

Electronic Communication in Tetrathiafulvalene (TTF)/C₆₀ Systems: Toward Molecular Solar Energy Conversion Materials?

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ABSTRACT

The covalent connection of the electron acceptor C₆₀ to *p*-quinonoid π -extended tetrathiafulvalenes (exTTFs) has allowed for the preparation of new photo- and electroactive conjugates able to act as artificial photosynthetic systems and active molecular materials in organic photovoltaics. The gain of aromaticity undergone by the π -extended TTF unit in the oxidation process results in highly stabilized radical ion pairs, namely, C₆₀^{•-}/exTTF^{•+}. Lifetimes for such charge-separated states, ranging from a few nanoseconds to hundreds of *microseconds*, have been achieved by rationally modifying the nature of the chemical spacers. These long-lived radical pairs are called to play an important role for the conversion of sunlight into chemical or electrical power.

Introduction

Photosynthesis, the natural process in which two thermodynamically demanding processes, the oxidation of water and the reduction of carbon dioxide, take place by means of a complex sequence of light harvesting, photo-induced charge separation, and catalysis events, serves as

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an inspiration for the development of artificial systems capable of mimicking this efficient biological process of converting inexpensive, nonpolluting, and inexhaustible energy. Considering that photosynthesis produces 10²² kJ/year of biological material, about 100 times more than the food needed for mankind, by converting only 0.02–0.05% of the solar incident energy, it is clear that artificial photosynthetic systems should play an active role in affecting the correlation between energy supply and energy demand.¹ That influence is stressed by the fact that the progress made in the construction of synthetic models, capable of efficiently emulating photosynthesis, has also been applied to the fabrication of molecular-scale optoelectronic devices and especially in the field of organic photovoltaics (PVs).²

Common to artificial photosynthetic model systems and to the active layer of photovoltaic cells are the following aspects: (i) efficient harvesting of the solar spectrum, (ii) unidirectional energy transfer, (iii) vectorial charge transfer, and (iv) motion of charge carriers (electrons and holes). All of these processes evolve between different classes of photo- and electroactive molecules (i.e., electron acceptors and donors) and produce ultimately a metastable state, that is, a charge-separated radical ion pair state. The basic requirement for an artificial reaction center to function efficiently consists in the connection of photo- and electroactive donor and acceptor units by means of a linker that controls their

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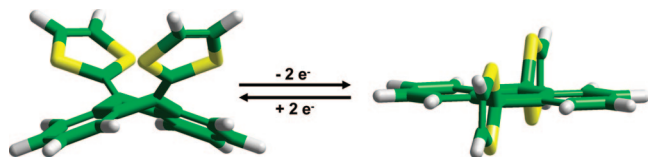


FIGURE 1. Geometry of the ground state (left) and dicationic state (right) of exTTF (**1**).

electronic interactions and, hence, the electronic coupling as well as the rates and yields of electron transfer.^{3,4}

Several sophisticated and versatile synthetic strategies have been pursued en route toward artificial photosynthetic and photovoltaic model systems.^{3,4} Herein, we will focus on our most relevant achievements in this field, with particular emphasis on the search for the stabilization of the radical ion pairs generated upon light irradiation.

The physicochemical properties of [60]fullerene and its derivatives,⁵ accepting up to six electrons in solution at moderate reduction potentials to form stable anionic species, simultaneously, exhibiting very low reorganization energies in charge-transfer reactions, and simultaneously, showing remarkable electron-mobility features, prompted us to pursue the preparation of conjugates, in which this all-carbon framework acts as an outstanding electron acceptor. On the other hand, we have chosen the *p*-quinonoid analogue of tetrathiafulvalene (TTF),⁶ 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (abbreviated as exTTF, **1**), as the electron-donating counterpart. Unlike many known electron donors, such as porphyrins, aniline derivatives, ferrocenes, phthalocyanines, π -conjugated oligomers, etc.,⁷ TTF and its *p*-quinonoid π -extended congener (exTTF) undergo aromatization upon oxidation (Figure 1). Such aromatization affords thermodynamically stable radical-cationic and -dicationic species at relatively low oxidation potentials.^{8,9} Furthermore, the formation of aromatic species upon oxidation is accompanied by dramatic geometrical changes, which stabilize either the ion radical pair or the dication species.

Theoretical calculations, performed at the semiempirical (PM3), the *ab initio* Hartree–Fock (HF/6-31G*), and the density functional theory (DFT, B3-P86/6-31G*) levels, shed light on the geometry and electronic features of the radical-cation species of exTTF (**1**) and a related benzoannulated series.^{9b} These studies corroborated that the exTTF unit, upon losing a single electron, turns into a more aromatic radical-cation intermediate while still retaining to some extent its *p*-quinonoid character.

Nonetheless, the interest of TTF derivatives for the fabrication of solar energy conversion devices relies on their charge-transport properties. In fact, organic field effect transistors prepared from some of those derivatives feature some of the higher hole mobilities found for solution-processed materials.^{10,11} This Account highlights the different strategies that we have followed in the quest for enhancing the lifetimes of the charge-separated states generated upon photoinduced electron transfer in C₆₀/exTTF conjugates. In addition to the photoinduced electron transfer that yields highly stabilized ion radical pairs,

the charge-transport mobilities exhibited for both donor and acceptor moieties, together with the possibility of tailoring the nature of the bridge, render them appealing candidates for their application in organic photovoltaics.

