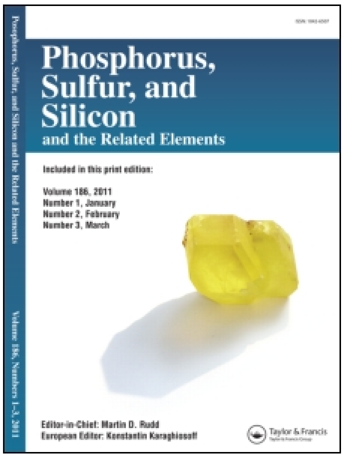

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Tetrathiafulvalene: A Paradigmatic Electron Donor Molecule

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*Tetrathiafulvalene (TTF) and its derivatives are exceptional building blocks in many areas of organic, supramolecular, and materials chemistry. Since the discovery ca. 30 years ago of the first "organic metal" tetrathiafulvalene-tetracyano-*p-*quinodimethane (TTF-TCNQ), a huge number of TTF derivatives have been synthetized.*

Although initial efforts were directed to enhance the electron-donating ability of TTF analogues to improve the conductivities of salts and charge-transfer (CT) complexes derived from them, the developments in synthetic TTF chemistry have made it possible to incorporate TTF into more sophisticated structures such as materials exhibiting intramolecular charge-transfer and nonlinear optical properties, sensors, molecular shuttles and devices.

Compounds in which TTF and electron-accepting molecules, especially C_{60}, are covalently tethered exhibit outstanding photophysical properties leading, upon photoexcitation, to charge-separated (CS) states showing remarkable lifetimes. In these systems, the gain of aromaticity upon oxidation of the TTF moiety has been used as a new concept for improving the stability of the charge-separated state, and, therefore, are of interest for the preparation of artificial photosynthetic systems as well as photovoltaic devices.

Keywords Conducting organic compounds; molecular shuttles; nonlinear optics; photoinduced electron transfer; sensors; tetrathiafulvalene

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INTRODUCTION

Tetrathiafulvalenes (TTFs) are well-known π-electron donors with a broad range of potential applications.[1] Since the field of organic metals was initiated ca. 30 years ago with the discoveries of high electric conductivity in a chloride salt of TTF[2] and metallic behavior in the charge-transfer complex tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF-TCNQ),[3] a huge number of TTF derivatives have been synthesized and TTFs are not any longer only a component of molecular conductors.[4] TTFs are versatile building blocks in many areas of organic, supramolecular, and materials chemistry.[5]

The parent TTF (**1**) is a nonaromatic 14π-electron molecule, which is easily oxidized to reversibly form the radical cation and dication species ($E^1_{1/2} = +0.34$; $E^2_{1/2} = +0.78$ V *vs.* Ag/Ag^+ in acetonitrile) (Figure 1). In contrast to the neutral TTF molecule, both the cation ($TTF^{\cdot +}$) radical and dication (TTF^{2+}) are aromatic in the Hückel sense as a result of the 6π-electron heteroaromaticity of the 1,3-dithiolium cation and, therefore, while $TTF^{\cdot +}$ and TTF^{2+} have a planar D_{2h} symmetry, neutral TTF has a boatlike equilibrium structure with C_{2v} symmetry.[6] However, neutral TTF can be folded along the S···S axes with a negligible energy cost, which explains the variety of conformations experimentally observed for neutral TTF.[7]

