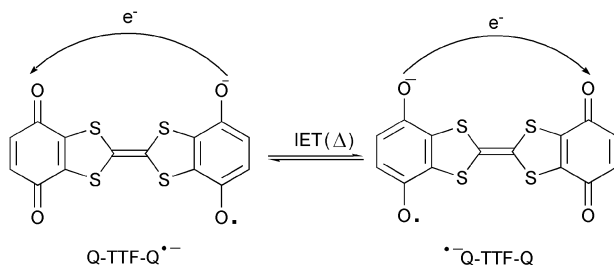


Fig. 11 Intramolecular electron transfer in **49** through a TTF bridge.

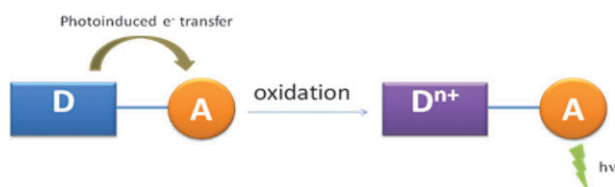
Pb^{2+} has been successfully demonstrated by alternating UV and visible light irradiations in the presence of spiropyran.

Another fascinating TTF-quinone assembly corresponds to the conjugated quinone-TTF-quinone triad **49** (Q-TTF-Q, Fig. 11), synthesized by Hudhomme *et al.*^{112,113} The intramolecular electron transfer process in the Q-TTF-Q $^{\cdot-}$ mixed-valence system was studied by temperature-dependent ESR spectroscopy. The results demonstrate that TTF, beside an evident ability for generating switching processes (*vide supra*), can also constitute a suitable molecular bridge for the promotion of intramolecular electron transfer between two redox centers.

4.2 Photoinduced electron-transfer within TTF-based D-A compounds: redox fluorescence switches

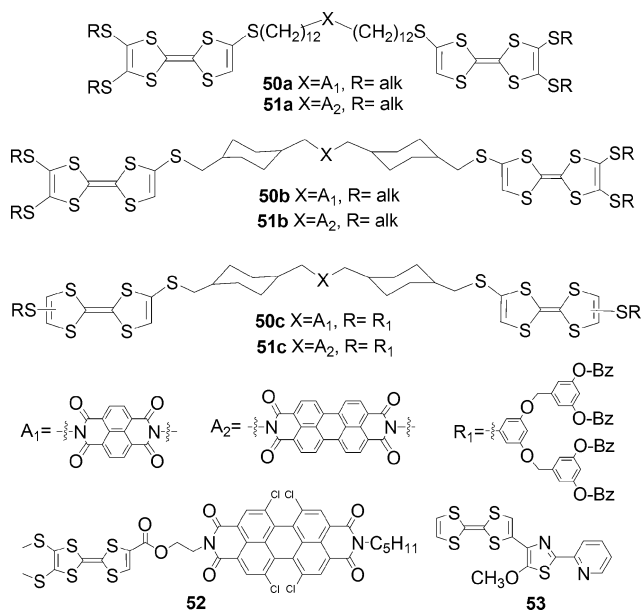
TTF-based D-A systems have also been extensively used in the recent years in order to play around photoinduced electron-transfer processes. Typically, when an electron acceptor moiety which emits fluorescence intrinsically is linked to TTF (D), the fluorescence due to the A moiety may be quenched because of a photoinduced electron transfer process (Scheme 24). Alternatively, these molecular systems are potentially of interest for photovoltaic studies. For instance, efficient photoinduced electron transfer and charge separation were reported for (D-A) TTF-fullerene dyad.^{14,103} An important added value provided by TTF relies on the redox behavior of this unit which can be reversibly oxidized according to two redox successive steps. Therefore, such TTF-A assemblies allow an access to redox fluorescence switches, for which the fluorescent state of the fluorophore A, can be reversibly switched on, upon oxidation of the TTF unit.

Compounds **50a-c**¹¹⁴ and **51a-c**¹¹⁵ contain naphthalene diimide and perylene diimide moieties, respectively. Due to



Scheme 24 Principle of a switchable, redox-controlled fluorescence in D–A systems (D = TTF).

the photoinduced electron transfer process, these compounds show rather weak fluorescence. Time-resolved fluorescence and absorption studies were performed and show that the lifetime of the long-lived charge-separated states generated in PhCN reaches 1100 ns. The oxidation of TTF into the corresponding $\text{TTF}^{\bullet+}$ should prohibit the photoinduced electron transfer between TTF and naphthalene diimide/perylene diimide moieties, and as a result the fluorescence of **50a–c** and **51a–c** should increase. However, in contrast to expectation, the fluorescence intensities decrease in both cases after oxidation. This can be ascribed to the fact that the $\text{TTF}^{\bullet+}$ units show absorptions in the range of 460–850 nm and thus a photoinduced energy transfer may occur from naphthalene diimide/perylene diimide to $\text{TTF}^{\bullet+}$, leading to fluorescence quenching.



The TTF–tetrachloride perylene diimide dyad **52** has been recently described for a similar purpose.^{116,117} The TTF moiety of **52** is oxidized into the corresponding $\text{TTF}^{\bullet+}$ and TTF^{2+} by applying potentials at 0.85 and 1.25 V vs. Ag/AgCl, respectively. Though the fluorescence intensity of tetrachloride perylene diimide (545 nm) decreases slightly after oxidation of TTF into $\text{TTF}^{\bullet+}$, it increases as expected, gradually, after further oxidation of $\text{TTF}^{\bullet+}$ into TTF^{2+} .¹¹⁶ Therefore, the fluorescence state of dyad **52** is directly dependent on the oxidation state of the TTF moiety (Fig. 12). Consequently, this dyad can be considered as a new reversible fluorescence-redox dependent molecular system.

