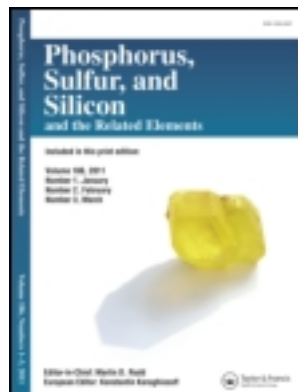


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Tetrathiafulvalene-Based Architectures: From Guests Recognition to Self-Assembly

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TETRATHIAFULVALENE-BASED ARCHITECTURES: FROM GUESTS RECOGNITION TO SELF-ASSEMBLY

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Abstract *The tetrathiafulvalene (TTF) unit has been successfully used for an incredibly broad range of applications. Beyond the well-established conducting properties of the corresponding cation-radical salts, this unit has appeared as a key redox-active component for various applications supported by its remarkable redox properties: a high π -donating ability and occurrence of three stable redox states. This article reviews the main contribution of the group of Angers to this field, highlighting results obtained in terms of redox-sensing as well as efforts carried out to reach new self-assembled TTF-based architectures.*

Keywords Calixarene; metallacycle; organogel; redox-responsive ligand; self-assembly; tetrathiafulvalene

INTRODUCTION

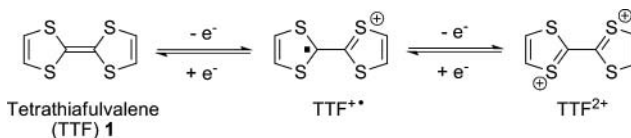
The tetrathiafulvalene (TTF, **1**) unit is fascinating by the fact that it combines a simple S-rich heterocyclic structure with an incredibly broad range of applications.^{1–5} In addition to the tremendous efforts that have been produced for four decades in designing new TTF derivatives programmed to improve the solid-state electroconducting properties of their oxidized salts,^{6,7} important developments have also been carried out for preparing molecular materials presenting various physical properties, such as magnetic,⁸ NLO,⁹ or photovoltaic¹⁰ properties for example.^{1–5,6,11} In the recent period, the remarkable π -donating solution properties of this unit have also been explored in a large number of redox-switchable molecular and supramolecular architectures, which we recently reviewed.¹² The ability of TTF to support such switchable processes comes from remarkable electronic properties, manifested by a high π -donating ability (low first oxidation potential E_1^{ox}) and the occurrence of two successive reversible one-electron redox steps ($E^1_{1/2}$, $E^2_{1/2}$), which give rise to three stable redox states (TTF, TTF^{•+}, TTF²⁺) (Scheme 1). This review will highlight recent illustrative efforts from our group in the preparation of TTF-based systems, regarding (1) the preparation of redox-responsive ligands, including ones incorporating

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All people from Angers and outside who have contributed to the results presented through various collaborations are warmly acknowledged. We thank the ANR PNANO “TTF-Based Nanomat” for financial support.

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calixarene-based scaffold, as well as (2) the use of self-assembly to produce electroactive organogels or metal-driven self-assembled molecular electroactive polygons.

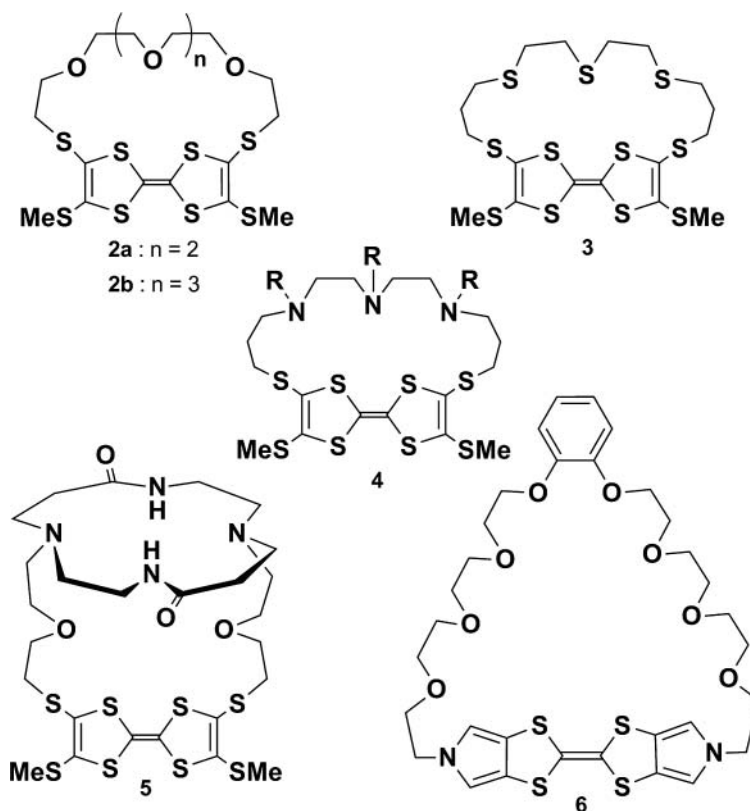


Scheme 1 The three redox states of TTF **1**.

