

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/49810551>

A Fully Conjugated TTF- π -TCAQ System: Synthesis, Structure, and Electronic Properties

ARTICLE *in* CHEMISTRY - A EUROPEAN JOURNAL · MARCH 2011

Impact Factor: 5.73 · DOI: 10.1002/chem.201002674 · Source: PubMed

CITATIONS

19

READS

28

9 AUTHORS, INCLUDING:



Jose Santos

Madrid Institute for Advanced Studies

21 PUBLICATIONS 392 CITATIONS

[SEE PROFILE](#)



Beatriz Illescas

Complutense University of Madrid

75 PUBLICATIONS 2,365 CITATIONS

[SEE PROFILE](#)



Javier Adrio

Universidad Autónoma de Madrid

87 PUBLICATIONS 1,929 CITATIONS

[SEE PROFILE](#)

A Fully Conjugated TTF- π -TCAQ System: Synthesis, Structure, and Electronic Properties**

José Santos,^[a] Beatriz M. Illescas,^[a] Nazario Martín,^{*,[a, b]} Javier Adrio,^[c] Juan C. Carretero,^{*,[c]} Rafael Viruela,^[d] Enrique Ortí,^{*,[d]} Fabian Spänig,^[e] and Dirk M. Guldi^{*,[e]}

Abstract: The synthesis of the first fully conjugated tetrathiafulvalene–tetracyano-*p*-quinodimethane ((TTF)–TCNQ)-type system has been carried out by means of a Julia–Kocienski olefination reaction. In particular, a tetracyanoanthraquinodimethane (TCAQ) formyl derivative and two new sulfonylmethyl-exTTFs (exTTF = 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole)—prepared as new building blocks—were linked. A variety of experimental conditions reveal that the use of sodium hexamethyldisilazane (NaHMDS) as base in THF afforded the *E* olefins with excellent stereoselectivity. Theoretical calculations

at the B3LYP/6-31G** level point to highly distorted exTTF and TCAQ that form an almost planar stilbene unit between them. Although calculations predicted appreciable electronic communication between the donor and the acceptor, cyclic voltammetric studies did not substantiate this effect. It was only in photophysical assays that the electronic communication emerged in the form of a charge-transfer (CT) absorption and emission. Once photoexcited

(i.e., the locally excited state or excited charge-transfer state), an ultrafast, sub-picosecond charge separation leads to a radical ion pair state in which the spectroscopic features of the radical cation of exTTF as well as the radical anion of TCAQ are discernable. The radical ion pair is metastable and undergoes a fast ((1.0 ± 0.2) ps) charge recombination to reconstitute the electronic ground state. Such ultrafast charge separation and recombination processes come as a consequence of the very short vinyl linkage between the two electroactive units.

Keywords: charge transfer • conjugation • donor–acceptor systems • olefination • tetrathiafulvalene

[a] Dr. J. Santos, Dr. B. M. Illescas, Prof. Dr. N. Martín
Departamento de Química Orgánica
Facultad de Ciencias Químicas, Universidad Complutense
Ciudad Universitaria, 28040 Madrid (Spain)
Fax: (+34) 91-394-4103
E-mail: nazmar@quim.ucm.es

[b] Prof. Dr. N. Martín
IMDEA-Nanociencia, Facultad de Ciencias
Universidad Autónoma, Cantoblanco, 28049 Madrid (Spain)

[c] Dr. J. Adrio, Prof. Dr. J. C. Carretero
Departamento de Química Orgánica, Facultad de Ciencias
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: (+34) 914973966
E-mail: juancarlos.carretero@uam.es

[d] Dr. R. Viruela, Prof. Dr. E. Ortí
Instituto de Ciencia Molecular, Universidad de Valencia
46980 Paterna (Spain)
Fax: (+34) 963543274
E-mail: enrique.orti@uv.es

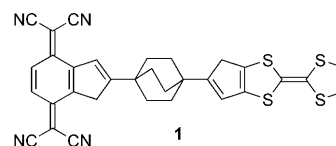
[e] Dr. F. Spänig, Prof. Dr. D. M. Guldi
Friedrich-Alexander-Universität Erlangen-Nürnberg
Department of Chemistry and Pharmacy
& Interdisciplinary Center for Molecular Materials (ICMM)
Egerlandstrasse 3, 91058 Erlangen (Germany)
Fax: (+49) 9131-852-8307
E-mail: dirk.guldi@chemie.uni-erlangen.de

[**] TTF = tetrathiafulvalene. TCAQ = tetracyanoanthraquinodimethane.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201002674>.

Introduction

Electron donors (D) and electron acceptors (A) have been studied in chemistry for many years. A particularly important aspect focuses on electronic interactions, either inter- or intramolecular. To this end, intermolecular interactions between D and A have resulted in the development of charge-transfer (CT) complexes and/or salts that exhibit electrically conducting, superconducting, and magnetic properties.^[1] The mode in which the two electroactive moieties interact in covalently connected D–bridge–A systems strongly depends on the type of connectivity that exists between them.^[2] D- σ -A systems, for example, in which the linkage between D and A is given by a bridge of sigma bonds, have received a great deal of attention. It was in 1974 that Aviram and Ratner postulated that a single molecule such as **1** (TTF- σ -TCNQ (TCNQ = tetracyano-*p*-quinodimethane); Scheme 1)



Scheme 1. Chemical structure of the proposed Aviram–Ratner rectifier (**1**) formed by TTF (tetrathiafulvalene) and TCNQ (tetracyano-*p*-quinodimethane) units covalently connected through sigma bonds.

could rectify the electrical current.^[3] In fact, this seminal paper has been considered to be a cornerstone of molecular electronics.^[4] D- σ -A-type systems have also been studied as artificial photosynthetic mimics. Here, photoexcitation is the inception of an electron transfer from the electron donor to the electron acceptor to afford a charge-separated state. The lifetime of the latter is essential for photovoltaic applications.^[5] Finally, the implications of D- σ -A systems on the field of organic molecular wires should be mentioned.^[6]