A similar tuning of fluorescence was also described for TTF–MPT (5-methoxy-2-pyridylthiazole) dyad **53**.¹¹⁸ Both

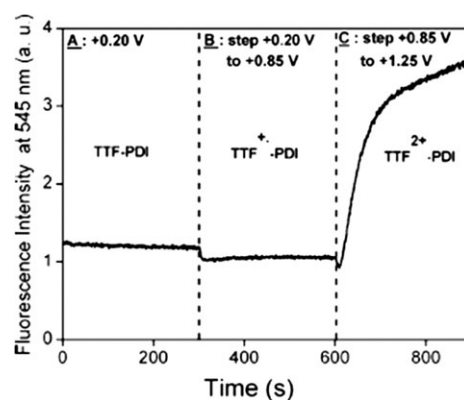
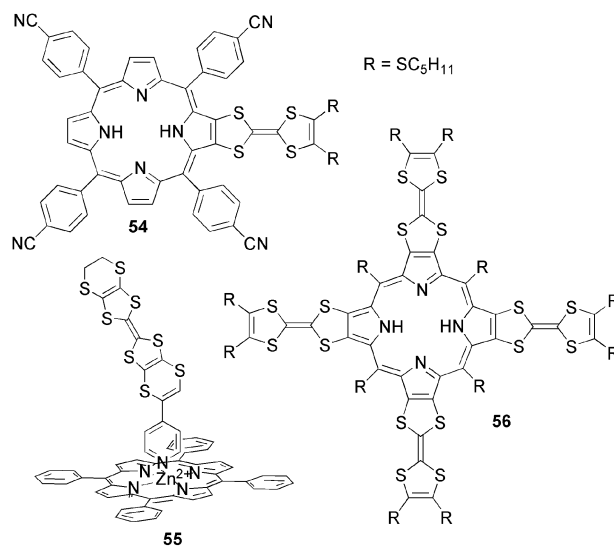


Fig. 12 Evolution of the fluorescence intensity at 545 nm ($c = 10^{-3}$ M in CH_2Cl_2) of dyad **52** at different oxidation states vs. time ($\lambda_{\text{exc}} = 490$ nm). Reproduced from ref. 116. Copyright 2005, American Chemical Society.

TTF –MPT and $\text{TTF}^{\bullet+}$ –MPT show weak fluorescence, but significant fluorescence enhancement is observed for TTF^{2+} –MPT. Moreover, the variation of the fluorescence of TTF–MPT in response to metal ions was also investigated. The corresponding fluorescence variation behaviors mimic the functions of several logic gates.

The TTF–porphyrin dyad **54** (Scheme 25) was described by the group of Odense.¹¹⁹ The fluorescence of **54** is significantly quenched by the photoinduced electron transfer process. Notably, the fluorescence intensity increases largely after addition of Fe^{3+} which oxidizes TTF into $\text{TTF}^{\bullet+}$. Further reduction of $\text{TTF}^{\bullet+}$ is not reported. Nevertheless, it is anticipated that the fluorescence of dyad **54** can be reversibly modulated by redox processes. In fact, the fluorescence of complex **55**, formed between Zn-tetraphenylporphyrin and a pyridine-substituted TTF (TTF–Py), can be reversibly tuned by sequential oxidation and reduction of the TTF moiety in TTF–Py.¹²⁰ It should be noted in this context that the synthetically challenging system associating a porphyrin ring fused to four TTFs (compound **56**) was also reported.¹²¹



Scheme 25 TTF–porphyrin assemblies.

TTF–phthalocyanines (Pc) assemblies **57a–g** (Scheme 26) were described by Bryce and co-workers. They contain TTF and silicon-phthalocyanine units.¹²² Photoinduced electron transfer occurs in these systems and result in rather weak fluorescence. Oxidation of TTF unit into the corresponding TTF^{•+} does not lead to fluorescence enhancement. This is attributed to the photoinduced electron transfer from the excited silicon-phthalocyanine to TTF^{•+}, referred as to *reversed electron transfer* by the authors. Conversely, chemical oxidation of the TTF units by FeCl₃ in ZnPc-(TTF)₄ (**58**) prepared by Liu, Decurtins and co-workers can induce fluorescence enhancement.^{123,124} Quite a substantial excess of FeCl₃ is needed to obtain maximum fluorescence intensity. This result means that, if not all four TTF units in **58** are transformed into TTF^{•+}, the fluorescence of Zn-Pc in **58** is still fully quenched.

Naturally, considering the intrinsic fluorescence properties of fused polyaromatic systems, substantial efforts can be found in recent literature for grafting of such units to redox-active TTF. Anthracene emits in the range of 380–450 nm; thus, the fluorescence spectrum of anthracene has rather small overlap with the absorption spectrum of TTF^{•+}.¹²⁵ It is anticipated that the fluorescence of the TTF–anthracene dyad can be reversibly modulated by redox reactions of TTF moiety. With this consideration in mind, some of us designed and synthesized the TTF–anthracene triad **59**¹²⁶ and its dyad analogue **60**.¹²⁵ Both **59** and **60** exhibit rather weak fluorescence. Following either chemical or electrochemical oxidation, large fluorescence enhancement is observed. As an example, Fig. 13A shows the fluorescence spectra of **59** after the solution was oxidized at 0.7 V vs. Ag/AgCl for different periods. Moreover, the fluorescence intensity decreases gradually if the resulting solution was then subjected to reduction at 0.2 V (Fig. 13B). The fluorescence intensity of triad **59** can be reversibly modulated for several cycles. A similar behavior was found in polymers bearing pendant TTF and anthracene moieties,¹²⁷ and the fluorescence of the triad with TTF and