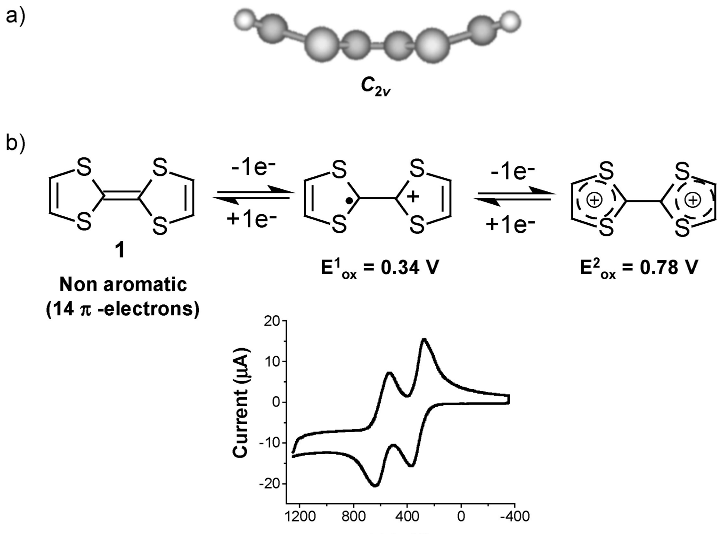


FIGURE 1 a) Boat conformation of TTF, b) electronic structure of neutral TTF and its cation, dication, and cyclic voltammogram of TTF in CH_3CN at 100 mVs^{-1}.

TTFs have been the base for the development of molecular conductors and superconductors[8] and their applications to the fields of molecular electronics and photoinduced electron transfer processes are currently a field of great interest.[5,9] During the past decade, the study of TTF derivatives has undergone an explosive growth of activity in the search for nonconventional applications. Thus, this paradigmatic molecule has been incorporated into different molecular systems based on host–guest interactions being able to act as sensors, molecular switches, or mediators for specific reactions.[10]

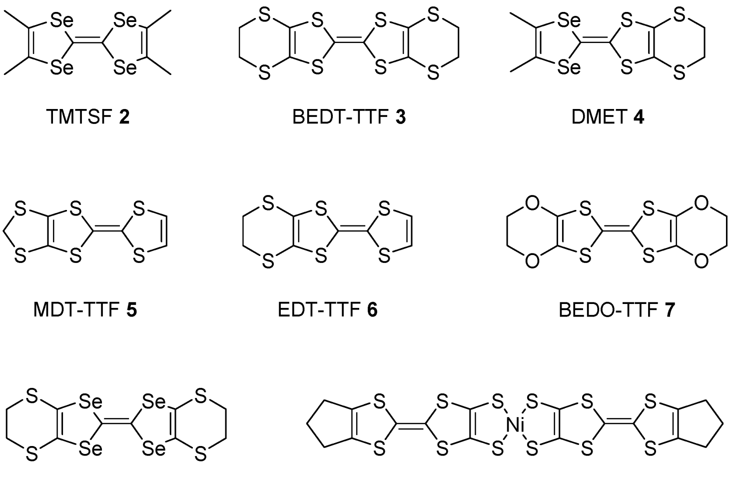
This account is a selective overview with a bias toward the interest and work of the authors on some relevant aspects of TTF-based materials, with the aim of demonstrating the well-known versatility and potential of this exceptional molecule as a rich electron-donor building block. In particular and as a representative example, an update on the recent application of TTFs in the search of Non-linear optical (NLO) properties and some recent examples of the photoinduced electron transfer process of TTF-containing fullerenes will be presented. During the past few years, partial aspects of the synthesis and properties of tetrathiafulvalenes have been reviewed and the most relevant articles were listed in our last review on TTF chemistry; we refer the reader to this paper for specific details.[5]

TTF IN ELECTRICALLY CONDUCTING MATERIALS

During almost three decades there has been considerable interest in molecular-based organic conductors and superconductors,[1,11] which was initiated with the previously mentioned findings of Wudl et al.[2] and Ferraris and coworkers.[3] Since then, a great milestone was achieved with the discovery of superconductivity in the charge-transfer (CT) salts containing TMTSF (tetramethyltetraselenafulvalene, **2**) or BEDT-TTF (or simply ET) [bis(ethylenedithio) tetrathiafulvalene, **3**] as a donor component, followed by the salts of unsymmetrical donors DMET [dimethyl(ethylenedithio)diselenadithiafulvalene, **4**) and MDT-TTF (methylenedithiotetrathiafulvalene, **5**), as well as the Ni $(dmit)_2$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) complex with EDT-TTF (ethylenedithiotetrathiafulvalene, **6**).[12]