[60]Fullerene/ π -Extended Tetrathiafulvalene (C₆₀/exTTF) Conjugates

First reports on C₆₀/TTF conjugates (**2**) date from 1996,¹² with details on their photophysics following in 2000.¹³ Photophysical studies showed lifetimes for the charge-separated state of about 2 ns, although being of the same magnitude than that observed in comparable fullerene electron-donor conjugates was, however, insufficient to warrant applications as active layers in organic solar cells.¹⁴

Following the aromatization principle undergone by the exTTF unit upon oxidation, we pursued the synthesis of C₆₀/exTTF conjugates **3** (Figure 2).¹⁵ Fluorescence and transient absorption spectroscopy confirmed that in **3** the fullerene singlet excited state deactivates indeed to the corresponding C₆₀^{•-}/exTTF^{•+} radical ion pair state. Lifetimes of around 200 ns (i.e., benzonitrile) are 2 orders of magnitude longer than the aforementioned C₆₀/TTF (**2**) systems! This stabilization is rationalized in terms of aromaticity as well as planarity that are gained during the transformation of the ground state into the radical-cation species.

The role played by the spacers is not just structural, because its chemical nature governs the electronic communication between the terminal units. Another important feature of the spacer is its modular composition, which allows for the alteration of the separation without affecting the electronic nature of the connection.⁷ In this regard, the different connectivities (for example, in **2b**, the 1,3-dithiole fragment is only separated from C₆₀ by two single bonds, and in **3**, the 1,3-dithiole/C₆₀ separation is given by six bonds) should be considered. Such topological differences raise a controversial question: is the gain of aromaticity/planarity of the donor responsible for the longer radical ion pair state lifetime in **3** or, in contrast, is this effect a simple consequence of a larger donor–acceptor separation? To address this central issue, we devised and tested C₆₀/exTTF conjugates **4** and **5** (Figure 2), where the topological features are reminiscent of those of **1**: the separation between the two electroactive components is limited by only two single bonds.¹⁶ Importantly, transient absorption measurements revealed radical ion pair state lifetimes in the range of 200 ns for Diels–Alder cycloadduct **4** as well as for fulleropyrrolidine **5**. In conclusion, the data prove the following points: (i) connecting exTTF at either its anthracene or its 1,3-dithiole functionality to C₆₀ exerts no appreciable impact on the radical ion pair state lifetime; (ii) the positive charge that resides on the one-electron-oxidized donor seems to be delocalized over the two 1,3-dithiole rings rather than localized on just one of them; and (iii) the aromatization principle that is applicable to the one-electron oxidation

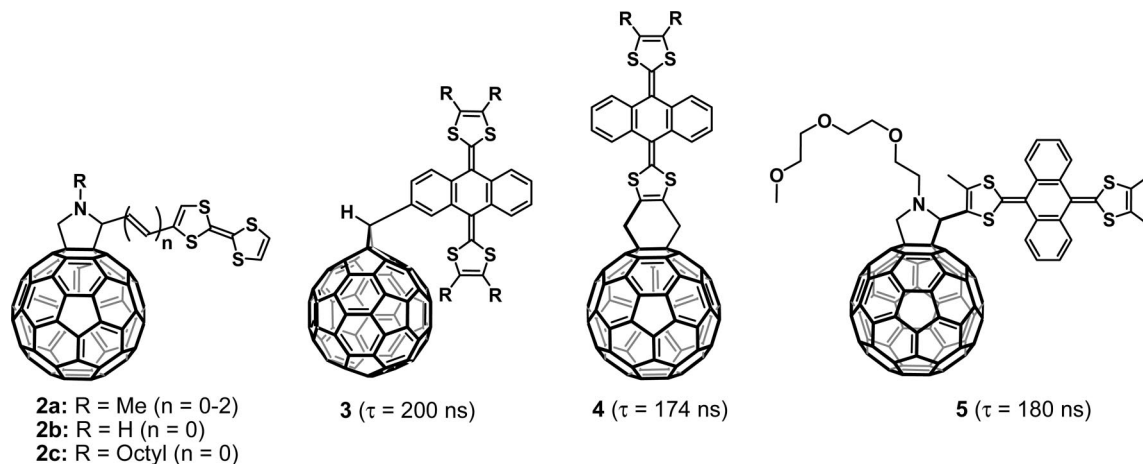
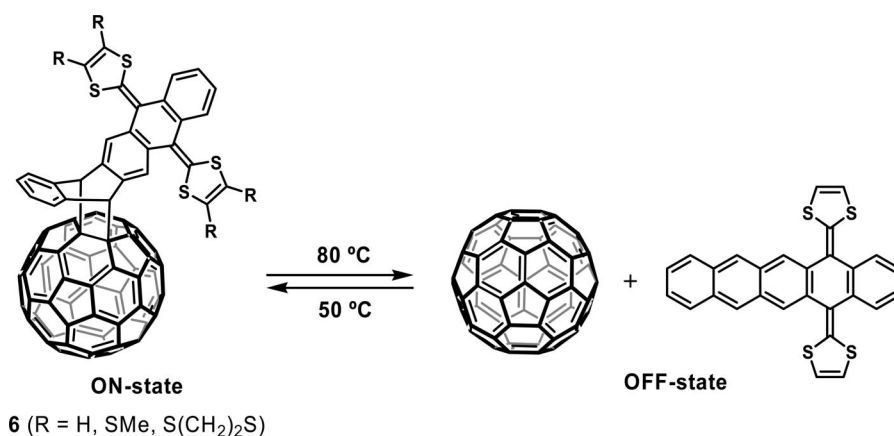


FIGURE 2. Topologically different C₆₀/TTF and C₆₀/exTTF conjugates, where R = H, SMe, or S(CH₂)₂S. Lifetimes for the respective radical ion pairs of C₆₀/exTTF **3–5** were measured in benzonitrile.