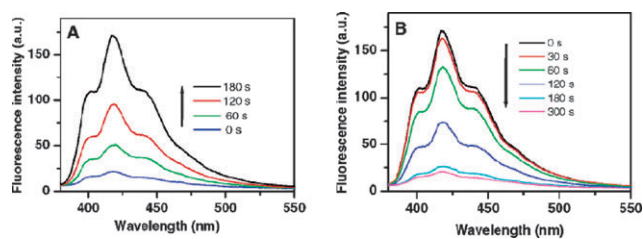
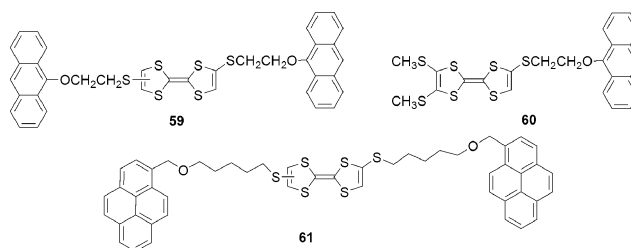


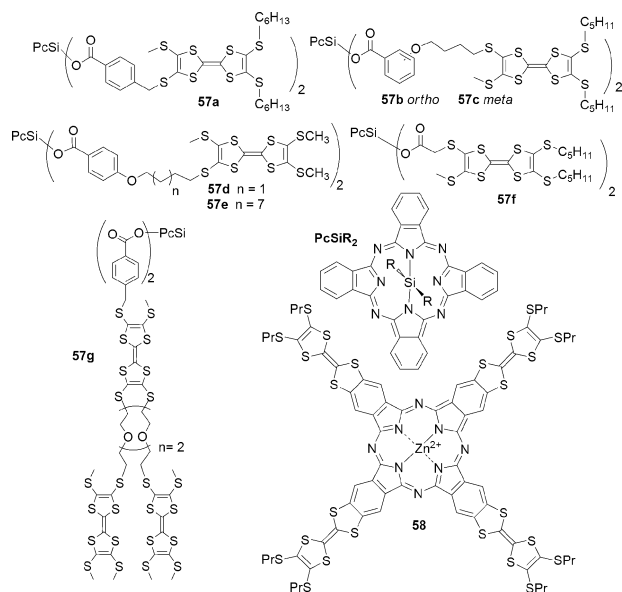
Fig. 13 Variation of fluorescence spectra of **59** upon oxidation (A) and upon subsequent reduction (B). Reproduced from ref. 126. Copyright 2004, American Chemical Society.

pyrene moieties **61**¹²⁸ can also be tuned depending on the redox state of the TTF moiety.

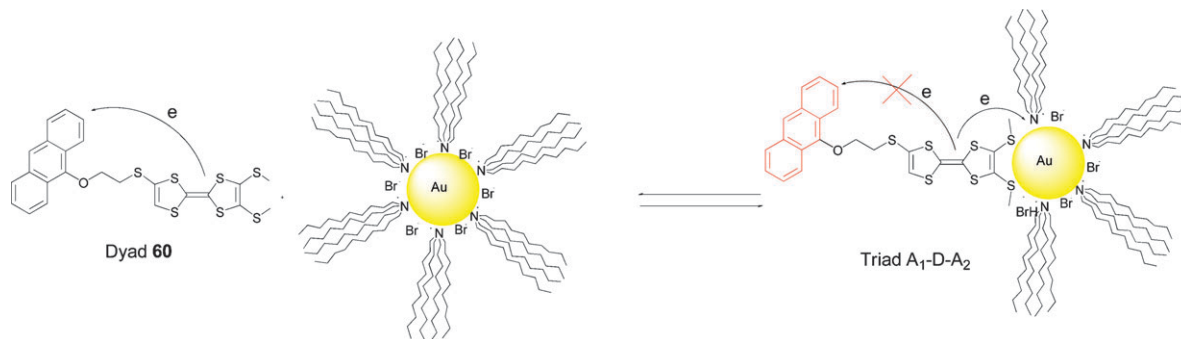


In addition to the use of the TTF–redox command, tuning of the photoinduced electron transfer within dyad **60** has been shown possible by the preparation of the corresponding derived-gold nanoparticles.¹²⁵ Cyclic voltammetric studies indicate self-assembly of dyad **60** on the surfaces of gold nanoparticles, likely through interactions of both methylthio groups with surface gold atoms as illustrated in Scheme 27. Since gold nanoparticles are strong electron acceptors, assembly of dyad **60** on the surfaces of gold nanoparticles leads to the formation of a triad A₁–D–A₂ and therefore modulates the photoinduced electron transfer between the excited anthracene and TTF units, which is confirmed by spectroscopic studies. Namely, the fluorescence intensity of the solution of dyad **60** increases gradually after introducing the gold nanoparticles to the solution. Moreover, it is also shown that the photo-dimerization of anthracene units is accelerated upon the assembly of **60** on the surfaces of gold nanoparticles.