A large number of metallic and superconducting organic solids are now known[8] and the basis for the rational design of new TTF-based electron donors over the past years has been the following: i) the realization of increased dimensionality of the conduction pathway in conducting materials, which was shown by the structural features of the superconducting ET salts with approximately isotropic conductivity in the donor sheet including the intermolecular $S\cdots S$ network (two-dimensional character), ii) the expectation of a decrease in the onsite Coulombic repulsion involved in the formation of a dicationic species, and iii) the novel suggestions for the donor-packing motif in the CT complexes and/or salts. Thus, major attempts to modify the TTF skeleton have been directed toward the extension of the π-conjugation, the introduction of single atoms as chalcogen and phosphorus, and the functionalization by substituents bearing —OH and/or —NRH groups that would enable intermolecular hydrogen bonding interactions. The resulting extended or functionalized TTF-type donor molecules have been reported in several reviews[8] and book chapters. In addition, replacing sulfur atoms with the lighter oxygen or with the larger and more polarizable selenium or tellurium[13] has still been a promising simple modification of the skeleton for the prototype sulfur-based TTF derivatives. For example, ET was transformed by substitution of the outer ring sulfur atom with oxygen atoms into BEDO-TTF [bis(ethylenedioxy)tetrathiafulvalene, **7**], which has yielded superconducting salts,[14] and the TSF (tetraselenafulvalene, **8**], which has also provided organic superconductors.[15]

It has been recently, however, when a difficult problem in the metallization of molecular crystals has been solved. In contrast to typical inorganic metals composed of single elements, such as sodium and copper, all of the examples of molecular metals consisted of more than two components. In 2001, Tanaka et al.[16] reported a single-component molecular metal, [Ni(tmdt)$_2$], **9** (TMDT, trimethylenetetrathiafulvalenedithiolate) (Figure 2). The intermolecular overlap integrals for this metal



TMTSF **2**
BEDT-TTF **3**
DMET **4**
MDT-TTF **5**
EDT-TTF **6**
BEDO-TTF **7**
BETS **8**
[Ni(tmdt)$_2$] **9**

FIGURE 2 Examples of TTFs for molecular-based organic metals.

showed that the system has a three-dimensional π band and, the room-temperature (RT) conductivity σ(RT) was determined to be 400 $\mathrm{Scm^{-1}}$, which is almost one order of magnitude greater than those of typical BEDT-TTF organic superconductors.[16]

NON-CONVENTIONAL APPLICATIONS OF TTF

Although the TTF molecule is synonymous with the development of molecular organic metals,[8] the significant advances in synthetic TTF chemistry have allowed incorporating TTF into macrocyclic and supramolecular structures, with the ultimate goal being to construct systems capable of acting as sensor, switches at the molecular level, or materials with interesting optoelectronic properties. In this section, we will briefly review the less-known but very promising "non-conventional" applications of TTF derivatives.

TTF as Cation Sensor

The construction of macrocycles containing TTF units has received considerable attention because such molecules may act as a host for which complexation of a neutral or ionic guest induces a change in the optical or redox properties of the system.[17] Effective control and monitoring of host–guest binding is relevant to the development of smart sensors and molecular devices. In this sense, Jørgensen et al.[10a] were the first to describe the ability of crown-ether annelated TTFs to host alkali metal cations with a concomitant increase of the first oxidation potential as indicated by cyclic voltammetry (CV) experiments. However, more than 250 equiv of cations were necessary to observe any shifts for these ligands. LeDerf et al.[18] and Bryce et al.[9] obtained similar results and it was concluded that the relative weak responses result from the weak coupling between the metal cation and the redox active fulvene center, and, in some cases, the unfavorable structural environment for complexation.[10]

Self-assembled monolayers (SAMs) are an attractive method for the assembly of electroactive molecular systems on solid supports, because they are easy to prepare and possess good stabilities.[19] Moore et al.[20] incorporated crown-ether groups into TTF-SAMs, and their use as potential metal ion sensors was clearly demonstrated. Positive potential shifts of the first oxidation wave of the TTF unit were observed upon metal binding, similar to those observed in solution, e.g., $\Delta E^{1/2}$ for Na^+ and $Ba^{2+} = 45$ mV. In these monolayers, if the potential scanned was limited to the first wave, the CV response was recorded for at least