Push-pull chromophores, in which π -conjugated bridges link D and A (D- π -A), constitute an important class of compounds. It is their properties as second- and third-order nonlinear optical (NLO) materials that stand out among many other physicochemical properties.^[7] The possibility of tuning their optical and electrochemical band gaps renders D- π -A systems as appealing components for future optical-processing device applications.^[8]

Among the different electron-donor units used for the preparation of D- π -A molecules that show NLO responses, 1,3-dithiole derivatives have been widely used since the pioneering work by the groups of Katz and Lehn.^[9] More recently, some of us introduced TTF as a donor in novel NLO materials.^[10] Similarly, π -extended TTF (2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF)) has also been used as an electroactive component in materials that exhibit second-order NLO features.^[11]

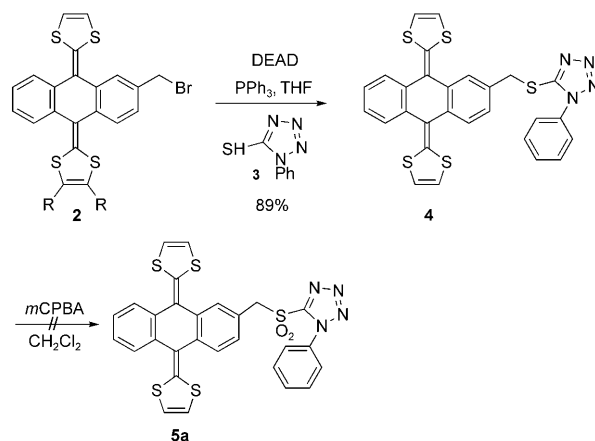
In the present paper, we report on a new family of D- π -A systems in which exTTF and tetracyanoanthraquinodimethane (TCAQ) are used as D and A, respectively. To the best of our knowledge, this is the first example in which exTTF and TCAQ derivatives are covalently connected through a fully π -conjugated bridge. The preparation of exTTF- π -TCAQ was a synthetic challenge, because no complementary exTTF and TCAQ derivatives endowed with suitable groups for further olefination reactions have so far been available. Theoretical calculations have been carried out at the density functional theory (DFT) level to gather information about the geometrical and electronic properties of the new push-pull exTTF- π -TCAQ system. As a complement, several physicochemical assays were conducted by means of electrochemistry and photophysics to confirm the electronic communication between D and A in the electronic ground state as well as in the electronic excited state.

Results and Discussion

Synthesis and characterization: The synthesis of the highly functionalized, fully conjugated target D- π -A **11** was not straightforward and required the previous preparation of the respective D and A fragments endowed with the appropriate functional groups to carry out the final olefination reaction under mild reaction conditions, compatible with the existing sensitive functionalization. For this purpose, we decided to prepare the new type of sulfonylmethyl-exTTF compounds (**5**) as potential highly reactive olefination part-

ners in the subsequent Julia-Kocienski reaction with the formyl-containing TCAQ. However, whereas the formyl-TCAQ is readily available following the synthetic protocol previously reported in our group,^[12] the preparation of the sulfones **5** proved to be more challenging and required us to test different synthetic approaches.

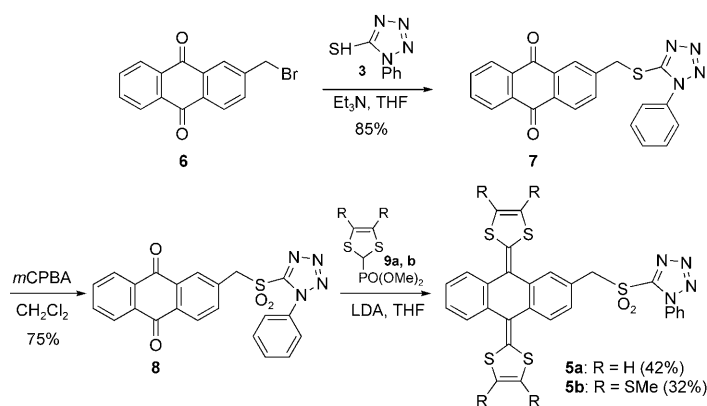
The first attempt to obtain **5a** was carried out from the previously reported compound 2-bromomethyl-exTTF (**2**; Scheme 2).^[13] Reaction of **2** with 1-phenyl-1*H*-tetrazole-5-



Scheme 2. Synthesis of sulfonylmethyl-exTTF **4**, and failed attempt to form sulfonylmethyl-exTTF **5a**.

thiol (**3**) in THF under Mitsunobu-type reaction conditions (PPh_3 /diethyl azodicarboxylate (DEAD)) led efficiently to sulfonylmethyl-exTTF **4**. However, the seemingly straightforward oxidation of **4** to the desired sulfone **5a** suffered from extensive decomposition regardless of the oxidant and reaction conditions. This experimental finding could be ascribed to the strong reducing character of the exTTF moiety, which, in the presence of an oxidant such as *meta*-chloroperoxybenzoic acid (*m*CPBA), would undergo an initial electron-transfer process with the formation of ion radical intermediates that would finally provide the observed complex crude reaction mixture.

The synthesis of sulfonylmethyl-exTTFs **5** was successfully achieved following an alternative synthetic strategy in which the TTF units were introduced after the thioether/sulfone oxidation (Scheme 3). Thus, the straightforward alkylation of thiol **3** with 2-bromomethylantraquinone (**6**) gave the sulfonylmethylantraquinone derivative **7**, which was later oxidized to sulfone **8** by using *m*CPBA (64% overall yield). The further Wadsworth-Emmons olefination reaction of the anthraquinone (AQ) derivative **8** with phosphonates **9a,b** to provide the desired sulfonylmethyl-exTTFs **5** proved to be highly dependent on the base and reaction conditions (see Table S1 in the Supporting Information). The best results were obtained by employing a great excess amount of phosphonate and lithium diisopropylamide (LDA; 6 equiv each) in THF. Under these conditions, compounds **5a,b** could be isolated in moderate yields after final silica gel chromato-

Scheme 3. Synthesis of sulfonylmethyl-exTTFs **5a,b**.