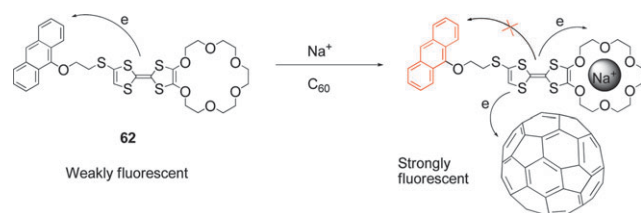
Efforts were also made to tune the photoinduced electron transfer process within the TTF–anthracene dyad by addition of C₆₀ to the solution. Indeed, C₆₀ is an electron acceptor and photoinduced electron transfer can occur efficiently between C₆₀ and TTF derivatives. The fluorescence increase observed for the TTF–anthracene dyad is rather small after introducing C₆₀ to the solution. Interestingly, it has been reported that the electron donating ability of TTF derivatives fused with a crown ether unit can be modulated by addition of suitable metal ions (see section 2.1). Actually, fluorescence modulation for the crown-TTF–anthracene dyad **62** is small by addition of Na⁺, in contrast to the expectation. However, in the presence of both Na⁺ and C₆₀ the fluorescence of dyad **62** can be largely enhanced. If C₆₀ and Na⁺ are regarded as two input signals, and the fluorescence of dyad **62** as the output signal, such fluorescence modulation mimics the performance of an “AND” logic gate (Scheme 28).¹²⁹



Scheme 26 TTF–phthalocyanines.



Scheme 27 Illustration of the assembly of the TTF–anthracene dyad **60** on the surfaces of gold nanoparticles and modulation of the photoinduced electron transfer process.



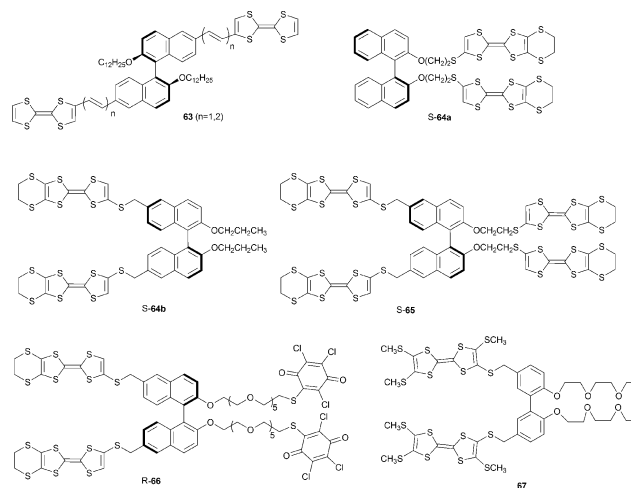
Scheme 28 Modulating the fluorescence of dyad **62** by addition of sodium ion and fullerene.

4.3 Chiroptical switches based on molecules with TTF moieties

Reversible interconversion can be realized among TTF, TTF^{•+} and TTF²⁺. Taking advantage of this feature, new molecular chiral switches have been recently constructed (Scheme 29). Pioneering works on this topic were led by Martin *et al.*, with systems presenting two TTF units connected through a rigid conjugated linker to the 3,3′ positions of the binaphthalene skeleton (**63**).^{130,131} Modulation of the chiroptical properties of these systems have not been reported. Chiral binaphthalene shows strong CD signal and the intensity is strongly dependent on the dihedral angle of the two naphthalene rings. With the respective features of binaphthalene and TTF in mind, the group of Beijing designed and investigated binaphthalene–TTF assemblies (*S*)-**64a**, (*S*)-**64b** and (*S*)-**65**.¹³² Within these compounds, it is expected that the dihedral angle on the chiral binaphthalene framework can be tuned according to the redox state of TTF units. The CD signal intensity of (*S*)-**64a** at 220 and 240 nm, successively increases and decreases after oxidation at the corresponding cation-radical and dication stages respectively. For (*S*)-**64b** and (*S*)-**65**, CD signal intensities at 235 and 250 nm decreases after sequential oxidation of TTF into TTF^{•+}/TTF²⁺, and a reversible variation of CD spectrum is also observed.

Chiral binaphthalene (*R*)-**66** bears two TTF and two trichloroquinone units.¹³³ It is expected from such system, that the variation of the D–A interaction in the presence of metal ions may induce a change of the dihedral angle between the two naphthalene rings. Both absorption and ESR spectral studies show that electron transfer occurs between TTF and trichloroquinone units in the presence of metal ions. Nevertheless, in contrast to expectation, the CD spectral change of (*R*)-**66** is rather small after addition of metal ions.

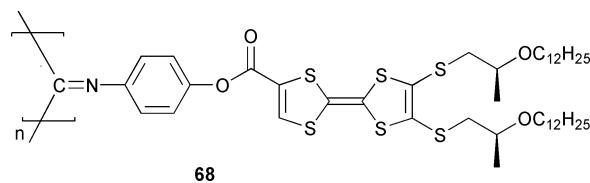
C₂-symmetric TTF-derivatives **67** were also prepared from the biphenyl platform by Delogu *et al.*¹³⁴ Based on the



Scheme 29 C₂-Symmetric TTF-based assemblies.

electrochemical investigations, the interaction between both TTF moieties can be modulated upon binding of Pb²⁺, due to rotation around the Ar–Ar bond.

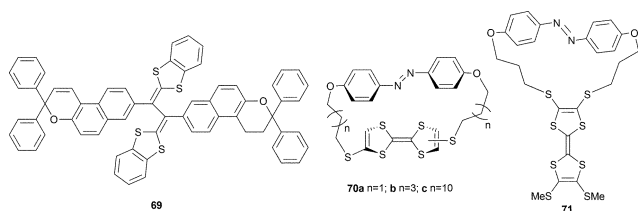
A chiral TTF-substituted poly(isocyanide) **68** was prepared by Amabilino *et al.*¹³⁵ Of interest is the fact that the CD spectrum of **68** can be tuned by changing the oxidation states of the TTF units in the side-chains. This polymer shows reversible interconversion between three univalent and two very broad mixed-valence redox states that have different chiroptical properties.