Scheme 1. Thermally Reversible Diels–Alder Cycloadducts **6**



of exTTF plays, indeed, a crucial role in the stabilization of the corresponding charge-separated states.

Diels–Alder cycloadduct **6** represents an interesting example of a thermal on–off electron-transfer switch. Photophysical assays corroborated the reaction pattern in **6**.¹⁷ In particular, the fullerene singlet excited state is subject to a rapid charge-transfer deactivation that yields a 200 ns lived C₆₀^{•−}/exTTF^{•+} radical ion pair state. Much more interesting are temperature effects. Diels–Alder cycloadduct **6** acts as an efficient, thermally reversible material, whose fluorescence switches as sketched in Scheme 1. In the on state, an activated charge transfer is the inception for a strong fullerene fluorescence quenching, when compared to a fullerene reference. Upon heating, **6** reverts to the starting materials and the charge transfer is deactivated. In this off state, unquenched fullerene fluorescence emerges.

Multichromophoric C₆₀/exTTF Conjugates: Improving the Stability of the Radical Ion Pairs

Despite the benefits and simplicity of integrating exTTF into electron donor–acceptor conjugates, practical PV applications require radical ion pair state stabilizations that reach into the range of microseconds and beyond.¹⁸

However, in the most common C₆₀-based conjugates, bearing different classes of electron donors, the lifetimes are, nevertheless, well below the range of microseconds.⁷

An elegant approach toward improving the charge separation/charge recombination ratio implies the linkage of two fullerenes to the two opposite termini of the electron donor. This family of fullerene derivatives, often named as dumbbells, has shown improved photophysical and photovoltaic performances.¹⁹ An additional benefit of symmetrical C₆₀ dumbbells is that they are synthetically easier to prepare than related asymmetric systems.²⁰ More interestingly, Blom and coworkers have recently demonstrated the C₆₀ content dependence for the performance of photovoltaic devices. In this regard, the electron mobility of the devices increases with the C₆₀ weight ratio up to 80%. However, this weight ratio has a sharp influence on the hole mobility of the electron-donor counterpart, too.²¹

C₆₀/exTTF/C₆₀ dumbbells (**7** in Figure 3)¹⁴ constitute an important donor–acceptor prototype: they assist in shedding light on the advantages toward charge-transfer properties that stem from using two rather than just one C₆₀, especially when they are compared to the simpler C₆₀/exTTF analogue (**8**).