RESULTS AND DISCUSSION

TTF-Based Redox-Responsive Ligands

The well-defined redox and electron-donating properties of TTF have positioned this unit as a key redox building block in the construction of redox-sensors for cationic guests.^{12–15} Pioneering work in this area using the TTF framework was performed in Odense, in the group of J. Becher and colleagues.^{16,17} Corresponding receptors are built from the covalent association of a binding subunit to an electroactive TTF derivative. A structural constraint for designing such assemblies lies in the need to ensure an efficient through-space or through-bond communication between both binding and redox subunits. On this basis, sensing of a given guest that has been trapped or even modulation of the host–guest binding constant can be expected. In most cases, such systems work on the basis of electrostatic interactions between the guest and the redox unit; binding a cation in the cavity close to the TTF core leads to an alteration of the π -donating ability of the latter. 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 ($E^1_{1/2}$) of the TTF subunit being seen. The synthetic methodology, initially developed in Odense,¹⁸ and using selective thiolate protection/deprotection sequences by use of bromopropionitrile and cesium hydroxide monohydrate, was applied in our case to the synthesis of *bis*-substituted TTF derivatives, which bear a binding unit lying along the long axis of the TTF skeleton. Crown-ether TTFs **2**^{19,20} and their sulfur analogue **3**²¹ (Scheme 2) exhibit high affinity for various targeted cations (typical K° values 10^3 – 10^4 M^{-1} in CH_3CN/CH_2Cl_2) as shown by ¹H NMR, UV-vis, and/or by MS titration studies. The recognition process could also be electrochemically monitored in the presence of stoichiometric (1:1) quantities of added metal cations. In particular, significant positive shifts in the first redox potential could be observed (e.g., $\Delta E^1_{1/2} = +45$ – 100 mV for **2** or **3**) (Figure 1). As expected from the hard/soft nature of interaction sites and from the size of the cavity, metal ion selectivity could be demonstrated as shown with **2a** vs. **2b** or **2a** vs. **3**;²¹ whereas the crown-ether systems **2a** and **2b** demonstrate a good affinity for group II metal ions (Sr^{2+} and Ba^{2+} , respectively), receptor **3** involving S-atoms binds preferentially the relatively soft cation Ag^+ , as well as do **4** and **5** with N-atoms (Scheme 2).^{22,23} Interestingly, in all cases, no variation in the second redox potential ($E^2_{1/2}$) is observed upon introduction of the cation in the electrolytic solution. This is ascribed to the expulsion of the metal ion at this potential. A similar behavior was observed with compound **6** (Scheme 2),²⁴ constructed around the bis(pyrrolo)TTF skeleton. In this case, a high affinity for Pb^{2+} ($\log K^\circ = 6.2$ in CH_2Cl_2/CH_3CN , 1/1), along with a remarkable electrochemical signature were found ($\Delta E^1_{1/2} = +140$ mV).



Scheme 2 TTF-based crown-ether derivatives 2-6.

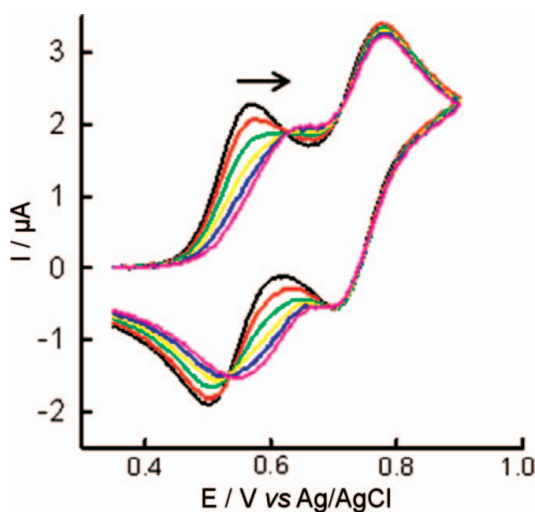


Figure 1 Cyclic voltammograms of compound **2b** in the presence of increasing amounts of $\text{Ba}(\text{ClO}_4)_2$ (from 0.0 to 1.0 equiv.). (Color figure available online.)

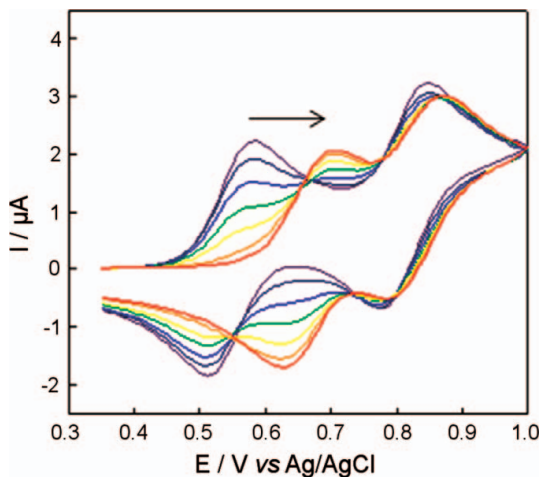
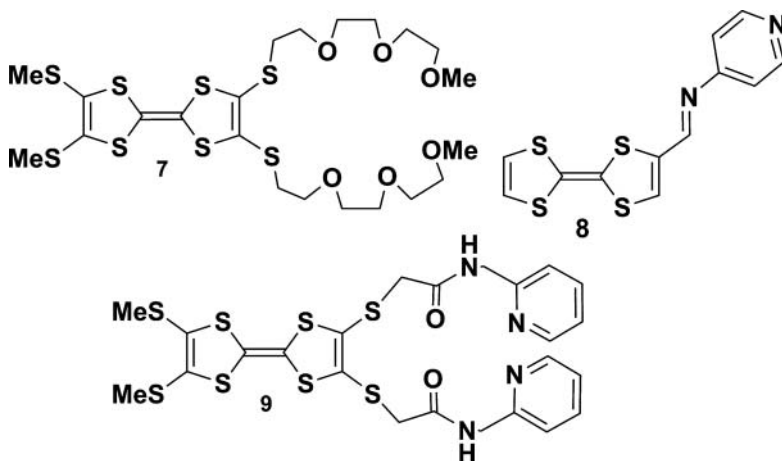


Figure 2 Cyclic voltammograms of compound **7** in the presence of increasing amounts of $\text{Pb}(\text{ClO}_4)_2$ (from 0.0 to 1.2 equiv.). (Color figure available online.)