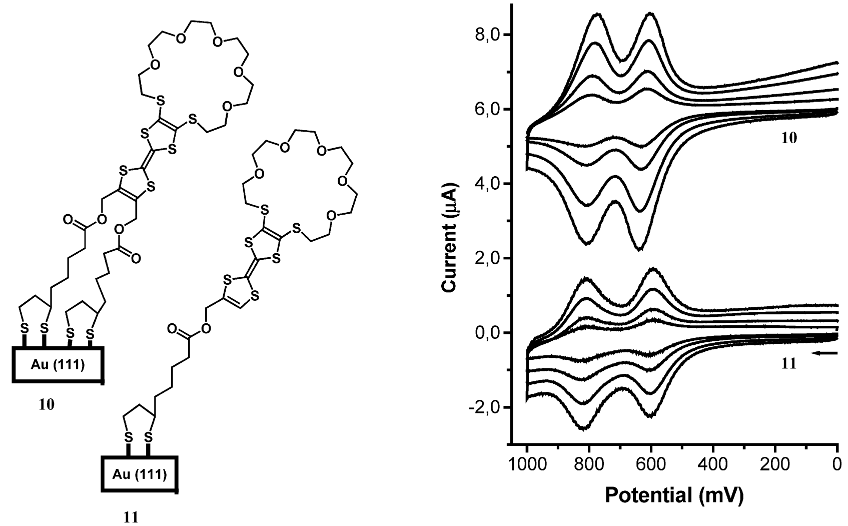


FIGURE 3 Crown-ether annelated TTFs used for assembly on electrode surfaces and CVs of SAMs of **10** and **11** in THF solutions containing 0.1 M $TBAPF_6$ at different scan rates (100 to 600 mVs^{-1}).

1000 cycles. However, the electroactivity gradually decreased when the potential was scanned beyond the first oxidation.[20]

Liu et al.[21] prepared the thioctic ester TTF derivatives **10** and **11**, which form remarkably stable SAMs with surface-confined electrochemistry (Figure 3). SAMs of these crown-TTF disulfides can recognize alkali metal ions, and they possess almost indefinite stability.[22] Thus, in THF containing MPF_6 (5.0 mM) anodic shifts were observed for the first and second oxidation potentials of **10**; M = Na: $\Delta E^1_{1/2} = +60$ mV, $\Delta E^2_{1/2} = +55$ mV; M = K: $\Delta E^1_{1/2} = +20$ mV, $\Delta E^2_{1/2} = +30$ mV. The shift of $E^2_{1/2}$ (not observed in other derivatives) was explained by surface aggregation or cooperativity effects between neighboring crowns in the SAM.

Molecular Shuttles and Devices

The emergence of supramolecular chemistry[23] has provided many elegant self-assembled interlocked compounds such as catenanes and rotaxanes in high yields.[24] Catenanes are molecules containing two or more interlocked rings, which cannot be separated without the breaking of a covalent bond. Rotaxanes contain a dumbbell-shaped component (a rod and two bulky stoppers) with a macrocyclic component encircled.

The stoppers prevent the macrocycle unthreading from the rod. In the absence of these stoppers the corresponding complex is called a pseudorotaxane.

Because the mechanically interlocked components of non-degenerate catenanes and rotaxanes can be induced to change their relative positions as a result of some external stimulus, they are ideally suited for the construction of molecular machines and the fabrication of molecular electronic devices.[25] The relative movements of the interlocked components can be triggered by chemical, electrochemical, and photochemical stimuli (input signal), forcing the molecule to switch between its two non-degenerate states (State 0 and State 1), which can distinghished spectroscopically (output signal).

Among the desirable features for the redox-controllable, amphiphilic [2]rotaxanes that have been employed for the fabrication of single-molecule thick electrochemical junctions in electronic devices are the siting of redox-active units along the rod section and the dumbbell component, and the presence of both hydrophobic and hydrophilic groups as stoppers at the ends of the dumbbell component. TTF's unique π-electron-donor properties, together with its ability to form a strong green 1:1 complex with the tetracationic cyclobis cpara-quot-p-phenylene ($CBPQT^{4+}$), have been responsible for TTF's incorporation into a considerable range of catenanes and pseudorotaxanes. Because these systems have been very recently reviewed by Becher and coworkers[10,26] we will only discuss one of the examples lately reported in the literature, the amphiphilic bistable [2]rotaxane **12**$\cdot 4PF_6$ (see Figure 4).[27]