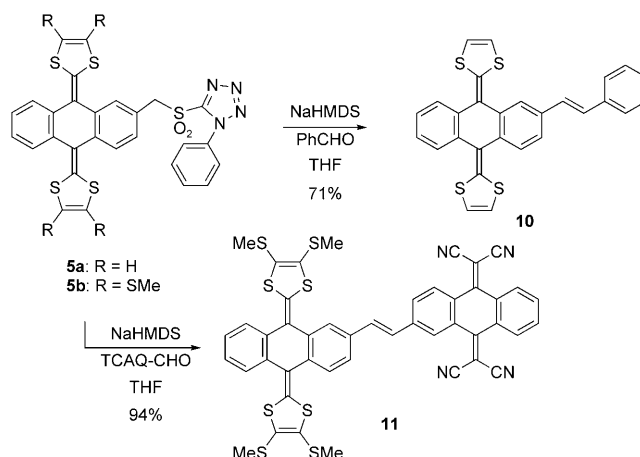
graphic purification (42 and 32% yield, respectively). At least in part, the difficulty of this reaction probably stems from the high acidity of the benzylic hydrogen atoms in α position to the sulfone functionality.

All new compounds were fully characterized on the basis of analytic and spectroscopic methods. The ^1H NMR spectra of sulfonylmethyl-exTTFs **5a,b** show, in addition to the aromatic protons, the presence of the exTTF moiety as two singlets around $\delta=6.3$ ppm for **5a** and the four SMe groups at around $\delta=2.40$ ppm for **5b**. The methylene group in α to the sulfone functionality appears as an AB system for **5a** ($\delta \approx 4.9$ ppm, $J=10.5$ Hz) and as a singlet at $\delta \approx 5.0$ ppm for **5b**. The chemical structure of compounds **5a,b** was ascertained by means of mass spectrometry, which showed the molecular ions at 602.0 and 786.0, respectively.

1-Phenyl-1*H*-tetrazol-5-yl sulfones **5a,b** are suitably functionalized for further Julia–Kocienski olefinations by reaction with formyl-containing compounds. This reaction leads to *E* olefins with excellent stereoselectivity when benzylic sulfones and aromatic aldehydes are employed.^[14] To check the performance of compounds **5a,b** in the Julia–Kocienski reaction, styryl-exTTF **10** was first synthesized by reaction of **5a** with benzaldehyde by employing sodium hexamethyldisilazane (NaHMDS) as base (THF, -78°C to RT; 71% yield).

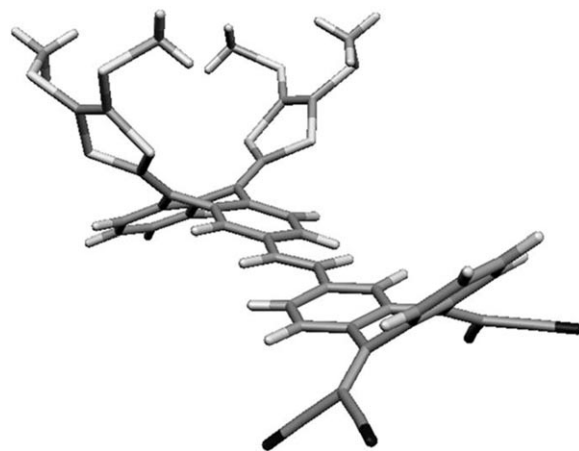
Next, we tested the Julia–Kocienski reaction in the synthesis of the desired exTTF- π -TCAQ derivative **11** (Scheme 4). Previous attempts in our group to prepare this type of compound, either by means of Wittig olefination or Heck coupling reaction between appropriately functionalized exTTF and TCAQ derivatives, were unsuccessful, likely due to the rapid formation of the charge-transfer complex formed between the two strong electroactive moieties. Gratifyingly, when we carried out the Julia–Kocienski reaction of **5b** with TCAQ-CHO under the mild reaction conditions developed for the model alkene **10** (NaHMDS, THF, -78°C), exTTF- π -TCAQ **11** was obtained as a black solid in almost quantitative yield (94%).

^1H and ^{13}C NMR spectra of compound **11** show the expected signals that correspond to both exTTF and TCAQ

Scheme 4. Synthesis of reference compound **10** and exTTF- π -TCAQ **11** by Julia–Kocienski olefination reaction.

moieties. In addition, the vinyl protons appear at $\delta=7.20$ ppm ($J=16.2$ Hz), thus confirming the *E* stereochemistry (see the Supporting Information).

Molecular and electronic structures: The molecular geometry of compound **11** was theoretically optimized starting from different geometrical conformations. The tetramethylthio-exTTF (TTM-exTTF) and TCAQ molecules of which **11** is comprised were also calculated as reference compounds. B3LYP/6-31G** calculations predicted that the most stable conformation of compound **11** corresponds to that depicted in Figure 1, in which the exTTF and TCAQ moieties are folded up and down, respectively. The conformation in which both moieties are folded in the same direction was found to be basically isoenergetic and differed less than 0.2 kcal mol^{-1} . Other possible conformations that resulted from the internal rotation around the C–C single bonds that link the ethylene bridge to the exTTF and TCAQ units were calculated within 2.0 kcal mol^{-1} .

Figure 1. Minimum-energy conformation calculated for **11** at the B3LYP/6-31G** level.

The exTTF unit in compound **11** adopts a butterfly- or saddlelike structure, similar to that calculated for unsubstituted exTTF,^[15,16] and consistent with the crystal structures observed for different exTTF derivatives.^[17–19] To relieve the short contacts between the sulfur atoms and the hydrogen atoms in the *peri* positions, the central ring of the anthracene unit folds in a boat conformation along the C9–C10 vector by an average angle of 38.4°. This value compares well to the X-ray value experimentally found for the TTM-exTTF molecule (38°),^[17] for which an almost identical value (38.3°) is theoretically calculated. The dithiole rings are tilted by 33.9° with respect to the plane defined by the anthracene atoms C11–C12–C13–C14. Furthermore, the dithiole rings are folded inward by 18.7° along the S–S axes.