Receptors involving an acyclic binding site are of interest since they allow a more straightforward synthetic approach (no need for high-dilution conditions), but also present higher solubility and greater conformational flexibility than for crown-systems. The TTF-based podand **7**^{25,26} shows a good affinity for Pb^{2+} ($\log K^\circ = 5.0$, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1/1)). In this case, the 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 ($\Delta E_{1/2}^1 = +120$ mV) corresponding to formation of the **7**- Pb^{2+} (1/1) complex (Scheme 3) at the expense of the free ligand **7** (Figure 2). Interestingly, the $E_{1/2}^2$ values remain constant, a finding that once again is interpreted in terms of cation expulsion taking place in this oxidized form. The binding constants for the different redox states of TTF could be evaluated as $\log K^\circ = 5.5$, $\log K^{+} = 3.3$ and $\log K^{2+} = 0$, respectively. Such behavior could 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.²⁵



Scheme 3 Molecular structure of acyclic receptors **7**–**9**.

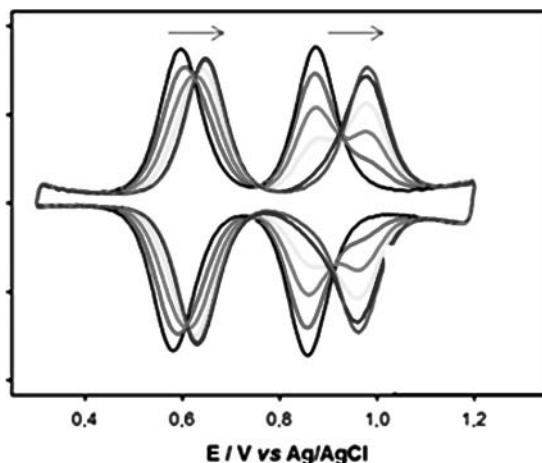
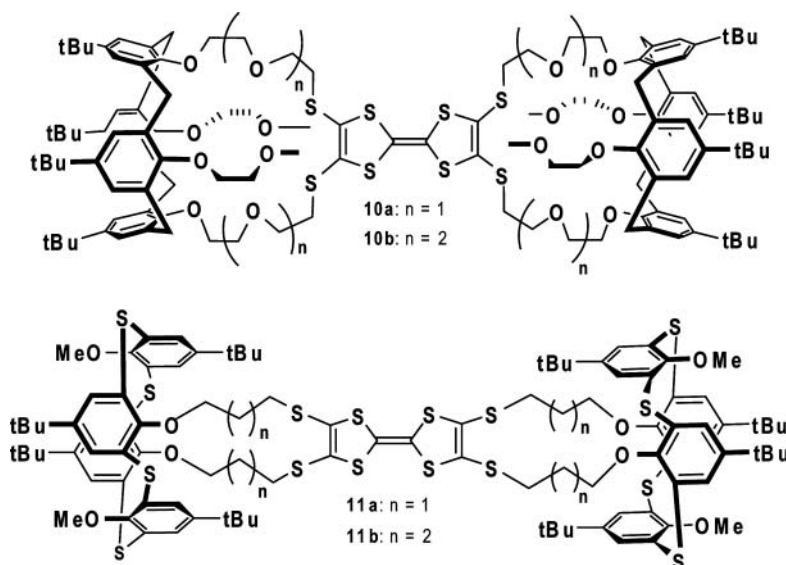


Figure 3 Deconvoluted cyclic voltammogram of compound **9** in the presence of increasing amounts of $\text{Cd}(\text{ClO}_4)_2$ (from 0.0 to 2.0 equiv.).

A considerable variety of TTF-pyridine derivatives have been described in recent years. We recently synthesized the TTF-pyridine ligand **8**,²⁷ which involves an imine linker (Scheme 3). This system shows a good sensing ability to lead(II). This aptitude clearly follows a different mechanism than the one described above for TTF-based receptors such as **2–6**, which is supported by electrostatic interactions. Indeed, chemosensor **8** exhibits a dual responsive behavior to metal binding, with both colorimetric (color change from yellow to purple) and electrochemical (positive shift of $E^{1/2}$) detections. These changes result from a strong modification of the intramolecular charge transfer, which takes place from the HOMO of the donating part (TTF) to the accepting pyridyl moiety upon metal coordination. Therefore, the recognition is based in this case on a through-bond interaction rather than on a through-space electrostatic interaction between the bound cation and the TTF moiety. Compound **9** (Scheme 3), which also incorporates pyridyl units, shows a high affinity for M(II) transition metal cations.²⁸ In the particular case of Cd^{2+} , this recognition ability is manifested by a remarkable four-wave voltammetric response (Figure 3), 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.