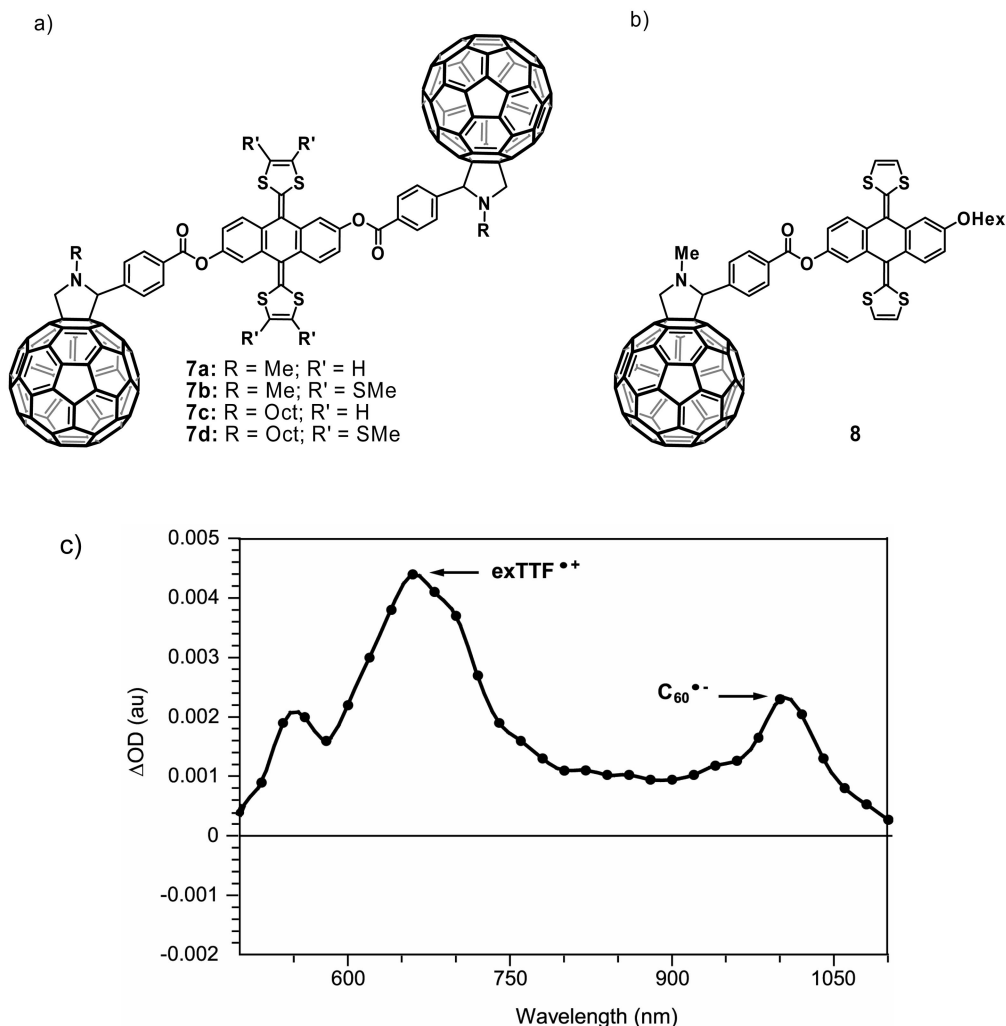


FIGURE 3. Chemical structures of (a) dumbbell-type triads **7** and (b) dyad **8** (showing the same primary structure as triad **7**). (c) Differential absorption spectrum [i.e., vis and near-infrared (NIR)] obtained upon nanosecond flash photolysis (355 nm) of **7a** in nitrogen-saturated benzonitrile with a time delay of 50 ns.

Photophysical experiments demonstrate that the C₆₀^{•-}/exTTF^{•+}/C₆₀ (**7**) and C₆₀^{•-}/exTTF^{•+} (**8**) transient species were formed through rapid and intramolecular charge-transfer processes that commence with the initial C₆₀ photoexcitation. When the lifetimes of C₆₀^{•-}/exTTF^{•+}/C₆₀ (i.e., 630 ns in benzonitrile) and C₆₀^{•-}/exTTF^{•+} (i.e., 480 ns in benzonitrile) are compared, a significant improvement turns out for the dumbbell structure. Therefore, although there is not a clear explanation for this experimental finding yet, the presence of a second C₆₀ induces a cooperative effect on the stabilization of the photogenerated radical ion pair state (Figure 3c).

In this realm, the charge-transfer properties of **7c** together with its high C₆₀ content encouraged us to use it as a photoactive material in a photovoltaic device. The architecture of the device consisted of a glass with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)-coated indium tin oxide (ITO) as a transparent hole collecting electrodes and LiF/Al as an electron-collecting back contact (Figure 4). A moderate rectification ratio was observed in the dark (60 at ±2 V), which is largely due to a substantial leakage of current. Under illumination

(75 mW/cm²), a short-circuit current density (J_{sc}) of 0.25 mA/cm², an open-circuit voltage (V_{oc}) of 0.32 V, and a fill factor (FF) of 0.27 were measured. With these parameters, a ~0.03% energy conversion was calculated.

Typically, the efficiency of charge transfer decreases exponentially with increasing bridge length. Any long-range electron-transfer processes, which are governed by a superexchange mechanism, are typically limited to distances of around 20 Å. At larger distances, the electron-transfer rate-determining electronic coupling is largely diminished and, consequently, is insufficient to compete with the intrinsic deactivation of the excited-state electron donor. Therefore, the motion of charges over distances larger than 20 Å would require considering alternative strategies. This task becomes particularly relevant to achieve radical ion pair state lifetimes in the range of microseconds. An appealing option is the incorporation of several electroactive units to form linear arrays, in which a relay of several short-range electron-transfer steps along well-designed redox gradients takes place instead of forcing the electron transfer through a single, concerted long-range step. In

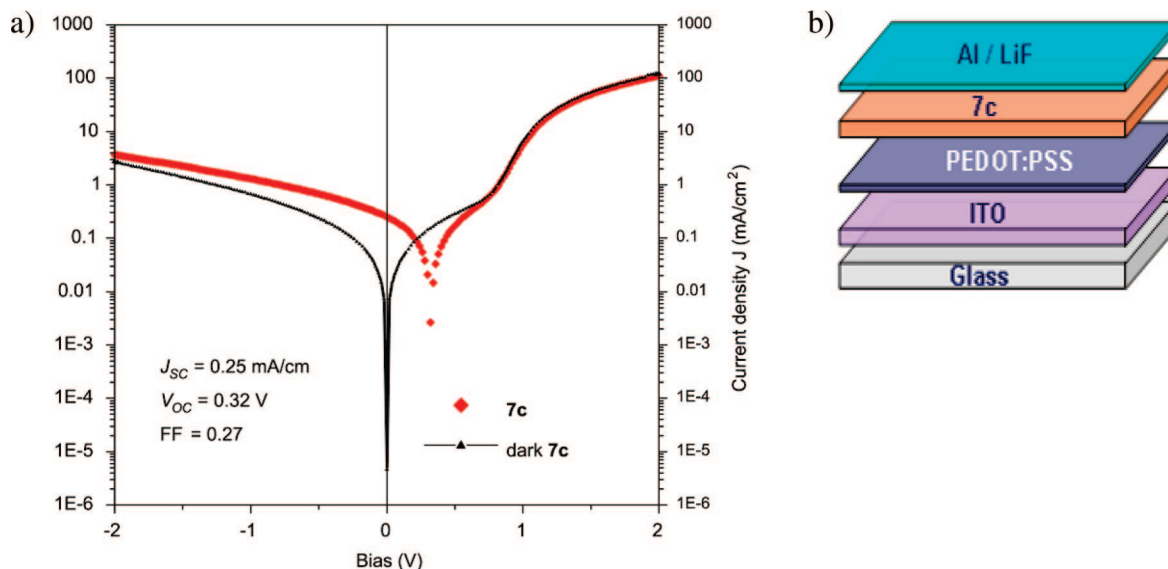


FIGURE 4. (a) Semilogarithmic plot of the J/V characteristics in the dark and under illumination and (b) schematic architecture for **7c** photovoltaic devices.