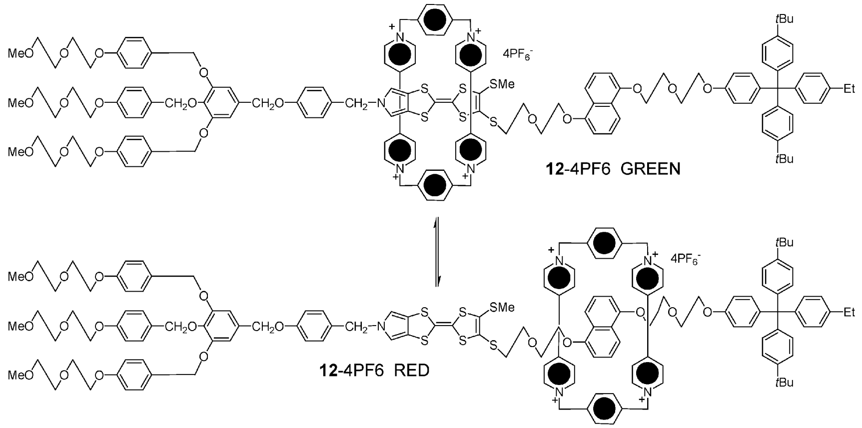


FIGURE 4 Molecular shuttle bearing a mono(pyrrolo)-TTF ring and a 1,5-dioxynaphthalene (DNP) unit as electron-rich residues.

The amphiphilic bistable [2]rotaxane **12**·4PF$_6$ was designed with CBPQT^{4+} as the ring component and with the dumbbell component, containing a mono(pyrrolo)-TTF unit and a 1,5-dioxynaphthalene (DNP) moiety within its rod section, terminated by the hydrophilic dendritic stopper at one end and a hydrophobic tetraarylmethane stopper at the other.[27] It turned out that the SMe group situated between the TTF and the DNP recognition sites adds a considerable activation barrier for the shuttling of the tetracationic cyclophane CBPQT^{4+} between the two recognition sites. In fact, the steric hindrance exhibit by the SMe group made it possible to isolate the translational isomers **12**·4PF$_6$·RED and **12**·4PF$_6$·GREEN and to study the kinetics of the shuttling of CBPQT^{4+} between the two recognition sites. The solid-state switches fabricated from this kind of amphiphilic [2]rotaxanes[28] are far superior to the switch fabricated from a TTF-based [2]catenane.[29]

TTF Derivatives as Non-linear Optics Materials

Push–pull systems of general structure D-π-A are being actively studied as NLO chromophores.[30] At the molecular level, donor π-conjugated bridge-acceptor (D-π-A) structures showing a charge-transfer process from the D to the A moiety and, therefore, a significant difference between both ground-state and excited-state dipole moments are the best candidates to attain high hyperpolarizabilities. These are electrooptic materials whose refraction index can be changed by the application of an electric field and are of interest as a result of their potential use in areas such as optical modulation, molecular switching, optical memory, and frequency doubling.[31]

In this context, we have recently proved the efficacy of TTF and π-extended TTFs (*ex*TTFs) as NLO-phore and different TTF[5,32] or exTTF-based[33] push–pull chromophores (see **13–20** in Figure 5) have been synthetized and their electrochemical and NLO properties studied.

We have studied the influence of different acceptors and spacers to optimize the non-linear optical response of these materials. An increase in the NLO properties was observed by using stronger electron acceptors attached to the TTF moiety, and the best results ($\mu\beta = 1350 \times 10^{-48}$ esu) were observed when the strong acceptor 3-(dicyanomethylidene) indan-1-one was used in combination with the TTF unit.[32e] As in other NLO materials, the $\mu\beta$ values increase in the series a < b < c, which shows the benefical effects of the extended conjugated chain on the molecular first hyperpolarizability.[33]

The UV/Vis spectra of all these derivatives showed a low-intensity charge-transfer band in the visible region, which is a prerequisite for the attainment of high β values.[34] In addition, these TTF-based NLO