4.4 TTF-based functional molecules with photoresponsive moieties

TTF derivatives with photoresponsive moieties have been described in recent years in order to study the interplay between photochromic and electrochemical properties. Brisset *et al.* described compound **69** which entails two naphthopyran units and an extended TTF vinyllog unit. However,

photoisomerization of **69** under UV light irradiation cannot take place efficiently.¹³⁶ On the other hand, heterocyclic compounds **70a–c** containing TTF and azobenzene moieties were synthesized, aimed at modulating the electron donating ability of TTF unit by light irradiation.¹³⁷ It is anticipated that the transformation of the *trans*-azobenzene to the corresponding *cis*-azobenzene unit would alter the steric strain within the TTF unit, and modifying therefore its electron donating. For compounds **70a** and **70b**, with short spacers, the first oxidation potential of the TTF unit can be reversibly tuned by alternating UV and visible light irradiations. Conversely, the first oxidation potential of the TTF unit remains unchanged upon UV and visible light irradiation for **70c**, bearing a longer spacer, because of the lack of steric strain whatever the azo-benzene configuration. Variation of the oxidation potential is also found to be negligible for compound **71** in which the azobenzene moiety is linked to vicinal positions on the TTF moiety.

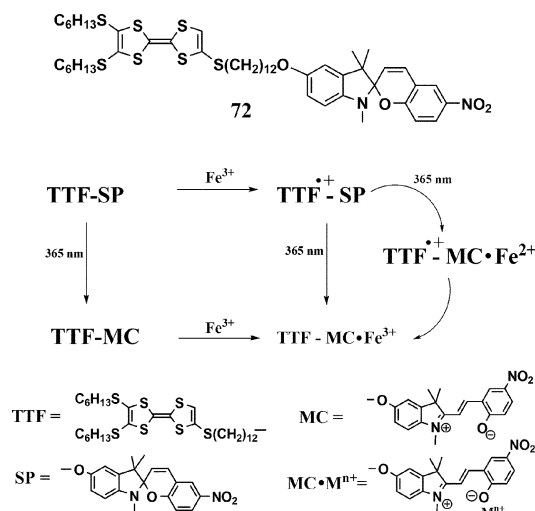


Above, we have discussed the tuning of the photoinduced electron transfer processes within dyads and triads according to the redox state of TTF, this being either chemically or electrochemically controlled. We have also demonstrated that the oxidation of TTF unit by Fe^{3+} can be photocontrolled in the presence of a spiropyran (SP) unit, which can be transformed into the merocyanine form (MC) that can further coordinate with metal ions. Oxidation of TTF–SP (dyad **72**) by Fe^{3+} led to $\text{TTF}^{\bullet+}$ –SP and Fe^{2+} . Interestingly, absorption spectral studies indicate that the $\text{TTF}^{\bullet+}$ was transformed into the neutral TTF unit after UV light irradiation. This was attributed to the electron-transfer reaction from $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{TTF}^{\bullet+}$ as schematically shown in Scheme 30.¹³⁸

4.5 Miscellaneous TTF-based switchable functional molecules: some illustrative examples

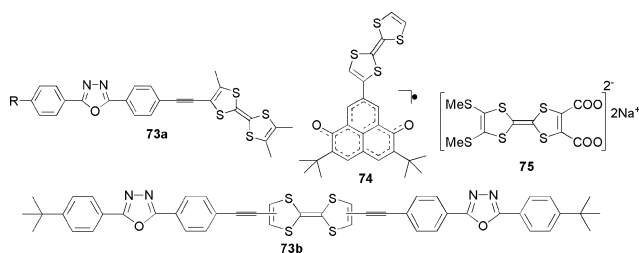
TTF derivatives including conjugated chromophores units have been reported. For example, TTF compounds **73a** and **73b** bearing diaryl-1,3,4-oxadiazole (OXD) units exhibit electrochromic properties.¹³⁹ Their absorption spectra can be reversibly tuned by electrochemical redox reactions at different potentials. Therefore, these compounds offer great potential as a new class of materials for electrochromic devices.

Compound **74** contains a 2,5-di-*tert*-butyl-6-oxophenalenoxyl stable neutral radical which is directly linked to a TTF moiety. In addition to being a stable radical, 2,5-di-*tert*-butyl-6-oxophenalenoxyl is also a good electron acceptor; thus, intramolecular electron transfer occurs within **74**. Interestingly, such intramolecular electron transfer is controlled



Scheme 30 Proposed mechanism for the photocontrolled oxidation of TTF by Fe^{3+} upon UV light irradiation.

by moderate change in the solvent environment and temperature.¹⁴⁰



TTF dicarboxylate salt **75** corresponds to a very simple, water-soluble structure. This compound exhibits pH sensitive redox properties.¹⁴¹ Particularly, a redox-coupled proton association/dissociation was found. Such behavior may find applications in electrochemically controllable chemical or physical processes, such as H^+ promoted fluorescent emission.