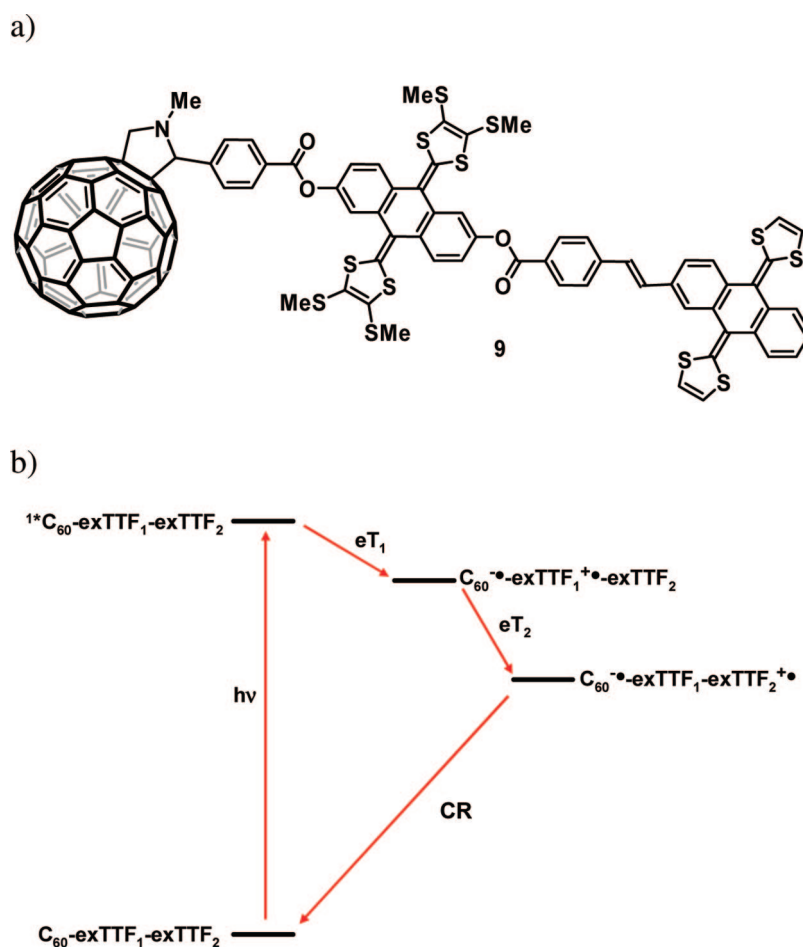


FIGURE 5. (a) Chemical structure of linear C₆₀/exTTF₁/exTTF₂ triad **9**. (b) Schematic diagram of the photophysical behavior of triad **9**.

fact, linear triads, tetrads, etc., involving fullerenes (i.e., electron acceptor) and several porphyrins and/or ferrocene (Fc) as donors, have led to remarkable results.²²

To this end, we have developed a series of C₆₀/exTTF arrays with different D_mA_n stoichiometries. Particularly noteworthy is the linear C₆₀/exTTF₁/exTTF₂ conjugate **9**

(Figure 5).²³ Here, a redox gradient was obtained by introducing methylthio (SMe) groups to the exTTF adjacent to the fullerene unit (i.e., exTTF₁), whereas a second unsubstituted exTTF (i.e., exTTF₂) is connected to this one, in a far off position from the fullerene. Fundamental in this context is that replacing the H atoms of the 1,3-