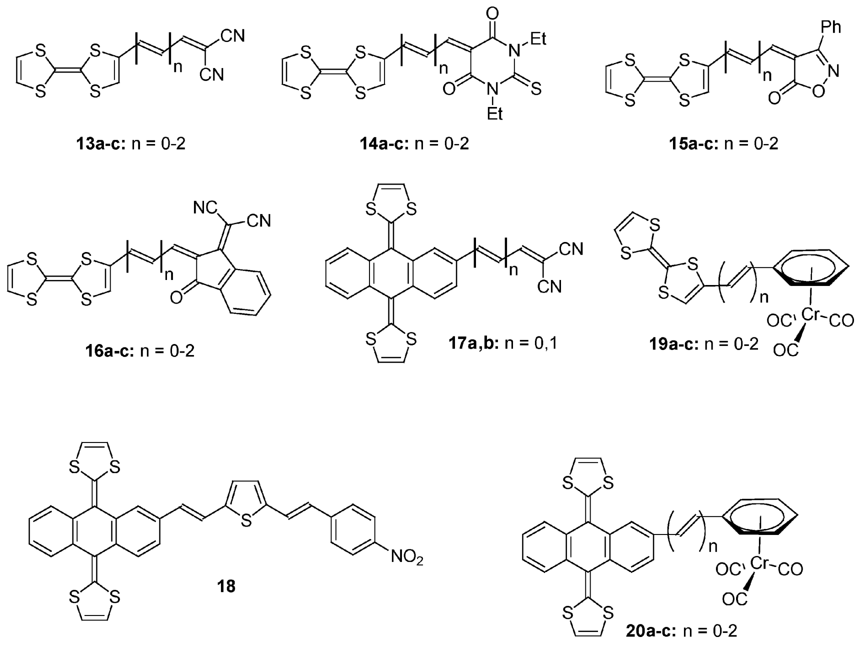


FIGURE 5 Selected TTF-containing NLO chromophores.

chromophores display good thermal stabilities that make them potential candidates for incorporation in poled polymers. With these promising results in hand, better $\mu\beta$ values are expected for TTF-containing materials in which more polarizable spacers and stronger acceptor units are included. On the other hand, the NLO responses of all the D-π-A systems presented in this article could be tuned by altering the electrochemical properties of either the whole molecule or just the electroactive moieties constituting the molecule. Those changes could be achieved by electrochemical (oxidation or reduction) methods together with varying the nature of the spacer. The inherent tailorability of such TTF derivatives would allow to reach very exciting materials possesing NLO properties.[35]

PHOTOINDUCED ELECTRON TRANSFER IN TTF-CONTAINING FULLERENES

The electron transfer between donor and acceptor molecules is the key step in very important natural processes such as photosynthesis, in which sunlight is converted into chemical energy.[36] However, a deeper study of the primary photosynthetic events has stimulated the active search for simpler models. On the other hand, the electron transfer process that occurs between both electroactive units is also responsible for the conversion of sunlight into power, which is the base of the functioning of organic solar cells.[37] The attainment of both goals requires bichromophoric molecules in which the presence of electron-donating and electron-accepting fragments connected through a spacer is necessary. Although other electron-accepting compounds can be used, fullerenes, and especially [60]fullerene, render a very appealing system for the preparation of photo- and redox-active model systems.[38] Thus, one of the most outstanding properties of [60]fullerene in electron transfer processes is that it accelerates the photoinduced charge separation and retards the charge recombination in the absence of light.

A large number of C_{60}-donor systems have been prepared in the search of electron transfer properties.[39] It is important to mention that most of the donor molecules used in the preparation of C_{60}-σ-donor systems have an aromatic character in the ground state, which is partially or totally lost upon oxidation to form the radical cation species. In contrast, TTF and its derivatives are non-aromatic molecules that, upon oxidation, form the 1,3-dithiolium cation that presents aromatic character (Figure 1). This gain of aromaticity in forming the radical cation and dication species of TTF in the oxidation process is an important improvement to further increase the stabilization of the charge-separated state.