Case of calixarene-TTF assemblies. The calix[4]arene moiety is known in the literature as a suitable scaffold for generating three-dimensional binding cavities capable of complexing various guests with high affinity. Modulating the guest binding properties as a function of TTF redox state requires first a high binding constant (K°) for the neutral state. In this context, we synthesized TTF-based receptors **10a,b** and studied their metal ion binding ability (Scheme 4).^{29,30} The cone structure of both calix[4]arene platforms **10a** and **10b** promotes the construction of two 3D pockets. Binding studies performed with these receptors revealed a good affinity for sodium cation. A slight increase in the $E^{1/2}$ value [$\Delta(E^{1/2}) = +30\text{mV}$] could be observed upon addition of NaClO_4 . Based on a similar concept, we recently studied in collaboration with B.-T. Zhao and colleagues

thiacalix[4]arene analogues **11** (Scheme 4).³¹ These bisthiacalix[4]arenes tethered by an electroactive TTF unit exhibit an electrochemical response upon introduction of Ag^+ .

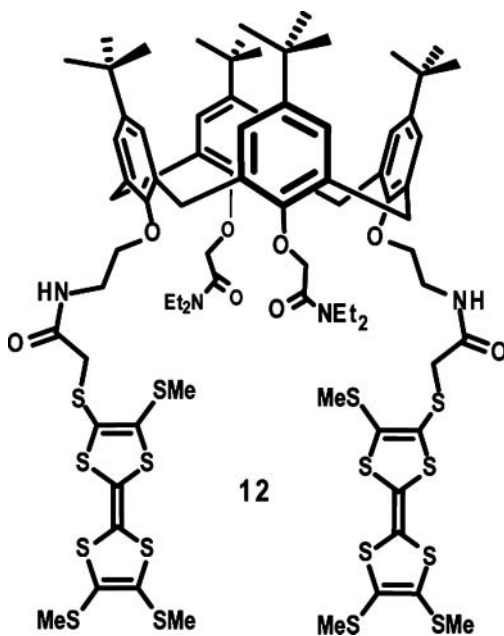


Scheme 4 Bis(thiacalix[4]arene) TTF receptors **10** and **11**.

The electroactive TTF core can also be used to contribute to anion recognition in redox-responsive ligands. The calixarene derivative **12** (Scheme 5), which encompasses two secondary amide H-bond donating sites, shows a good affinity for H_2PO_4^- and a cone structure that rigidifies upon anion binding.^{32,33} 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 in this case upon introduction of H_2PO_4^- .

Using the calix[4]arene scaffold, we also prepared derivatives **13**³⁴ and **14**,³⁵ which contain two and four pendant TTF moieties, respectively, at the lower rim of the cone (Scheme 6). A tetracarbonyl binding cavity, which is known to exhibit a strong affinity for alkali cations, is generated in both cases through ester and/or amide groups. This cavity is appropriate for Na^+ complexation, as shown by X-ray diffraction studies, which reveal that the metal cation is coordinated by eight oxygen atoms in both cases. The CV titration with Na^+ shows the expected positive potential shift of the first redox potential of TTF ($E^1_{1/2}$), and in addition is accompanied by a peculiar CV behavior manifested by a thinner redox wave when Na^+ is bound (Figure 4). This is assigned to a molecular conformation change upon complexation, from a flexible free ligand wherein the TTF units can interact at $E^1_{1/2}$, to a more rigid form upon sodium complexation, for which TTF units cannot interact anymore, and resulting in independent redox behavior. Systems **13,14** thus provide examples of redox-triggered molecular movement involving an additional input through metal cation binding.

Case of biphenyl-TTF assemblies. Moving to a biphenyl scaffold, C_2 -symmetric TTF-derivatives such as **15** were prepared in collaboration with G. Delogu and coworkers (Scheme 7),³⁶ and show an original electrochemical recognition process upon binding of Pb^{2+} , correlated to conformational changes occurring upon metal cation complexation. As in the previous examples (calixarene derivatives **13, 14**), the interaction between TTF moieties can be modulated upon binding of a metal cation (Pb^{2+}), due in this



Scheme 5 Structure of anion receptor 12.

case to a rotation around the Ar–Ar bond; such architectures constitute therefore interesting models to study long-distance conformational effects monitored electrochemically.

Case of π -extended-TTF derivatives. Efforts to new TTF-based responsive ligands have also been carried out through a design optimization of the redox-active unit. Examples were recently proposed with two conjugated analogues TTF **16**³⁷ (in collaboration with S. X. Liu and S. Decurtins) and **17**³⁸ (in collaboration with P. Frère) presenting a furanoquinonoid or a thienylene spacer between the 1,3-dithiol-2-ylidene rings (Scheme 8). Group

