EurJOC
European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201200115

A Straightforward Electroactive π-Extended Tetrathiafulvalene (exTTF) Building Block

Agustín Molina-Ontoria,[a] Raúl García,[a] Andreas Gouloumis,[a] Francesco Giacalone,[a] M. Rosario Torres,[b] and Nazario Martín*[a,c]

Dedicated to Professor Miguel Angel Miranda on the occasion of his 60 birthday

Keywords: Materials / Fused-ring systems / Conjugation / Donor-acceptor systems / Pi interactions / Olefination

The synthesis and X-ray structure of a new and readily available exTTF derivative (**6**) bearing a methyltriphenylphosphonium bromide moiety as a new building block for the construction of electroactive molecules is reported. The phosphonium salt **6**, which was prepared in one step from 2-hydroxymethyl-exTTF as a stable yellow solid in 84 % yield, efficiently undergoes Wittig olefination reactions with a variety of aldehydes to predominantly form the *E* isomer. Electronic spectra and cyclic voltammetry of the novel compounds reveal the electronic communication between the electroactive units.

Introduction

Since the first synthesis of tetrathiafulvalene (TTF) was developed just over forty years ago,[1] this planar and nonaromatic molecule has become one of the most important electron-donor species, forming radical cation and dication species at relatively low oxidation potentials that exhibit aromatic character. This gain of aromaticity upon oxidation has been successfully used for the preparation of a wide variety of stable charge-transfer salts and complexes showing electrical conducting and superconducting properties. Furthermore, TTF has also found application in other fields involving molecular, macromolecular, and supramolecular derivatives.[2]

Among the many structural modifications carried out on pristine TTF, extensions of the π-conjugated system between the two 1,3-dithiole rings, as well as laterally, by adding fused benzene rings to the central *p*-quinoid moiety has allowed the preparation of a unique type of π-extended TTF (exTTF) showing significant geometrical and electronic differences compared to the parent TTF molecule. Thus, exTTF is a highly distorted, out-of-planarity molecule adopting a butterfly-shape in the neutral state. Upon oxidation, the dication species is formed with a dramatic geometrical change and gain of aromaticity.[3]

exTTFs have been used for the preparation of a variety of compounds of interest in fields such as electrically conducting materials,[4] nonlinear optics,[5] sensors,[6] photovoltaics,[7] molecular wires,[8] and organogels,[9] in which the electronic properties of exTTFs are the key issue. We have taken advantage of the curved geometry of neutral exTTF for the design of molecular tweezers and macrocycles bearing two exTTF units that efficiently recognize fullerenes through concave–convex π–π interactions.[10] Furthermore, these exTTF-containing receptors have proven to be the best purely organic hosts for fullerenes found so far, with binding constants as high as $10^7\ \mathrm{M}^{-1}$ in chlorobenzene.[11] More recently, a molecular tweezer involving only one exTTF unit covalently connected to two crown ethers has revealed an excellent association constant through cooperative π–π and n–π supramolecular interactions.[12]

Despite the aforementioned interest in exTTF derivatives, the number of suitably functionalized exTTFs for further chemical transformations is low, which constrains the use of this important type of electron donor for further applications. In this work we describe an efficient and straightforward synthesis of exTTFs endowed with a phosphonate group, and its further Wittig olefination reaction with a variety of aldehydes, thus broadening the synthetic scope of this molecule. Furthermore, the electronic and electrochemical properties of the novel electroactive compounds complement the synthetic work.

---

[a] Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid,
28040 Madrid, Spain
Fax: +34-913-944-103
E-mail: nazmar@quim.ucm.es
[b] CAI Difracción de Rayos-X, Facultad de Ciencias Químicas, Universidad Complutense de Madrid,
28040 Madrid, Spain
[c] IMDEA – Nanociencia, Campus de Cantoblanco, Universidad Autónoma de Madrid,
28049 Madrid, Spain

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200115.

Results and Discussion

A variety of exTTF derivatives bearing a functional group that is suitable for further chemical transformations have been synthesized so far. Among them, the presence of a formyl group, as in **3**, has allowed a number of olefination reactions to be carried out by reaction with phosphonium salts and phosphonates through Wittig type reactions. Olefination reactions are important tools for the chemical modification of exTTFs because they allow conjugated exTTF derivatives to be prepared that facilitate good electronic communication with an acceptor unit in a variety of Donor–Acceptor systems. Therefore, it is important to endow the exTTF unit with a suitable functional group to carry out further olefination reactions with carbonyl-containing functional groups, thus complementing the synthetic approach and significantly broadening the scope of this olefination reaction.