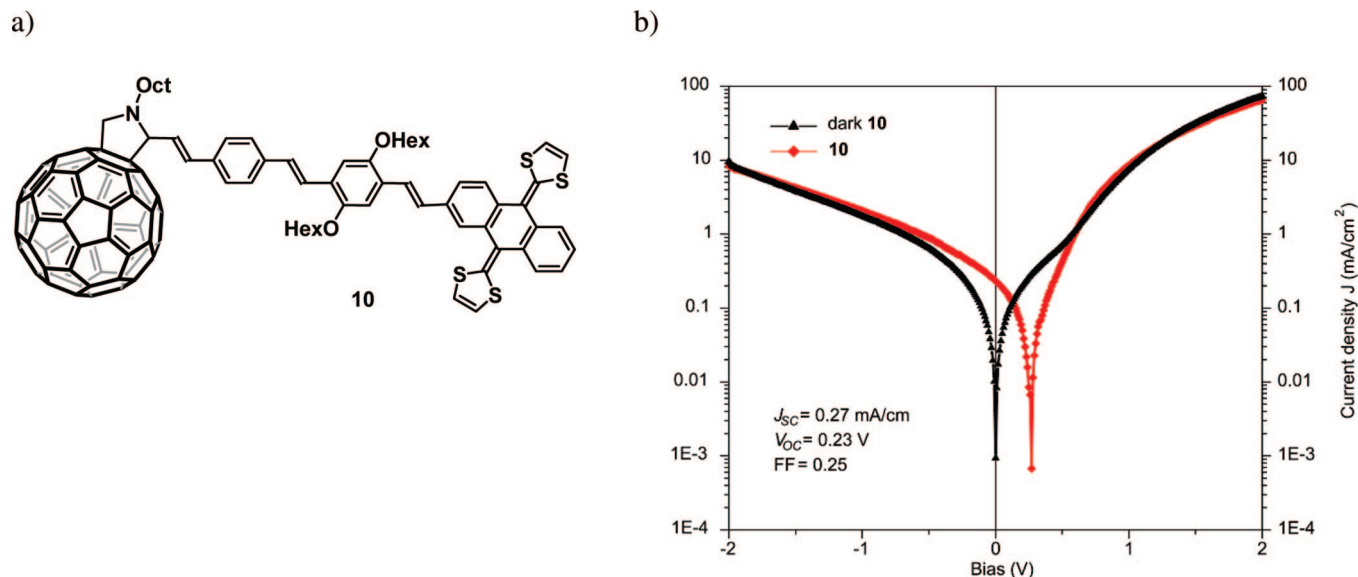


FIGURE 6. (a) Chemical structure of triad **10**. (b) Semilogarithmic plot of the J/V characteristics for pure **10**.

dithiole rings of exTTF with, for example, $-\text{SCH}_3$ groups, creates consequences in anodically shifted oxidation potentials (i.e., ca. 250 mV).^{9b}

Steady-state and time-resolved photolytic techniques confirm that, upon photoexcitation of the fullerene chromophore in **9** as well as in its analogue **8**, a rapid ($1.25 \times 10^{10} \text{ s}^{-1}$) and efficient charge separation generates a radical ion pair state. Typical lifetimes range between 54 and 460 ns, with the longer values found in more polar solvents, indicating dynamics located in the “normal region” of the Marcus curve. Such values correspond to a nearly 3-fold stabilization relative to what has been gathered for **3–5**. Next, subsequent charge shifts transform in **9** the adjacent radical ion pair (i.e., $\text{C}_{60}^{\bullet-}/\text{exTTF}_1^{\bullet+}/\text{exTTF}_2$) into the distant radical ion pair (i.e., $\text{C}_{60}^{\bullet-}/\text{exTTF}_1/\text{exTTF}_2^{\bullet+}$) (Figure 5b),²⁴ for which we determined lifetimes of up to 111 μs in *N,N*-dimethylformamide (DMF). In the $\text{C}_{60}^{\bullet-}/\text{exTTF}_1/\text{exTTF}_2^{\bullet+}$ state, a larger donor–acceptor separation (center–center distances $\sim 30 \text{ \AA}$) minimizes the coupling between the reduced acceptor and the oxidized donor. Analysis of the charge recombination kinetics shows that a stepwise mechanism accounts for the unusually long lifetimes.

In a photovoltaic context, it is necessary to control the assembly of donor–acceptor hybrids, both in solution and at surfaces. Varying the distance and the morphology, for example, of these structures changes the band-gap energies, electronic conduction, or transport features. The formation of long-lived radical pairs is just one of the many aspects to consider for the preparation of efficient PV devices. The weak light absorption of the previous $\text{C}_{60}/\text{exTTF}$ hybrids seems to be the main cause of the low PV performances. Because the conversion of sunlight into chemical energy requires an efficient absorption and transduction of incident light by antennae systems,^{3,7c,25} a further step in the construction of suitable $\text{C}_{60}/\text{exTTF}$ ensembles should include the linking of both redox units by means of a light-harvesting moiety acting as an antenna.²⁶

A leading example of $\text{C}_{60}/\text{antenna}/\text{exTTF}$ arrays is compound **10**, in which a π -conjugated *p*-phenylenevinylene oligomer links the C_{60} and exTTF fragments (Figure 6).^{27,28} As expected, an energy gradient assists in funneling the singlet excited-state energy from the antenna to the fullerene, which, in turn, powers an exothermically driven charge-transfer reaction that yields a 465 ns lived radical ion pair state, $\text{C}_{60}^{\bullet-}/\text{antenna}/\text{exTTF}^{\bullet+}$, in benzonitrile.

A reasonably strong absorbing maximum at 451 nm ($\epsilon = 49\,000 \text{ mol}^{-1} \text{ cm}^3 \text{ dm}^{-1}$) and a notable radical ion pair lifetime led us to evaluate the PV response of **10**. A prototype PV device was fabricated using **10** as the only photoactive molecular material. However, only modest device performances ($J_{\text{sc}} = 0.27 \text{ mA/cm}^2$; FF = 0.25; and $V_{\text{oc}} = 0.23 \text{ V}$; an efficiency conversion of $\sim 0.02\%$) (Figure 6b) were observed.²⁹ These values have been attributed to excessive losses because of, for example, charge recombination, as seen in a variety of $\text{C}_{60}/\text{donor}$ conjugates.³⁰

To compare the electronic transport properties with the previous systems, we synthesized the $\text{C}_{60}/\text{antenna}/\text{exTTF}$ conjugates **11** and **12** and performed a detailed kinetic analysis on these derivatives. In these structures, a chiral binaphthyl unit, which breaks the electronic communication between C_{60} and exTTF,³¹ and an *o*-1,4-dialkoxy-2,5-bis[2-(2-thienyl)vinyl]benzene fragment, respectively, (see Figure 7) were used as bridges between the C_{60} and exTTF units.³² The light-harvesting features of binaphthyl and *o*-1,4-dialkoxy-2,5-bis[2-(2-thienyl)vinyl]benzene are evidenced by strong absorption features in the blue spectral region ($\lambda_{\text{max}} \sim 465 \text{ nm}$).