Finally, we want to emphasize that the parent TTF is itself suitable for generating switchable processes. This can be advantageously explored in the context of molecular electronics and more specifically for logic gates construction. For instance, the way that absorption spectra change in association with the interconversion between TTF, $\text{TTF}^{\bullet+}$ and TTF^{2+} , mimics the function of a half-adder.¹⁴² TTF can be transformed into $\text{TTF}^{\bullet+}$ or TTF^{2+} , respectively, by either application of the correct oxidation potential or reaction with a suitable stoichiometric amounts of chemical oxidants such as NOPF_6 which can be regarded as two input signals. The absorptions at 350 nm (due to TTF^{2+}) and 435 nm (due to $\text{TTF}^{\bullet+}$) can be considered as two outputs. The absorption changes at 350 nm and 435 nm upon external inputs, can be interpreted as “AND” and “XOR” logic gates, respectively.

4.6 Some aspects of redox-controlled gelation and relevant molecular assemblies

Considering the well-established anisotropic character of transport properties in TTF-based crystals (mixed-valence

cation-radical salts), many efforts have been produced to induce organization in alternative soft materials.^{1–2,11} For example, the assembly of functional molecular TTF-based nanostructures on surfaces provides a powerful response, as recently reviewed.¹⁴³ In addition, preparation of nanostructures (gels, nanowires) by self-assembly of TTF derivatives is presently the subject of intensive attention. In those cases, molecules are assembled through noncovalent interactions such as hydrogen bonding, ionic interactions and π - π stacking. Self-assembly of molecules with TTF moieties has been investigated mainly from two aspects: (1) development of low-molecular-weight gelators (LMWGs) and tuning of the gel formation through an external stimulus (oxidation); (2) formation of conducting fibers and nanowires.

Significant advances have been described by several groups in recent years on this topic. Previous works were reported in 1994 by Jørgensen *et al.*¹⁴⁴ with the gel formation of bis-arborol substituted TTF in ethanol–water or DMF–water. Molecules are in this case self-assembled into bandlike structures with a length of tens of microns and diameters in the 30–100 nm range. More recently, analogous compounds have produced thin films,¹⁴⁵ which after oxidative doping show moderate levels of conductivity, indicating that a significant degree of supramolecular order is present, with π - π stacking of the TTF cores.

Compound **76** with one TTF and one urea group can gel several organic solvents such as cyclohexane and 1,2-dichloroethane.¹⁴⁶ The reaction of **76** with TCNQ in cyclohexane leads to a dark-green gel. On the contrary, formation of the charge-transfer complexes in polar solvents causes the disappearance of the gel state. Direct oxidation of the TTF group either chemically or electrochemically also results in destruction of the gel state while the gel state can be restored by reduction, followed by heating and cooling (Fig. 14). Therefore, the gel formation with **76** can be tuned as a function of the redox state of the TTF moiety.

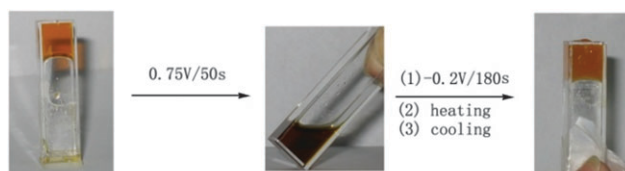
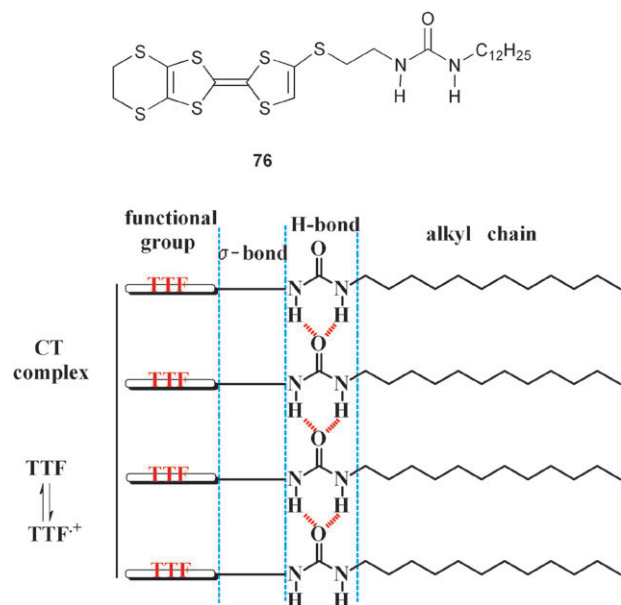
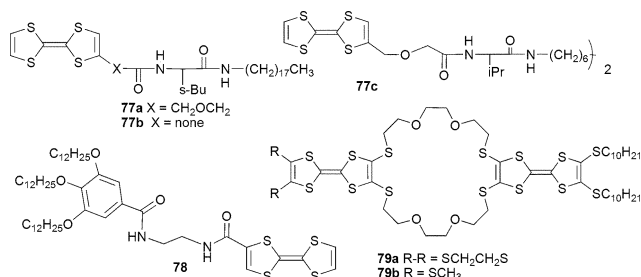


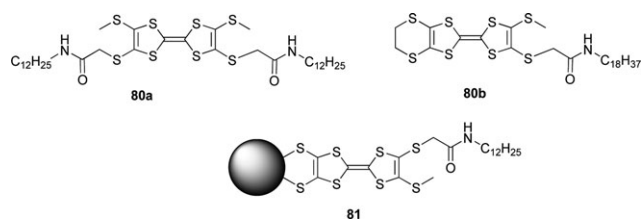
Fig. 14 A TTF-based gelator; reversible transition of gel into solution by electrochemical oxidation and reduction.