The first C_{60}-TTF dyad (**21**, $n = 0$) was simultaneous and independently reported by Prato[40] and Martín[41] in 1996. Since then, other C_{60}-TTF derivatives such **22–25** (Figure 6) have been published in the search of photoinduced electron transfer processes.[5,42]

We have recently reported the photophysics of the TTF-containing dyads **21**[42b] and **25**.[42c] Absorption of light in these dyads leads to the formation of the fullerene excited singlet state, which undergoes an intramolecular electron transfer to form the charge-separated (CS) state. Evidence for the electron transfer process comes from steady-state and time-resolved photolysis. It is worth mentioning that an increase of the stabilization of the CS state takes place by gaining aromaticity upon oxidation of the TTF moiety. Charge recombination proceeds mainly via formation of the fullerene triplet excited state because of the strong second-order vibronic spin-orbit coupling induced by the presence of the sulfur atoms of the TTF unit. This charge-recombination behavior forming a fullerene triplet excited state is different than most of the previously reported C_{60}-based dyads bearing donor moieties other than TTF.[39]

The lifetimes of the charge-separated states in all these C_{60}-TTF dyads are in the range of 1–2 ns, which is similar to that found in other

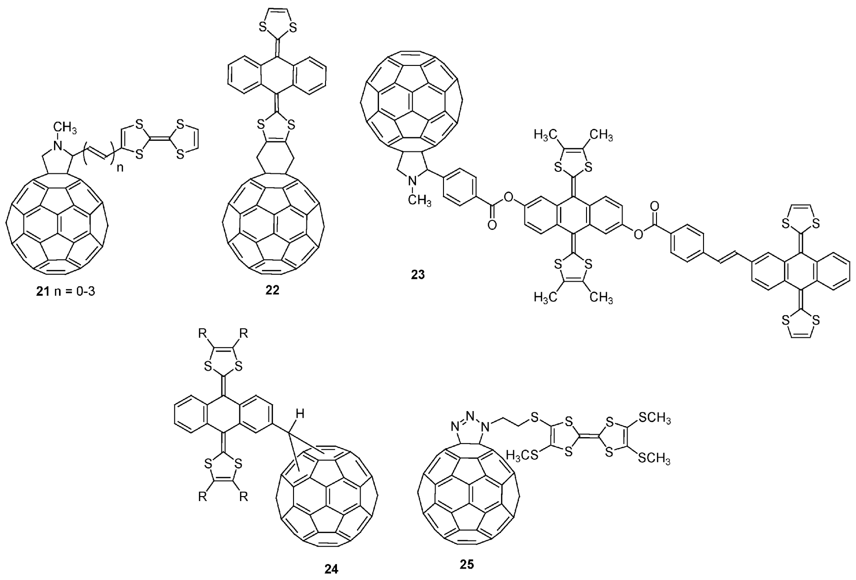


FIGURE 6 Representative examples of TTF-containing fullerenes for photovoltaic applications.

C_{60}-based tetraphenylporphyrin dyads (~0.5 ns) endowed with similar spacers.[39]

All the C_{60}-TTF dyads reported so far connected both electroactive units *via* covalent bonds. However, in nature, noncovalent interactions play a crucial role by providing a meaningful organization principle to regulate size, shape, and function down to the nanometer scale. In this regard, a series of H-bonded $C_{60}\cdots$TTF architectures (**26** and **27**) (Figure 7) have been reported and their electrochemical and photophysical properties studied.[43] To modulate the molecular architecture, two chemical spacers of different lengths (i.e., phenyl *versus* biphenyl) as well as two functional groups (i.e., ester *versus* amide) have been used.

In these cases, the photophysical measurements revealed the formation of the $C_{60}^{\cdot -} \cdot TTF^{\cdot +}$ radical ion pairs in a through-space electron-transfer manner. The lifetime measured for the radical ion pair states are in the range of hundred of nanoseconds, thus being in the same order of magnitude as those reported for covalently linked C_{60}-TTF dyads.[40–42]

In further studies, we found that C_{60}-based dyads bearing a π-extended TTF fragment (**22**, **24**), which upon oxidation form very stable cationic species, exhibit a highly remarkable stability of the CS state