The TCAQ moiety in compound **11** also adopts a saddlelike structure to alleviate the steric contacts between the cyano groups and the *peri* hydrogen atoms. The anthracene unit is folded up along the C9–C10 vector by 35.6°, and the C(CN)₂ units are tilted down by an average angle of 30.9° with respect to the C11–C12–C13–C14 plane. These folding angles are in very good correlation with the X-ray values reported for the TCAQ molecule (33.9 and 30.4°, respectively).^[20]

The lateral benzene rings of the anthracene unit in both the exTTF and the TCAQ moieties present an aromatic structure because all the C–C bonds have a length of (1.40 ± 0.01) Å. It is important to note that the benzene rings in the central part of the molecule are conjugated through the ethylene bridge and form an almost planar *trans*-stilbene unit (see Figure 1).

Figure 2 shows the atomic orbital (AO) composition of the highest-occupied (HOMO–2 to HOMO) and lowest-unoccupied (LUMO to LUMO+2) molecular orbitals of **11**. The HOMO (–5.10 eV) and HOMO–1 (–5.63 eV) are localized on the electron-donor exTTF unit and are calculated at slightly lower energies than the HOMO (–4.90 eV) and HOMO–1 (–5.43 eV) of the TTM-exTTF molecule. In contrast, the LUMO (–3.64 eV) and LUMO+1 (–2.71 eV) spread over the electron-acceptor TCAQ unit and are obtained at slightly higher energies than the LUMO (–3.75 eV) and LUMO+1 (–2.80 eV) of the TCAQ molecule. Therefore, compound **11** presents a small HOMO–LUMO energy gap of 1.46 eV, and low-energy charge-transfer absorption bands are to be expected in the electronic spectrum. The electronic communication between the donor and acceptor units in **11** is evidenced by the shift to lower energies of the HOMOs and to higher energies of the LUMOs and by the charge transfer of 0.10 e that takes place from the exTTF-ethylene environment to the TCAQ moiety in the electronic ground state. It is also to be noted that the HOMO–2 and the LUMO+2 are mainly localized over the central stilbene unit, and their AO compositions are indeed similar to those calculated for the HOMO and LUMO of stilbene.

Electrochemistry: The redox properties of exTTF–TCAQ (**11**) were examined by cyclic voltammetry (CV) and com-

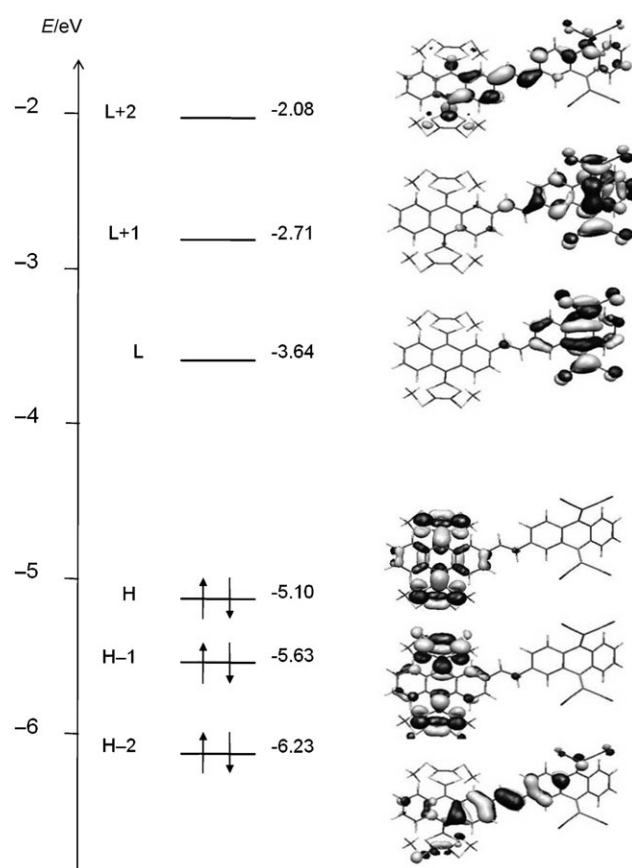


Figure 2. Electron-density contours (0.03 ebohr^{–3}) and orbital energies calculated for the HOMOs and LUMOs of **11** at the B3LYP/6-31G** level. H and L denote HOMO and LUMO, respectively.

pared with those of TTM-exTTF and TCAQ (Figure 3 and Table S2 in the Supporting Information). The measurements were carried out in dichloromethane as solvent, using a glassy carbon working electrode, a standard Ag/AgNO₃ reference electrode, and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte.

Both exTTF and TCAQ undergo, in contrast to related TTF and TCNQ, single two-electron redox processes that lead to the corresponding dication (exTTF²⁺) and dianion

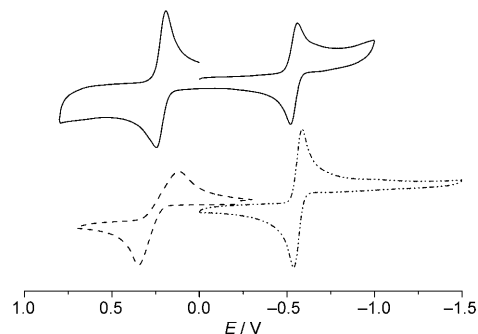


Figure 3. Cyclic voltammograms of **11** (—), TTM-exTTF (----), and TCAQ (–·–·) recorded in CH₂Cl₂ at 100 mV s^{–1} containing 0.1 M *n*Bu₄NClO₄ as supporting electrolyte.

(TCAQ²⁻) species. To this end, TTM-exTTF shows a quasi-reversible two-electron oxidation around +0.23 V ($E_{1/2}$), whereas the TCAQ reference undergoes a reversible ($\Delta E \approx 41$ mV) two-electron reduction around -0.56 V ($E_{1/2}$) that corresponds to the formation of the dianion.