TTF derivatives **77a–c** containing amino acid residues do not show excellent gelling ability in common organic solvents.¹⁴⁷ Nevertheless, gelation occurs for aromatic liquid crystals and stable fibrous aggregates are formed. Iodine-doping has been successfully carried out with the self-assembled fibers, leading to the formation of 1D charge-transfer complexes. The conductivities of these 1D materials are in the range of 10^{-5} – 10^{-6} S cm⁻¹. Shinkai *et al.* described TTF derivative **78** possessing a 3,4,5-trialkoxybenzoic fragment.¹⁴⁸ This compound shows fine gelating properties in hydrocarbon solvents. It is assembled into one-dimensional fibers with less than 20 nm in width and more than several micrometers in length. Interestingly, the I₂-doped nanowires composed of **78** shows a characteristic absorption band at 1750 nm due to the mixed-valence state of the stacked TTF core.



Derivatives **79a–b** do not include typical gelating segments, but instead are amphiphilic bis-TTF annulated macrocycles.¹⁴⁹ Compound **79a** can form redox-active organogels. Although it possesses no hydrogen-bonding sites, the strong π - π and S–S interactions may enable the gel formation. It is interesting to note that bis(methylthio)-substituted bis-TTF annulated macrocycle **79b** is incapable of forming organogels under the same conditions. Amabilino and co-workers have very recently reported a new TTF-based gelator involving secondary amide functions (**80**), which can form transparent organogels in hexane or decane.¹⁵⁰ The intermolecular hydrogen bonding and van der Waals interactions due to the –CONH– amide unit and the long alkyl chain contribute to the gel formation. The xerogel is composed of nanofibers which can be doped by exposure to iodine vapor. After doping, a mixed-valence state containing neutral and cation radical species is formed as indicated by absorption spectral studies. The nanofibers show electrical conducting property and the conductivity increases further by annealing. The same group has also reported very recently hybrid gels of **80b** and

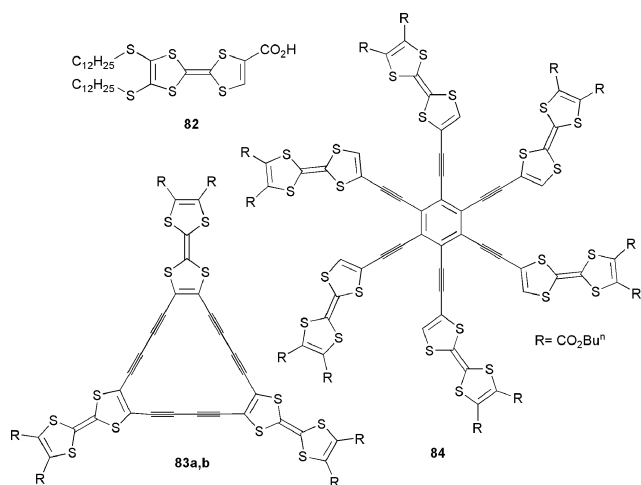
81.¹⁵¹ It appears clear from the TEM images that the nanoparticles are included within the fibers.



Besides forming gels, self-assembly of **80a** and **80b** also leads to well-defined nanofibers when deposited on HOPG, providing a noncovalent control for bottom-up assembly of functional supramolecular wires, as supported by STM studies.^{143,152–154}

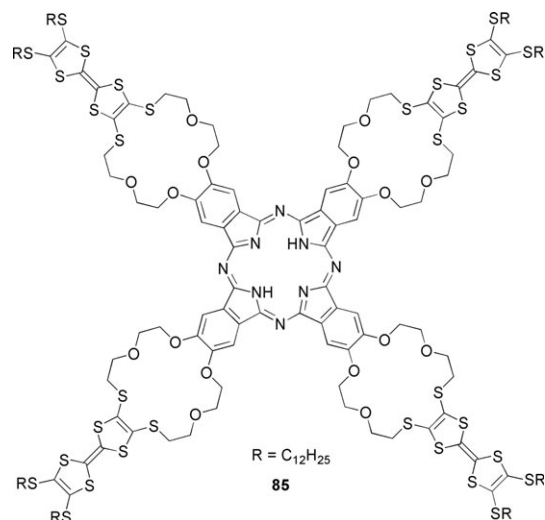
The group of Iyoda has also described gel formation from several TTF derivatives, and recently reported a related high-light review.¹⁵⁵ Interestingly, the very simple TTF–carboxylic acid **82** can gel hexane and cyclohexane to form fibrous structures. Compound **82** shows solvatochromism both in solution and in the fibrous state.¹⁵⁶

The appealing TTF[18]annulene structure **83** has been synthesized independently by Iyoda and Coll.¹⁵⁷ (**83a**, R = CO₂C_nH_{2n+1}, n = 4,8) and by Nielsen and Diederich *et al.*¹⁵⁸ (**83b**, R = nHex). Annulenes **83a** show unusual solvatochromic and thermochromic properties based on their self-aggregation behavior in solution. They can be assembled into fibrous structure from an aqueous THF solution.¹⁵⁷ Comparison of ¹H NMR and absorption spectroscopy for the two series (**83a** and **83b**) confirms the critical role of the ester group (R) of **83a** in promoting additional intermolecular dipolar interactions to the aromatic π-stacking self-assembly process.



On the other hand, hexakis(tetrathiafulvalenylethynyl)benzene **84** presenting a flexible disk-like structure, exhibits a strong self-aggregation tendency. Nanowires fabricated from the solution of **84** have a hexagonal columnar structure, reflecting the lateral and π–π stacking interactions. It should be noted that the corresponding salt **84**^{•+}·ClO₄[–] can also self-assemble into fibrous structure.¹⁵⁹

The assembly of TTF-substituted phthalocyanine **85**¹⁶⁰ was also reported. Absorption spectral studies clearly indicates the aggregation of **85** can occur in solution. Moreover, **85** can gel a mixture of dioxane and chloroform. Even more interesting is that the self-assembly of **85** leads to the formation of helical tapes nanometers wide and micrometers long.