Dyads **11** and **12** were first investigated in solution. Both systems exhibit, upon photoexcitation, the formation of the corresponding $\text{C}_{60}^{\bullet-}$ and $\text{exTTF}^{\bullet+}$ radical ion pair states. Lifetimes as different as 25 and 0.7 μs (CH_2Cl_2) were determined for **11** and **12**, respectively. These observations could be accounted for by the different electronic coupling between the redox-active units (i.e., C_{60} and exTTF).

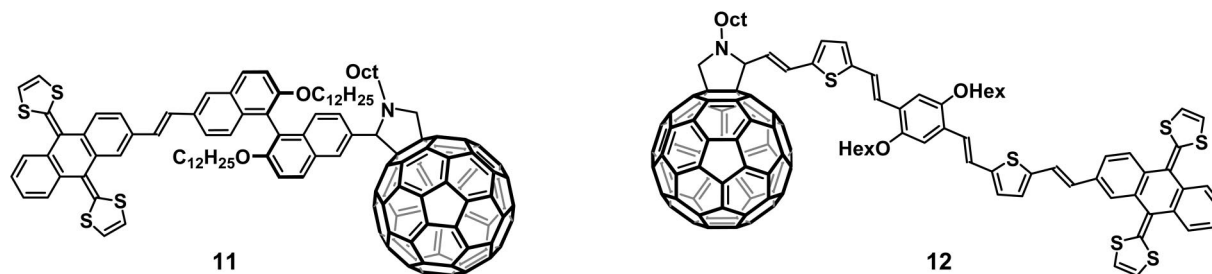


FIGURE 7. Topologically different C₆₀/antenna/exTTF dyads **11** and **12**.

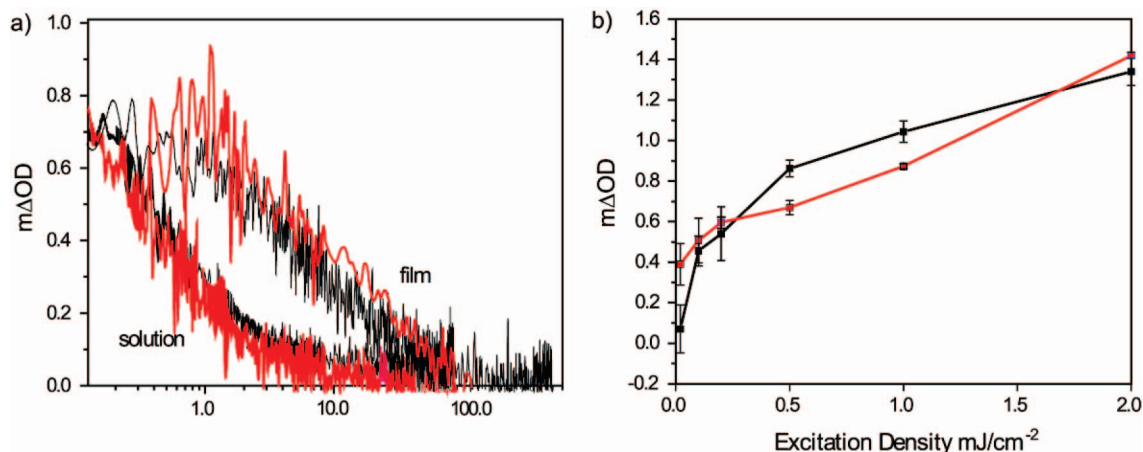


FIGURE 8. (a) Electron recombination dynamics at high (black line) and low (red line) excitation densities for a dichloromethane solution and film of dyad **12**. The signals have been normalized to clearly exhibit the dynamics ($t = 0.1 \mu\text{s}$). (b) Laser-power dependence of the transient absorption signal for dyad **12** ($\lambda_{\text{probe}} = 830$, and $\lambda_{\text{ex}} = 355$ nm); red line, film; black line, solution.

This work in solution was followed by solid-state measurements. In particular, molecular films were fabricated by drop casting **11** and **12**. Unlike **12**, in which a significant light scattering prevents the determination of a precise absorption spectrum (Figure 8), ground-state absorption of **11** in solution and in the solid state is identical. In addition, the recombination dynamics determined for **11** in film are approximately 10 times faster than those observed in solution ($\tau_{\text{film}} = 2.1 \mu\text{s}$ versus $\tau_{\text{solution}} = 25 \mu\text{s}$). In sharp contrast, the recombination dynamics for **12** in the film are one order of magnitude slower than those observed in solution ($\tau_{\text{film}} = 7 \mu\text{s}$ versus $\tau_{\text{solution}} = 0.7 \mu\text{s}$). Moreover, its decay is largely nonexponential and independent upon excitation density.

The planar and conjugated nature of the bridge in **12** could induce the formation of molecular aggregates by means of aromatic stacking interactions. The noncovalent species thus formed would be responsible for the considerable light scattering observed in the absorption spectra of the films. Atomic force microscopy studies, in fact, corroborate this assumption and would also explain the nonlinear behavior observed for the film studies.³²

The accelerated recombination dynamics for **11**, accounted for by an efficient *intermolecular* electronic coupling between the C₆₀^{•-} and exTTF^{•+} radical pairs, prevents an attractive application in the fabrication of PV devices. In contrast, the slow recombination dynamics observed for **12** in the solid film, which could be due to the dissociation of the photogenerated radical pairs to free carriers, and subsequent trapping of them on low-energy

sites within the film can contribute to a higher efficient photovoltaic device function.

exTTF-Modified Single-Walled Carbon Nanotubes (SWNTs) for Light-Induced Electron-Transfer Interactions

Our most recent contribution en route to versatile donor-acceptor nanosized ensembles for photoinduced electron transfer has been the preparation of carbon nanotubes (CNTs) endowed with TTF (**13**) or π -extended TTF (**14**) electron-donor moieties.