For **11**, oxidation is discernable at +0.22 V ($E_{1/2}$) together with a reduction at -0.54 V ($E_{1/2}$). Both redox processes are reversible and involve two electrons. Electrochemically, we could not detect any appreciable impact on the oxidation and reduction of exTTF and TCAQ, respectively, despite the presence of both electroactive moieties that are connected through a conjugated ethylene bridge. The electrochemical band gap for **11** is approximately 0.80 V, which resembles those of related TTF-TCAQ systems.^[21]

The nature of the HOMO and LUMO, which are respectively localized on the electron-donor and -acceptor units (Figure 2), indicates that oxidation of **11** should mainly affect the exTTF moiety, whereas reduction concerns the TCAQ moiety. In a first approach, Koopman's theorem enabled us to relate the HOMO and LUMO energies with the electrochemical potentials of the first oxidation and reduction processes, respectively. Using this theorem and in contrast to what is experimentally observed, more positive/negative oxidation/reduction potentials had to be expected for **11** due to the lower energy of the HOMO (-5.10 eV) and the higher energy of the LUMO (-3.64 eV) than TTM-exTTF (-4.90 eV) and TCAQ (-3.75 eV), respectively. The reason for this apparent discrepancy is that Koopman's theorem is a one-electron approach and does not apply to the oxidation/reduction processes of **11**, which involve two electrons.

The dication and dianion species of **11** were computed at the B3LYP/6-31G** level to provide a deeper understanding of the oxidation/reduction processes. As depicted in Figure 4a, the minimum-energy structure calculated for **11**²⁺ corresponds to a conformation in which the TCAQ unit remains folded and the exTTF unit adopts an orthogonal conformation similar to those previously found for exTTF dications both theoretically^[15,16,22] and experimentally.^[18,19] Upon oxidation, the exocyclic C=C bonds that connect the dithiole rings to the anthracene unit elongate from 1.365 Å in neutral **11** to 1.482 Å in charged **11**²⁺. This lengthening allows for the rotation of the dithiole rings to minimize the steric interactions, and, as a consequence, the anthracene unit becomes planar. In the resulting conformation, the dithiole rings are nearly perpendicular to the anthracene plane and the SMe groups lie in the plane of the dithiole rings. This disposition of the SMe groups was already reported for the TTM-TTF dication.^[23,24] The net atomic charges calculated for **11**²⁺ by using the natural population analysis (NPA) algorithm indicate that the electrons have been mainly removed from the SMe-dithiole rings, which accumulate a charge of +0.91 e each, whereas the anthracene unit remains mainly neutral (+0.05 e). The exTTF moiety in **11**²⁺ is therefore constituted by an aromatic anthracene unit (14 π electrons) substituted by singly charged dithiole rings. This minimizes the coulombic repulsion between the posi-

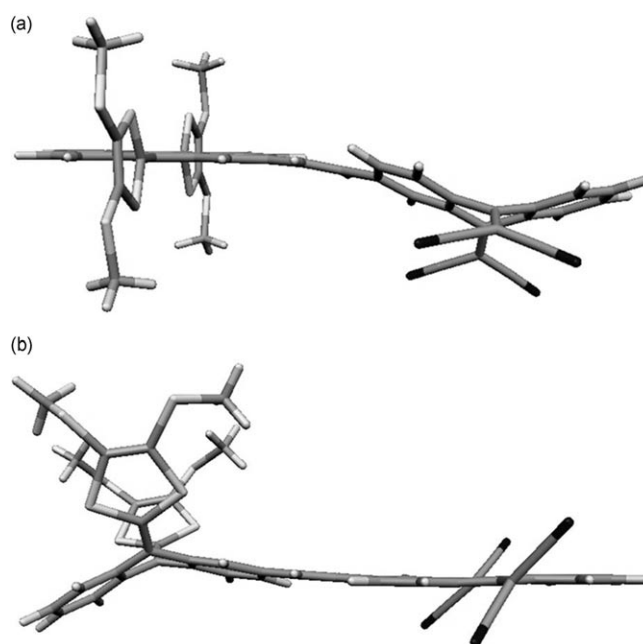


Figure 4. Minimum-energy conformations calculated for a) **11**²⁺ and b) **11**²⁻ at the B3LYP/6-31G** level.

tive charges in the dication and explains the fact that almost identical oxidation potentials are observed for **11** and for the reference compound TTM-exTTF.

Reduction of **11** to the dianion produces structural changes on the molecular geometry similar to those predicted upon oxidation, but they are now localized on the electron-acceptor TCAQ unit (see Figure 4b). For **11**²⁻, the exTTF unit preserves the saddlelike structure of the neutral molecule and the TCAQ unit becomes planar with the C(CN)₂ groups twisted out of the anthracene plane by an average angle of 45°. As for the exTTF unit, this geometrical reorganization is made possible by the elongation of the C=C exocyclic bonds that link the C(CN)₂ groups to the anthracene unit that lengthen from approximately 1.380 Å in **11** to approximately 1.475 Å in **11**²⁻ and allow rotation of the C(CN)₂ groups. The NPA charges calculated for **11**²⁻ indicate that the extra electrons are mainly supported by the C(CN)₂ groups (-1.80 e).