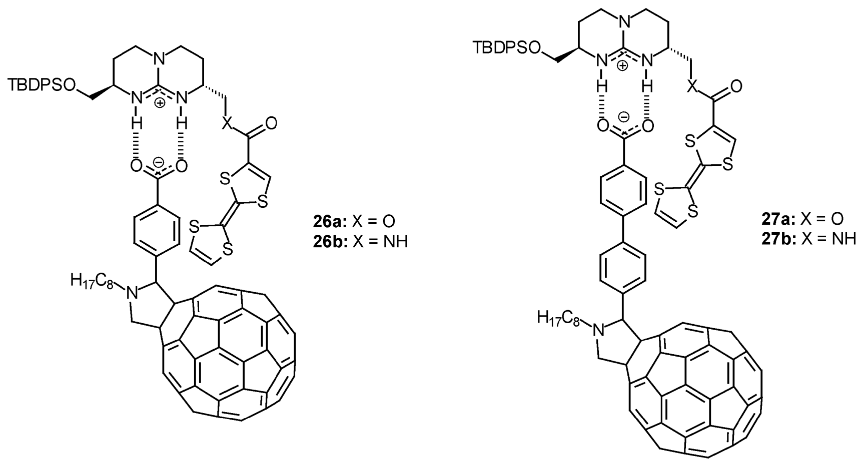


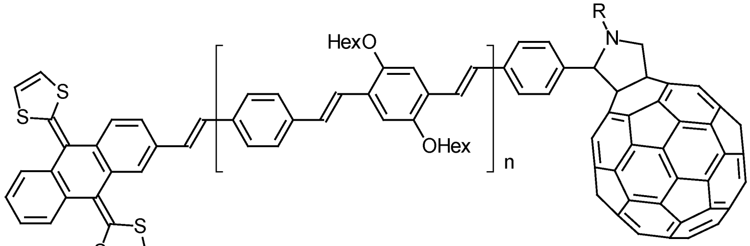
FIGURE 7 Structures of H-bonded $C_{60}\cdots$TTF dyads (**26** and **27**).

(200 ns in benzonitrile) that is improved in around two orders of magnitude in comparison with other C_{60}-TTF dyads.[5]

Very recently, TTF and its derivatives have been also used in the preparation of the first electroactive triads of type C_{60}-exTTF$_1$-exTTF$_2$ (**23**).[44] Excitation of the fullerene moiety in **23** yields the first singlet excited state $^1C_{60}$-exTTF$_1$-exTTF$_2$, which undergoes photoinduced electron transfer to give the adjacent charge separated state $C_{60}^{\cdot -}$-exTTF$_1^{\cdot +}$-exTTF$_2$. A second electron transfer from exTTF$_2$ competes with charge recombination to form the final $C_{60}^{\cdot -}$-exTTF$_1$-exTTF$_2^{\cdot +}$ state that eventually recombines to the ground state.[44] Remarkable lifetimes were measured for the final charge-separated state of triad **23** with values ranging from 50 to 100 μs in benzonitrile. These values are among the highest lifetimes found for electroactive C_{60}-based triads,[39,45] and can be accounted for by the additional stabilization provided by the gain of aromaticity and planarity of the π-extended TTF unit upon oxidation.

Finally, it is worth mentioning the series C_{60}-wire-exTTF architectures **28** reported very recently by our research group (Figure 8).[46] The photophysical measurements carried out for these compounds revealed a charge-transfer process indicating not only a rather weak distance dependence one but also a wire-like behavior. Those properties make these molecular-sized compounds suitable candidates for their application as molecular wires and therefore pave the way for using TTF derivatives in nanotechnology.

In summary, biomimetic models of type C_{60}-TTF dyads and triads, in which both electroactive moieties are connected through either



28: n = 1-3

FIGURE 8 C_{60}-wire-exTTF ensembles (**28**).

covalent or noncovalent spacers, have been used as models for further preparation of artificial photosynthetic systems as well as solar energy conversion devices. The search for novel photovoltaic devices and artificial photosynthetic systems is currently a major task in chemistry and the photophysical properties showed by dyads and triads involving TTF and π-extended TTFs are among the most outstanding found for these purposes.

CONCLUSIONS

The electron-donor ability of TTF has been employed since its discovery in the early 70s in a huge number of organic, polymeric, and supramolecular systems, in order for these to act as organic conductors, sensors, molecular switches, or electrooptical devices. The recent developments in both synthetic TTF chemistry and supramolecular chemistry offer great opportunities in the design and construction of future redox active molecular and supramolecular systems and, in this regard, TTF is still a molecule that needs to be studied in depth.

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