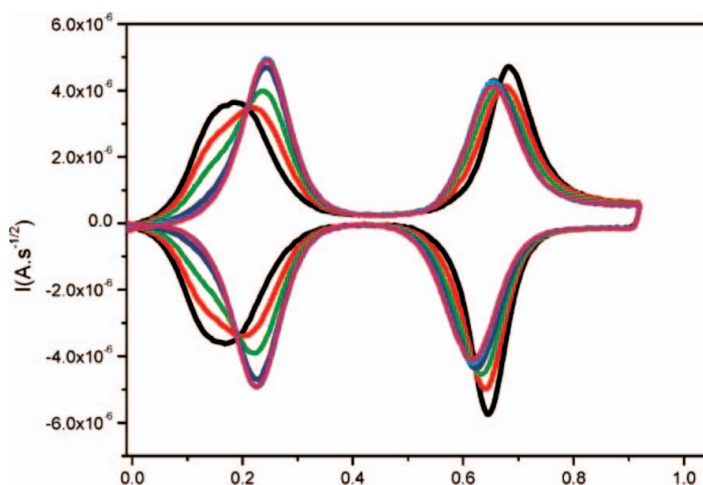
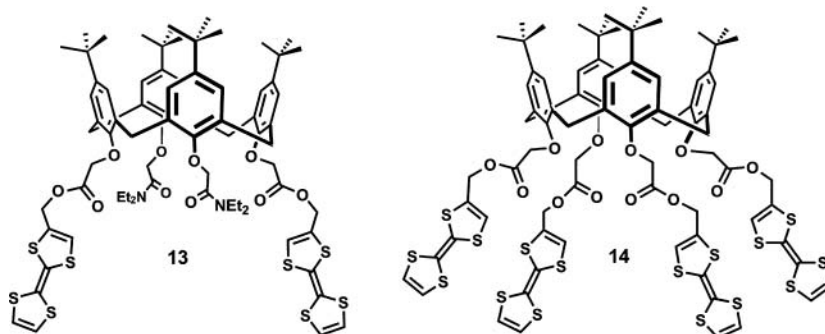
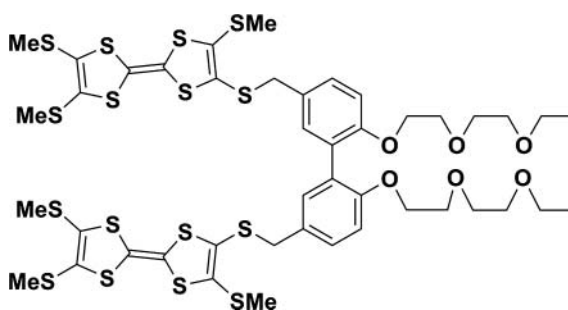
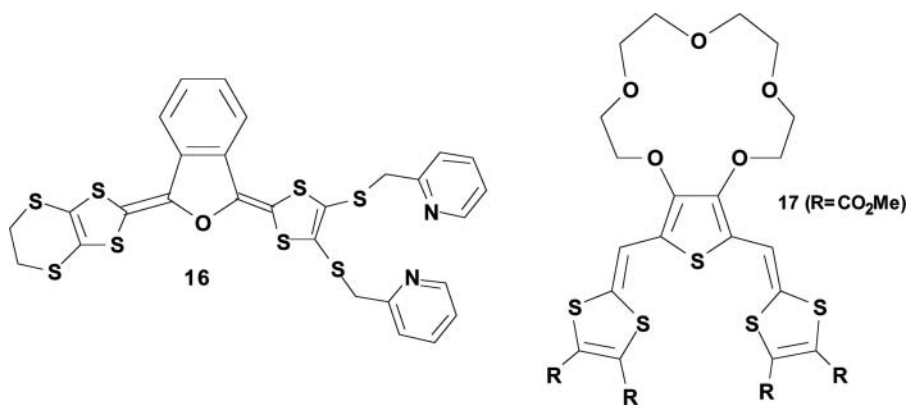
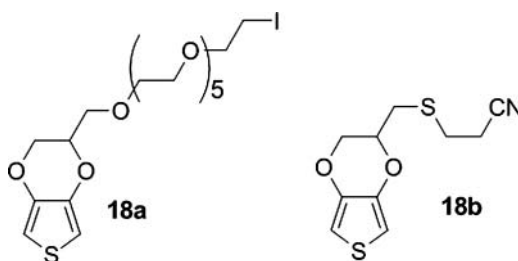


Figure 4 Deconvoluted cyclic voltammogram of compound **13** in the presence of increasing amounts of NaClO₄ (from 0.0 to 1.0 equiv.). (Color figure available online.)

Scheme 6 Molecular structure of receptors **13** and **14**.Scheme 7 Biphenyl-TTF receptor **15**.Scheme 8 Receptors incorporating extended TTF derivatives **16** and **17**.

I and II cations are efficiently detected by **17** (Na^+ or Ba^{2+} : $\Delta(E_{1/2}^1) = +90$ mV), according to a process very similar to that for parent TTF derivatives **2–6**. In the case of **16**, various M(II) cations could be recognized through pyridyl coordination. In particular, introduction of Pb^{2+} , Pd^{2+} , Ni^{2+} was accompanied by a remarkable four-wave behavior, 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, and accounts for the increased charge delocalization and the lowered coulombic repulsion within oxidized states of such a conjugated system.