Photophysics: The electronic absorption spectra of exTTF-TCAQ (**11**) reflect the well-known absorptions of exTTF, with absorption maxima at 376 and 445 nm, redshifted about 10 nm in comparison to the reference,^[19] and TCAQ, with maxima in the UV region of the spectrum at 345, 302, and 280 nm,^[17] marginally redshifted.^[25] Additionally, new absorption features evolve in the red part of the spectrum, that is, between 500 and 800 nm, in which neither exTTF nor TCAQ absorbs. When varying the solvent polarity from nonpolar toluene to polar acetonitrile, the maximum of this new band shifts from about 590 nm to 620 nm. In light of the aforementioned results and in analogy with previous results,^[26] we assigned this new band to a charge-transfer feature, namely, a redistribution of charge density from the

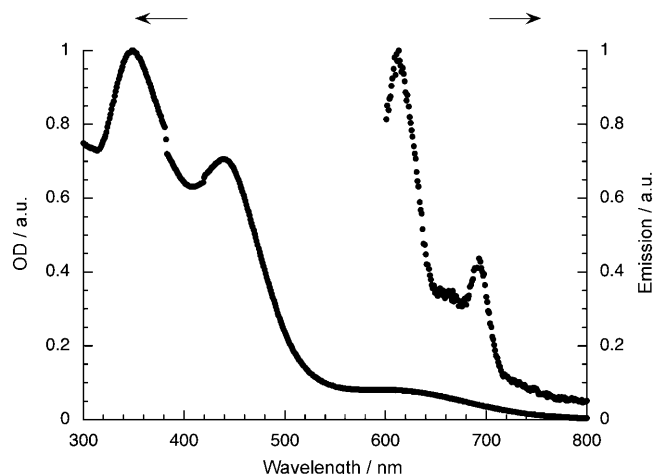


Figure 5. Absorption and emission ($\lambda_{\text{exc}} = 600$ nm) spectra of **11** recorded in toluene.

electron-donating exTTF to the electron-accepting TCAQ (Figure 5).

Vertical transitions to the lowest-energy electronic states were calculated for **11** in the presence of the solvent using the time-dependent DFT (TD-DFT) approach and the B3LYP/6-31G**-optimized ground-state geometry. TD-DFT calculations predict four CT states above 500 nm that result from electron excitations from the HOMO and HOMO–1, localized on the exTTF moiety, to the LUMO and LUMO+1, localized on the TCAQ unit. The first excited state corresponds to the HOMO→LUMO excitation and is calculated too low in energy (around 950–1000 nm) with an oscillator strength (f) of 0.08. The second excited state results from the HOMO–1→LUMO transition and occurs around 700 nm ($f=0.07$). The third and fourth excited states are very close in energy and result from a mixing of the HOMO–2→LUMO and HOMO→LUMO+1 excitations. The participation of the HOMO–2, which spreads over the central stilbene unit (Figure 2), enhances the intensity of the electronic transitions. The fourth state, which bears most of the intensity ($f=0.27$), shifts from 568 nm in toluene to 559 nm in acetonitrile.

The confirmation for the CT hypothesis came from fluorescence studies. Although the emissions of exTTF and TCAQ are almost completely quenched, a new emission in the 600 to 700 nm range—depending on the solvent—is discernable. In Figure 6, a 3D fluorescence plot of **11** is shown. Here, the strongly quenched exTTF emission around 500 nm is followed by the much stronger CT emission, with its maximum at 650 nm, as it evokes from the correlating CT absorption, respectively in THF.

Next, ultrafast laser flash photolysis experiments were carried out by employing either the 387 nm excitation wavelength (to photoactivate the singlet excited states of **11**) or the 660 nm excitation wavelength (to excite exclusively the CT transition).

Photoexcitation of exTTF at 387 nm generates an exTTF-centered excited state. Spectral characteristics of this very

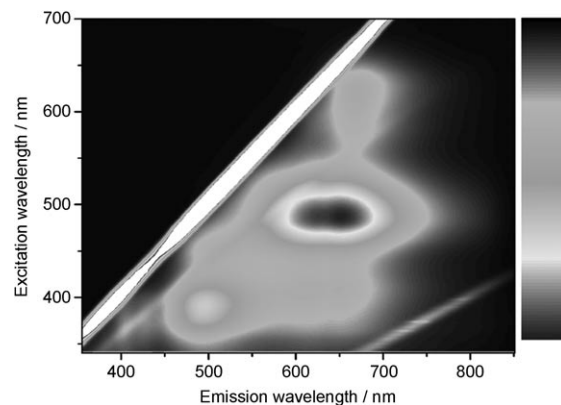


Figure 6. Three-dimensional fluorescence plot of **11** recorded in THF under argon (this figure is reproduced in color in the Supporting Information).

shortlived excited state (1.2 ps) are transient maxima around 465, 605, and 990 nm, as well as transient bleaching at around 450 nm (not shown). The short lifetimes (i.e., after 5 ps, no transient absorption remains) are rationalized by the presence of the sulfur atoms, with a strong second-order vibronic spin–orbit coupling. Going beyond our femtosecond experiments (i.e., 3 ns) we tested exTTF in nanosecond experiments following 355 nm excitation. However, outside of the 10 ns time window of the instrumental time resolution, no notable transients were detected.

When investigating **11** (Figure 7), instantaneously upon photoexcitation at 387 nm the singlet excited state features of exTTF are discernable (vide supra). These features of the localized exTTF excited state transform within the next 0.2 ps into a new transient with a minimum at 450 nm, maxima at 480/620 nm, and a shoulder at 680 nm. The transient—including the 450 nm minima and 680 nm shoulder—is in perfect agreement with the pulse-radiolysis-generated exTTF^{•+} radical cation (Figure S1 in the Supporting Information),^[27] whereas the transition at 620 nm is assigned to the TCAQ^{•–} radical anion (Figure S2).^[25] Notably, the additional spectral features of TCAQ^{•–} in the visible region with a minimum around 480 nm are buried beneath the much stronger exTTF^{•+} fingerprint. The correspondingly formed exTTF^{•+}–TCAQ^{•–} radical ion-pair state is shortlived and decays through recovery of the ground state. Times of 0.2 ps and (1.0±0.2) ps have been determined for the charge-separation and charge-recombination processes, respectively, in THF. Likewise, excitation at 660 nm, which generates the excited state of the CT state, causes these to convert into those of the exTTF^{•+}–TCAQ^{•–} radical ion-pair state (Figure S3).