The unique electronic, physicochemical, and mechanical properties of CNTs render them ideal candidates for molecular-scale electronic applications. In this context, controlled modification of their surface with multifunctional groups, chromophores, electron donors, biomolecules, etc., is required to fully realize their potential in nanotechnology. Chemical functionalization is an especially attractive goal because it contributes toward the improvement of CNT solubility and CNT processability and allows for the unique properties of CNTs to be coupled to those of other materials.³³

SWNTs endowed with covalently linked TTF or exTTF derivatives were prepared using simple esterification reactions (see Figure 9 for representative examples).³⁴ Time-resolved spectroscopy helped to identify the reduced SWNT and oxidized TTF and/or exTTF as metastable states in a series of novel donor-acceptor nanoconjugates.

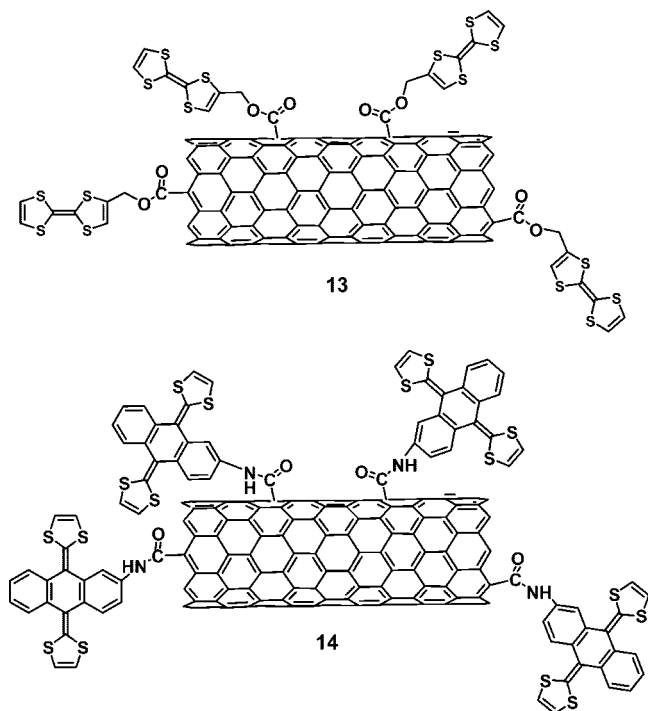


FIGURE 9. Examples of covalently linked SWNT/TTF and SWNT/exTTF nanoensembles.

Following nanosecond excitation of fine dispersions of SWNT/TTF and SWNT/exTTF in tetrahydrofuran (THF), the well-known signatures of the TTF and exTTF radical cations were observed at 440 and 660 nm, respectively. In the NIR region of the spectrum, the radical-cation absorptions of the donor fragments are negligible and the van Hove singularities of SWNTs constitute the major absorbing species. Overall, remarkable lifetimes, in the range of hundreds of nanoseconds, are noted. Most important is that we have achieved, *for the first time* in SWNTs endowed with electron-donor fragments, a control over the rate of electron transfer (i.e., charge separation and charge recombination) by either systematically altering the relative donor–acceptor separations or integrating different electron donors.

Whereas covalent functionalization may cause dramatic changes for the electronic properties of SWNTs, π – π interactions between the aromatic surfaces of both electroactive molecules leave the graphitic structure intact. Preliminary results indicate that the supramolecular approach also produces efficient electron-transfer processes, forming stable ion radical pairs.³⁵ These results pave the way toward the use of CNTs as appealing and promising materials for PV applications.

Summary and Outlook

Pairing [60]fullerene with the potent electron-donor TTF and more specifically with its *p*-quinonoid congener (exTTF) has resulted in an outstanding family of photo- and electroactive conjugates of interest for applications in research areas, such as artificial photosynthesis and photovoltaics. The aromatization undergone by the exTTF unit upon oxidation is a crucial factor in the stabilization

of the photogenerated radical ion pairs, i.e., C₆₀^{•–} and exTTF^{•+}. The combination of exTTF with C₆₀ in diverse stoichiometries and by means of different linkers allows for long-lived charge-separated states to be reached with lifetimes ranging from nanoseconds to hundreds of *microseconds*. These long-lived radical pairs are known to play a critical role in the conversion of sunlight into chemical power (photosynthesis) or electricity (photovoltaics). Nonetheless, those values, most of them extracted from solution studies, cannot be directly extrapolated to the solid state, and hence, a thorough study of this family of C₆₀-based systems in film is required to find a better and more detailed understanding of the relationship existing between the molecular structure, electron-transfer dynamics, and device function. In this realm, further work is coming relative to the incorporation of new supramolecular exTTF-based nanoensembles to this family.³⁶ Although the energy conversion efficiencies reported thus far for molecular photovoltaic devices are far away from the values published for those polymer-containing bulk heterojunction solar cells, for which values around 5% have recently been reported,² we do expect that the investigations presented in this Account could contribute positively to the implementation of this functional family of compounds to attain improved energy conversion efficiencies in molecular materials.

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