Immobilization on surfaces. Considering practical aspects of chemical sensors and devices, a critical next step concerns the possibility to immobilize the functional active group (receptor) onto 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. We achieved immobilization of the above TTF-based receptors either by preparing self-assembled monolayers (SAMs), by electrodeposition of persubstituted dendrimers, or by preparation of substituted electroconducting films. In the first case, SAMs were prepared from receptors **2b** and **7** substituted with alkylthiol grafting sites.^{39,40} The corresponding monolayers demonstrated sufficient stability on the gold substrate as well as good sensing abilities for Ba²⁺ and Pb²⁺ cations. Compound **2b** was also immobilized onto a platinum surface through electrodeposition of dendrimeric molecules persubstituted on their periphery with up to 96 TTF units (collaboration with J.-P. Majoral, A.-M. Caminade et al.).⁴¹ The resulting modified electrodes presented a nice electrochemical response to Ba²⁺. Finally, thick films of receptors **2b**⁴² and **7**²⁵ could be obtained on a conducting surface by electropolymerization. They were prepared from the redox-active receptor attached to a poly(ethylenedioxythiophene) (PEDOT) or to a polypyrrole skeleton. In the latter case, the corresponding modified electrode allows for tuning of the binding/expulsion process for a given cation.²⁵ In this context, and in line with the post-polymerization functionalization process that we previously described from the pentaethyleneglycol functionalized EDOT monomer **18a**,⁴³ we recently demonstrated the efficiency of the new functionalized EDOT derivative **18b** (Scheme 9), bearing a highly nucleophilic masked thiolate function for generating various functionalized PEDOT-based films, either through direct electropolymerization or through a post-polymerization functionalization process.⁴⁴



Scheme 9 Synthetically versatile EDOT monomers **18a,b**.

A TTF-Based Organogel

Supramolecular polymers based on the TTF unit are also of interest, in particular to prepare organic conducting nanostructures like wires. Thus, a new approach consisting in designing TTF-based organogelators so as to prepare new conducting materials has been recently developed.^{45–47} Indeed, upon evaporation of the solvent from an organogel, a network of nanofibers—i.e., a xerogel—is generated and can be converted into a conducting material upon oxidation. Such nanowires are of utmost interest in the context of miniaturization and more generally, in nanotechnologies.⁴⁸ In this regard, our contribution, in collaboration with the group of D. B. Amabilino, consisted in preparing and studying a multifunctional gelating TTF-pyrene conjugate **19** in which various intermolecular interactions are competing, namely S...S contacts, H-bonding, hydrophobic, and π - π interactions

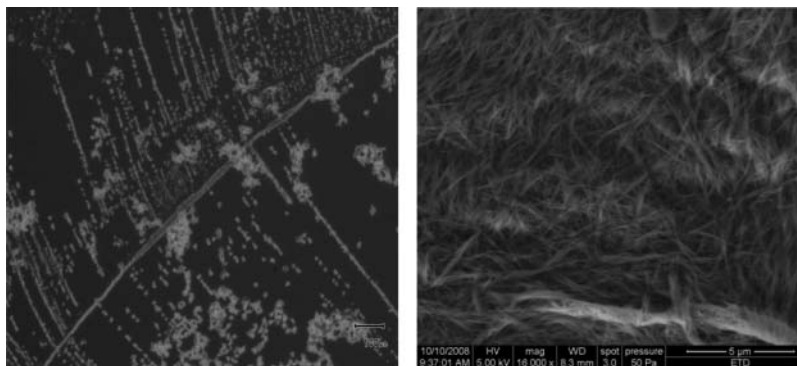
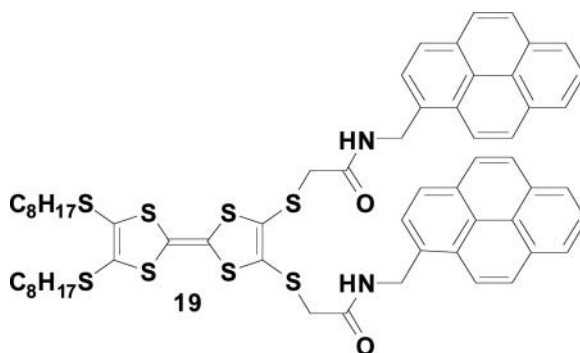


Figure 5 Aggregates obtained by cooling a hot solution of **19** (9.1×10^{-4} mol.L $^{-1}$) in acetone observed by polarized optical microscopy (left); xerogel obtained after THF evaporation observed by SEM (right).

(Scheme 10).⁴⁹ As illustrated in Figure 5, this structural peculiarity allowed the obtention of (i) varied nanostructures from bad solvents (e.g., acetone and dioxane) and (ii) organogels in miscellaneous solvents (e.g., tetrahydrofuran and chlorobenzene).



Scheme 10 Molecular structure of TTF-pyrene organogelator **19**.

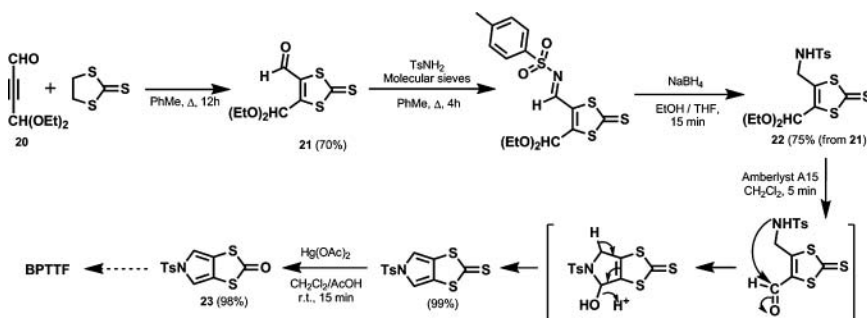
The corresponding xerogels were subsequently doped to the radical-cation state, affording conducting materials that were fully characterized by infrared absorption, electronic paramagnetic resonance, and current-sensing atomic force microscopy (CS-AFM). These studies enabled us to confirm robustness of the (weak rearrangement occurred upon iodine doping) as well as the efficiency of the doping process. Nicely, a correlation between the EPR signal line width and xerogel conductivity was observed in most solvents, showing that the larger the EPR signal, the lower the resistivity. This work opens a large avenue to stimuli-responsive organogels and xerogels given the structure of compound **19**, which consists of a redox-active unit linked to a versatile fluorophore (pyrene) through a bisamide bridge suitable for anion recognition.