The ultrafast charge-separation and charge-recombination dynamics are a result of the very short vinyl linkage. This provides not only strong electronic coupling, as it is discernable in form of CT absorption and emission, but also planarity of the molecule. As discussed above, an almost planar *trans*-stilbene unit is formed between the exTTF and TCAQ units through the ethylene bridge (Figure 1). Electronic de-

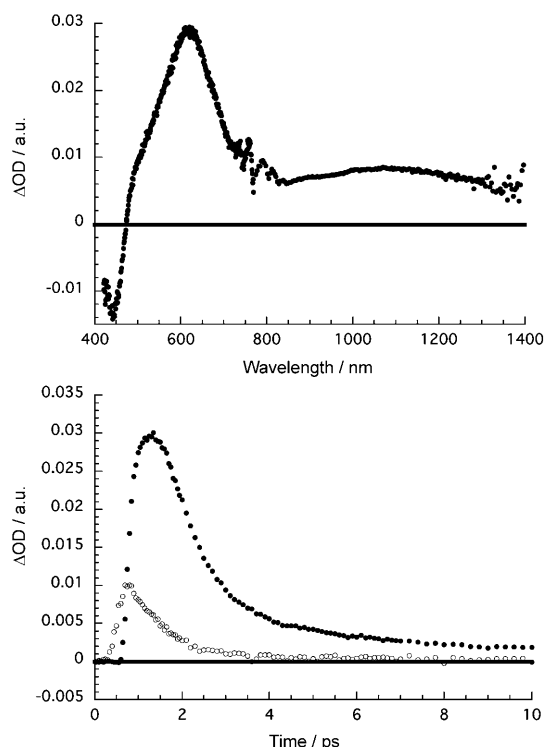


Figure 7. Top: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **11** in THF under argon with a time delay of 1.5 ps. Bottom: time absorption profiles of spectra shown above at 630 nm (filled circles), and 1060 nm (empty circles) monitoring the charge separation and charge recombination.

localization across this π -conjugated unit therefore enables strong interactions between the donor and acceptor parts of the molecule.

Conclusion

In summary, we have carried out the synthesis of a new building block for exTTFs, namely, sulfonylmethyl-exTTFs (**5**), suitably functionalized for Julia–Kocienski olefination reactions with different aldehydes. The reaction proceeds with an excellent stereoselectivity of the resulting *trans* olefin. As a proof-of-principle, the reaction of **5b** with the formyl-containing TCAQ afforded for the first time a fully conjugated TTF- π -TCAQ-type system (**11**). Theoretical calculations at the B3LYP/6-31G** level show a highly distorted molecule **11** at the exTTF and TCAQ moieties with an almost planar central stilbene unit. Importantly, the central vinyl spacer guarantees efficient connection of the electroactive donor and acceptor in the electronic ground state, and in turn gives rise to the formation of charge-transfer (CT) bands—both in absorption and emission—in the visible region of the spectrum. These experimental findings were nicely supported by TD-DFT calculations, which predict four CT states above 500 nm that result from electronic excitations from the HOMO and HOMO–1, localized on the exTTF moiety, to the LUMO and LUMO+1, localized on

the TCAQ unit. As a complement, the electronic excited state was probed by means of femtosecond transient-absorption spectroscopy. To this end, **11** reveals in the excited state ultrafast charge separation (0.2 ps)—that is, the formation of the radical cation of exTTF and the radical anion of TCAQ—and fast charge-recombination ((1.0 ± 0.2) ps) processes. The exTTF^{•+}–TCAQ^{•–} radical ion-pair state is formed either through a localized exTTF excited state or excited CT state.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (SFB 583), Cluster of Excellence (EAM), the Office of Basic Energy Sciences of the U.S., the MICINN of Spain (project nos. CTQ2008-00795/BQU, CTQ2009-08790, CTQ2009-07791, and Consolider-Ingenio CSD2007-00010 on Molecular Nanoscience), the CM (project nos. P-PPQ-000225-0505 and S2009/PPQ-1634), and the EU (FUNMOL FP7-212942-1) is greatly appreciated. J.S. is indebted to the MEC for a research grant.

- [1] a) Special issue on “Molecular Conductors” (Ed.: P. Batail), *Chem. Rev.* **2004**, *104*, 4887–5782; b) For a review on magnetic materials, see: J. S. Miller, *Inorg. Chem.* **2000**, *39*, 4392–4408; c) J. M. Williams, J. R. Ferrar, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo, *Organic Superconductors (including Fullerenes)*, Prentice Hall, Englewood Cliffs, **1992**; d) M. R. Bryce, *Chem. Soc. Rev.* **1991**, *20*, 355–390; e) P. Day, M. Kurmoo, *J. Mater. Chem.* **1997**, *7*, 1291–1295.
- [2] For general reviews, see: a) J. Garín, N. Martín in *TTF Chemistry. Fundamentals and Applications of Tetrathiafulvalene*, (Eds.: J. Yamada, T. Sugimoto), Springer, **2004**; b) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416–1455; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372–1409.
- [3] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277–283.
- [4] Special issue on “Organic Electronics and Optoelectronics” (Eds.: S. R. Forrest, M. E. Thompson), *Chem. Rev.* **2007**, *107*, 923–1386.
- [5] a) Special issue on “Organic Photovoltaics” (Eds.: J. L. Brédas, J. R. Durrant), *Acc. Chem. Res.* **2009**, *42*, 1689–1857; b) N. Martín, L. Sánchez, M. A. Herranz, B. Illescas, D. M. Guldi, *Acc. Chem. Res.* **2007**, *40*, 1015–1024; c) J. L. Segura, N. Martín, D. M. Guldi, *Chem. Soc. Rev.* **2005**, *34*, 31–47; d) J. L. Delgado, P.-A. Bouit, S. Filippone, M. A. Herranz, N. Martín, *Chem. Commun.* **2010**, *46*, 4853; e) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461; f) M. R. Wasielewski in *Photoinduced Electron Transfer*, (Eds.: M. A. Fox, M. Chanon), Elsevier, Amsterdam, **1988**.
- [6] a) D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski, N. Martín, *Chem. Soc. Rev.* **2009**, *38*, 1587–1597; b) E. A. Weiss, M. R. Wasielewski, M. A. Ratner, *Top. Curr. Chem.* **2005**, *257*, 103–134; c) D. K. James, J. M. Tour, *Top. Curr. Chem.* **2005**, *257*, 33–62.
- [7] S. Barlow, S. R. Marder in *Functional Organic Materials*, (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, **2007**, pp. 393–437.
- [8] M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248.
- [9] a) H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King, H. M. Gordon, *J. Am. Chem. Soc.* **1987**, *109*, 6561–6563; b) M. Blanchard-Desce, I. Ledoux, J.-M. Lehn, J. Malthête, J. Zyss, *J. Chem. Soc. Chem. Commun.* **1988**, 737–739.
- [10] a) R. Andreu, A. I. de Lucas, J. Garín, N. Martín, J. Orduna, L. Sánchez, C. Seoane, *Synth. Met.* **1997**, *86*, 1817–1818; b) A. I. de Lucas, N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, *Tetrahedron* **1998**, *54*, 4655–4662; c) J. Garín, J. Orduna, J. I. Rupérez, R. Alcalá, B. Villacampa, C. Sánchez, N. Martín, J. L. Segura, M. González, *Tetrahedron Lett.* **1998**, *39*, 3577–3580; d) M. González, N. Martín, J. L. Segura, J.