5. Summary and outlook

The unique electronic characteristics of TTF and its derivatives have produced in the recent years a large number of switchable molecular systems, which are remarkably different in nature. These achievements have installed this unit as a key building block for various applications in molecular and supramolecular chemistry. This feature article has intended to summarize the most recent developments in this respect. These include topics as different as chemical sensing, triggered molecular motions, controlled switching of various spectroscopic properties and controlled gelling processes.

Therefore, in addition to the development of new conducting materials which is still very active,¹¹ TTF and its derivatives deserve further studies, in particular, in the following directions:

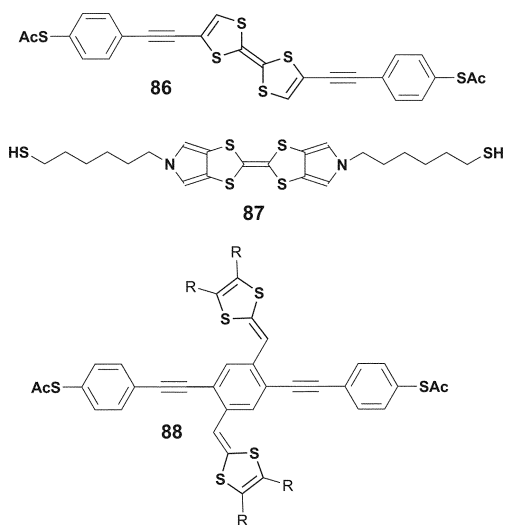
- *Multifunctional switchable architectures*: It is anticipated that sophisticated molecular switchable systems will be built by integrating TTF and other functional moieties. Such switchable systems can be employed to mimic the functions of molecular level devices such as molecular switches, machines and logics.^{161,162}

- *Sensing*: New selective and sensitive chemo- and biosensors may be designed with these switchable systems, as shown for instance with recent electrochemical biosensors from TTF-based self-assembly monolayers.^{163,164} Moreover, particularly promising results have been very recently published with the first synthesis of TTF-modified DNAs.¹⁶⁵ They can form stable double strands and a photo-induced electron transfer is demonstrated by fluorescence quenching in TTF/pyrene modified hetero-hybrids. These results are important for the development of redox-active, oligonucleotide-based diagnostics and optical sensors.

- *Surface modification*: In addition to studies led in solution, immobilization of TTF or derivatives onto substrates is of intense interest. In particular, the formation of redox-responsive surfaces are potentially useful for developing chemical sensors and for redox-controlled delivery of ions and molecules. Some examples have been proposed in this article; nanofibers deposited on surfaces, which provide a noncovalent control for bottom-up assembly of functional supramolecular wires constitute a very promising area in this field.

- *Gels and fibers*: New self-assemblies of TTF-containing functional molecules in solution into multilevel structures will receive more and more attention; in particular, it is interesting to examine the responses of these nanostructures towards redox reactions and charge-transfer interactions. A nice illustration has been recently proposed with a cholesterol-stoppered bistable [2]rotaxane incorporating a TTF unit, which forms organogels and which liquefy upon oxidation.¹⁶⁶

- *Molecular electronics*: Conjunction of the well-defined redox behavior of TTF and the recent finding of a high conductance¹⁶⁷ and efficient electron-transfer properties through TTF bridges,¹¹² focus a strong current interest in the framework of molecular electronics. Due to their easy chemical modification, TTF derivatives have recently been shown as good candidates for OFET (organic field-effect transistor) preparation.^{168,169} Another major challenge is to make use of single molecules that function as switches on metal surfaces in response to an external trigger. In this context, conjugated TTF systems such as **86**,¹⁷⁰ **87**¹⁷¹ or cruciform analogue **88**^{172,173} containing thiol end-groups for anchorage on gold surface, have recently been described, opening promising perspectives as molecular wires/transistors.



- *Synthetic chemistry*: As far as electron transfer processes are concerned, the peculiar electronic properties of TTF can be used as a synthetic tool in chemistry, in replacement of metals in a low oxidation state. Very promising results have also been recently reported through an original use of tetrathiafulvalene-oxazoline ligands,¹⁷⁴ in iridium catalyzed enantioselective hydrogenation of arylimines¹⁷⁵ and in palladium catalyzed asymmetric allylic alkylation,¹⁷⁶ opening new horizons towards the synthetic world.

- *Electron-rich receptors in host-guest chemistry*: Finally, considering the highly π -donating character of TTF and its planar geometry, this system will certainly find new developments as a key building-block for the construction of electron-rich receptors, for recognition of electron deficient guests. Construction of TTF-based interlocked systems has already seen tremendous developments.^{18–25} In addition, recent relevant examples of host structures for TTF-based guests have been described, that involve various three-dimensional cavities (cucurbituril derivatives,¹⁷⁷ capsules,¹⁷⁸ metal-assisted self-assembled cages,¹⁷⁹ and nanotubes¹⁸⁰). On the principle of reciprocity, there is now a strong interest in designing related electron-rich three-dimensional cavities, which involve TTF side-walls for receiving electro-deficient guests.

Acknowledgements

The topics covered by this feature article constitute key issues of a program entitled *TTF-based Nanomat* which is supported by the Agence Nationale de la Recherche (ANR – PNANO: ANR-07-NANO-030-01). In addition, this research topic has been developed in the frame of the COST D31 Action (WG 0014/05: *From a topological control in TTF-based macrocycles towards functional chemical systems*).

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