Metal-Driven Self-Assembly of TTF-Based Components

The coordination-driven self-assembly methodology has proven to be of particular interest for preparing highly organized architectures, including molecular polygons and

polyhedrons.^{50–56} This methodology constitutes an efficient alternative to classical covalent multistep synthesis for preparing structures that are otherwise very challenging to reach. Use of this strategy needs the previous synthesis of functional ligands (e.g., based on the pyridyl unit), which are then associated to complementary metallic salts of defined geometries (e.g., square planar Pt(II) and Pd(II) salts). Coordination results in metal-assembled entities of controlled shape. Besides the synthetic challenge, the resulting host architectures, which possess predefined geometries, present suitable characteristics in terms of molecular recognition.

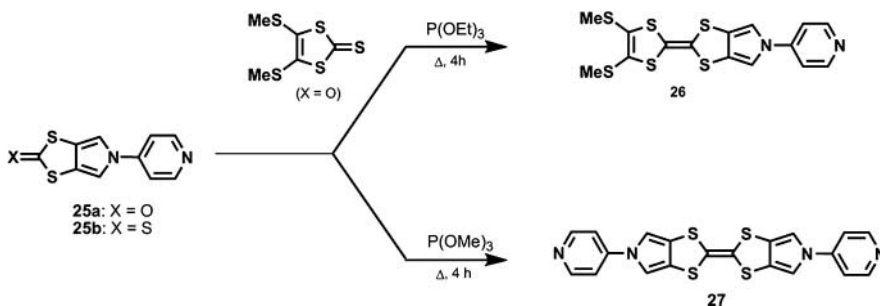
The π -donating ability of tetrathiafulvalene (TTF) derivatives is well-established (*vide supra*), and has projected this unit as a key redox building block for the construction of various redox-switchable ligands.¹² On this basis, we recently used the metal driven self-assembly technique to reach a new class of receptors incorporating two⁵⁷ or four⁵⁸ TTF-based redox units in a predefined geometry, through coordination to Pd(II) or Pt(II) phosphine corners. Whereas one pyridyl moiety allows preparation of tweezers-like structures, two pyridyl units are required on the periphery of the TTF backbone to prepare molecular polygons. Several TTF derivatives bearing two pyridyl coordinating moieties are described.^{27,59–61} Nevertheless, considering the propensity of bis-substituted TTF derivatives to undergo a *Z/E* isomerization upon oxidation to $\text{TTF}^{+\bullet}$ or by protonation,^{20,62,63} we have instead focused our interest on the non-isomerizable N,N'-disubstituted derivatives of bis(pyrrolo)tetrathiafulvalene (BPTTF). The synthesis of BPTTF, a unit that occupies a growing place among electroactive supramolecular architectures,⁶⁴ involves a cycloaddition between ethylenetrithiocarbonate and an electrophilic alkyne as the initial step. In the original synthesis by the group of J. Becher and colleagues,⁶⁵ the cycloaddition is carried out using dimethyl acetylenedicarboxylate as the electron-poor alkyne. We proposed recently⁶⁶ an alternative straightforward synthetic route to BPTTF using acetylene dicarbonyl mono(diethyl)acetal **20** (scheme 11).^{67,68} The choice of this alkyne avoids a subsequent oxidation step along the synthetic pathway. The key step in this route relies on the treatment of amine intermediate **22** by Amberlyst 15. Three successive elementary reactions are involved along this step: acetal deprotection, ring closure, and aromatization. Using this procedure, the N-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrol-2-one **23**, a key intermediate to bispyrroloTTF (BPTTF) derivatives could be obtained in less than three days, in a global yield of 51% from acetylene dicarbonyl mono(diethyl)acetal **20** (Scheme 11).



Scheme 11 Synthetic route to N-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrol-2-one **23**, a precursor of BPTTF.

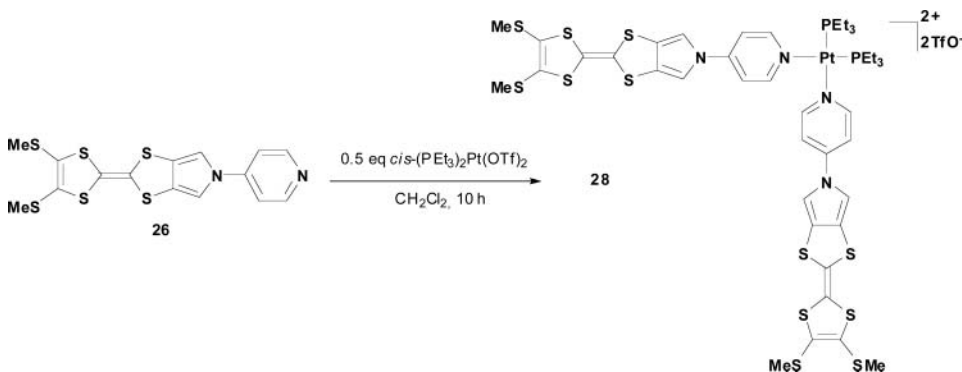
Using a similar methodology, we recently proposed⁵⁷ a general access to N-aryl-1,3-dithiolo[4,5-*c*]pyrrole-2-thione derivatives, key building blocks to N-aryl pyrroloTTF derivatives. In particular, this strategy allowed preparation of the N-pyridyl derivatives

25a,b, which were coupled in refluxing triethylphosphite, to afford the target mono- and bispyridyl ligands **26** and **27**, respectively (Scheme 12).