- Garín, J. Orduna, *Tetrahedron Lett.* **1998**, 39, 3269–3272; e) M. González, N. Martín, J. L. Segura, C. Seoane, J. Garín, J. Orduna, R. Alcalá, C. Sánchez, B. Villacampa, *Tetrahedron Lett.* **1999**, 40, 8599–8602; f) M. González, J. L. Segura, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, V. Hernández, J. T. Navarrete, *J. Org. Chem.* **2001**, 66, 8872–8882.
- [11] a) M. A. Herranz, N. Martín, L. Sánchez, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, C. Sánchez, *Tetrahedron* **1998**, 54, 11651–11658; b) M. Otero, M. A. Herranz, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, *Tetrahedron* **2002**, 58, 7463–7475.
- [12] B. M. Illescas, N. Martín, *J. Org. Chem.* **2000**, 65, 5986–5995.
- [13] T. Furuta, H. Torigai, M. Sugimoto, M. Iwamura, *J. Org. Chem.* **1995**, 60, 3953–3956.
- [14] C. Aïssa, *Eur. J. Org. Chem.* **2009**, 1831–1844.
- [15] N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, *J. Org. Chem.* **1998**, 63, 1268–1279.
- [16] M. C. Díaz, B. M. Illescas, N. Martín, R. Viruela, P. M. Viruela, E. Ortí, O. Brede, I. Zilbermann, D. M. Guldi, *Chem. Eur. J.* **2004**, 10, 2067–2077.
- [17] A. S. Batsanov, M. R. Bryce, M. A. Coffin, A. Green, R. E. Hester, J. A. K. Howard, I. K. Lednev, N. Martín, A. J. Moore, J. N. Moore, E. Ortí, L. Sánchez, M. Savirón, P. M. Viruela, R. Viruela, T.-Q. Ye, *Chem. Eur. J.* **1998**, 4, 2580–2592.
- [18] a) M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse, A. I. Karaulov, *Angew. Chem.* **1990**, 102, 1493–1495; *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 1450–1452; b) S. Triki, L. Ouahab, D. Lorcy, A. Robert, *Acta Crystallogr. Sect. C* **1993**, 49, 1189–1192; c) M. R. Bryce, T. Finn, A. S. Batsanov, R. Kataky, J. A. K. Howard, S. B. Lyubchik, *Eur. J. Org. Chem.* **2000**, 1199–1205; d) C. A. Christensen, A. S. Batsanov, M. R. Bryce, J. A. K. Howard, *J. Org. Chem.* **2001**, 66, 3313–3320.
- [19] A. E. Jones, C. A. Christensen, D. F. Perepichka, A. S. Batsanov, A. Beeby, P. J. Low, M. R. Bryce, A. W. Parker, *Chem. Eur. J.* **2001**, 7, 973–978.
- [20] U. Schubert, S. Hünig, A. Aümüller, *Liebigs Ann. Chem.* **1985**, 1216–1222.
- [21] J. Wu, S. Liu, A. Neels, F. Le Derf, M. Sallé, S. Decurtins, *Tetrahedron* **2007**, 63, 11282–11286.
- [22] M. C. Díaz, B. M. Illescas, N. Martín, I. F. Perepichka, M. R. Bryce, E. Levillain, R. Viruela, E. Ortí, *Chem. Eur. J.* **2006**, 12, 2709–2721.
- [23] C. Wartelle, R. Viruela, P. M. Viruela, F. X. Sauvage, M. Sallé, E. Ortí, E. Levillain, F. Le Derf, *Phys. Chem. Chem. Phys.* **2003**, 5, 4672–4679.
- [24] a) H. Endres, *Z. Naturforsch. B* **1986**, 41, 1437–1442; b) K. Brunn, H. Endres, J. Weiss, *Z. Naturforsch. B* **1988**, 43, 224–230; c) P. G. Jones, *Z. Naturforsch. B* **1989**, 44, 243–244.
- [25] A. M. Kini, D. O. Cowan, F. Gerson, R. Moeckel, *J. Am. Chem. Soc.* **1985**, 107, 556–562.
- [26] a) P. de Miguel, M. R. Bryce, L. M. Goldenberg, A. Beeby, V. Khodorkovsky, L. Shapiro, A. Niemz, A. O. Cuello, V. Rotello, *J. Mater. Chem.* **1998**, 8, 71–76; b) M. A. Herranz, S. González, I. Pérez, N. Martín, *Tetrahedron* **2001**, 57, 725–731; c) G. Zerza, A. Cravino, H. Neugebauer, N. S. Sariciftci, R. Gómez, J. L. Segura, N. Martín, M. Svensson, M. R. Andersson, *J. Phys. Chem. A* **2001**, 105, 4172–4176.
- [27] D. M. Guldi, L. Sánchez, N. Martín, *J. Phys. Chem. B* **2001**, 105, 7139–7144.

Received: September 17, 2010
Published online: February 3, 2011