Scheme 12 Synthesis of the mono- and dipyriddy BPTTF derivatives **26** and **27**.

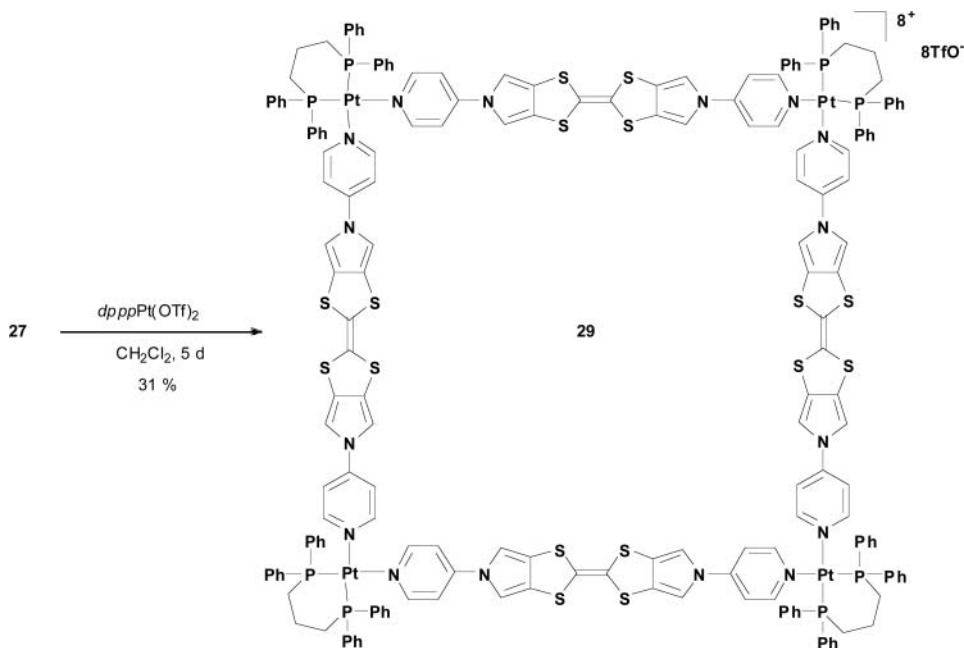
After obtaining the monotopic and ditopic ligands **26** and **27**, we could proceed to their metal-directed self-assembly through coordination to *cis*-blocked square planar Pt(II) and Pd(II) complexes.⁵⁷ In the case of **26**, rigid and orthogonal MPTTF dimers such as **28** were obtained, featuring electron-rich tweezers-like structures (Scheme 13). The two redox-active units behave independently, showing no detectable intramolecular interaction by cyclic voltammetry and by thin layer cyclic voltammetry studies. Interestingly, the orthogonal electron-rich dimer **28** presents a good affinity for the electron accepting C_{60} [$\log K = 3.15$ (CH_2Cl_2) with a 1/1 stoichiometry] as checked by UV-vis titration studies. It is worth noting that high third-order nonlinear optical responses could be found from these orthogonal dimers.⁶⁹ In addition, such corner systems constitute interesting models for the construction of higher symmetrical metalla-assembled systems such as molecular squares.



Scheme 13 Synthesis of dimer **28**.

The latter could be obtained from treatment of ditopic ligand **27** with a *cis*-blocked dpppPt(II) complex, which produces polygon **29** (Scheme 14).⁵⁸ To the best of our knowledge, this functional metallocsupramolecular square is the first described that incorporates strong π -donating side-walls. The redox behavior of this assembly presents the usual feature of BPTTF derivatives, with two successive reversible redox processes. Therefore this

molecular square allows a measure of control over the global charge surrounding the internal cavity, since each of the four constituting BPTTF redox-units can be oxidized twice. This renders this self-assembled square particularly attractive as a very easily oxidizable π -donating macrocyclic model, complementary to the extensively studied reducible ones generally based on the bipyridinium unit.



Scheme 14 Synthesis of the redox-active molecular-square **29**.

CONCLUSIONS

The unique electronic characteristics of TTF and its derivatives have installed this unit as a key building block for various applications in recent issues of molecular and supramolecular chemistry.¹² Through selected examples of our research activity in Angers, we have illustrated in this review this versatility, focusing on as different topics as redox-responsive ligands, self-assembled redox-active organogels, and construction of metal-driven self-assembled electroactive molecular polygons. Beyond those examples, and in addition to the development of new conducting materials, which is still very active,⁶ TTF and its derivatives still deserve further developments in various fields. There is no doubt that new self-assemblies of TTF-containing functional molecules in solution into multilevel structures, as well as nanofibers deposited on surface for bottom-up assembly of functional supramolecular wires, will receive more and more attention in relation with molecular electronics, as will single molecules that function as switches on metal surfaces.^{70–74} Regarding the tunable redox properties of TTF, switchable architectures engaged in sensing processes, such as molecular clips and tweezers,⁷⁵ will certainly know new developments, in particular by taking benefit of the electron-rich character of this unit, well-suited for recognition of electron deficient guests.

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