In a first approach, we have recently reported the synthesis of a series of exTTFs bearing a sulfone reactive group (**4**) and their further Julia–Kocienski reaction with aldehydes (Figure 1).[13] Although formation of the product proceeds reasonably well in moderate to good yields, formation of the starting sulfone was found to be a somewhat capricious reaction that occurs in relatively low yields, thus preventing the use of these sulfones as general starting materials for further chemical modifications.

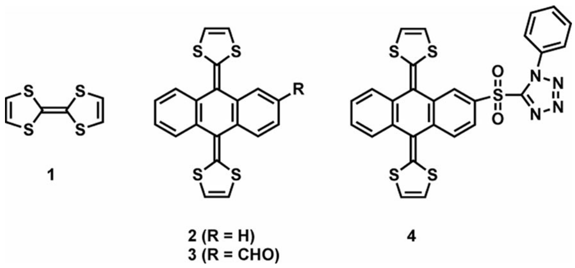
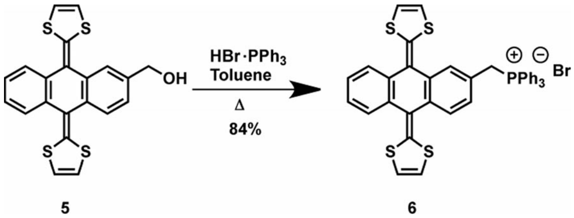


Figure 1. Tetrathiafulvalene (TTF) **1**, exTTF **2**, and some derivaties (**3** and **4**) that are suitably functionalized for further olefination reactions.

In this work, we report on the synthesis and X-ray structural characterization of a readily available exTTF derivative bearing a methyltriphenylphosphonium bromide moiety as a new building block for the construction of electroactive molecules endowed with the exTTF moiety. The synthesis of the phosphonium salt was carried out in one step from 2-hydroxymethyl-exTTF (**5**)[14] by reaction with triphenylphosphane hydrobromide in toluene at reflux. Thus, **6** could be obtained as a stable yellow solid in 84% yield (Scheme 1). Furthermore, the synthesis of **6** has been carried out on a gram scale without any significant variation in the obtained yield (see the Experimental Section).

Phosphonium salt **6** was characterized on the basis of its analytical and spectroscopic data. Thus, the ^{1}H NMR spectrum shows the presence of the 1,3-dithiole protons as a singlet at δ = 6.99 ppm and two doublets at δ = 6.93–6.75 ppm. The methylene protons are diastereotopic, appearing as two triplets at δ = 5.68 and 5.47 ppm due to the coupling with the phosphorus atom.



Scheme 1. Synthesis of phosphonium salt **6** from 2-hydroxymethyl-exTTF (**5**).

The structure of **6** was unambiguously confirmed by X-ray diffraction of a single crystal formed from a solution of acetonitrile (Figure 2).

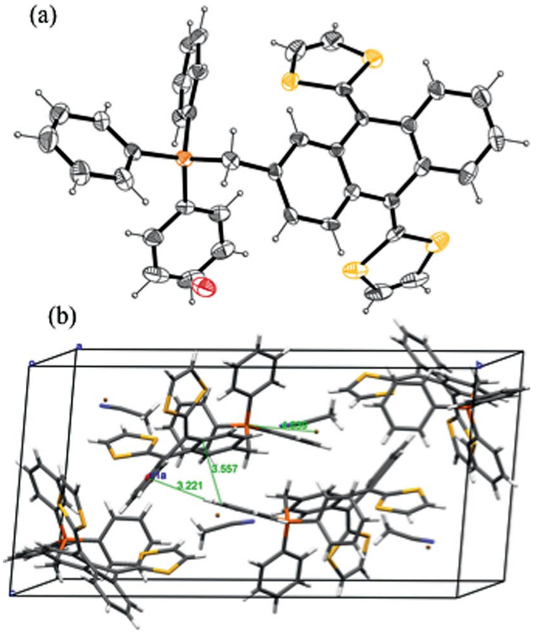


Figure 2. (a) Crystal structure of methyltriphenylphosphonium-exTTF bromide (**6**); (b) Unit cell. S (yellow), C (green), H (white), P (orange), Br (red).

The molecular geometry shows that the central ring folds into a boat conformation and the molecule adopts a butterfly structure in which the benzene rings point downward and the dithiole rings point upward. The crystallographic analysis performed on compound **6** revealed no significant deviations in the bond lengths or angles from X-ray or theoretical calculations data previously reported for pristine exTTF (for detailed data, see the Supporting Information).[15,3b,3c] The crystal packing can be described as cationic columnar assemblies along the “a” axis, in which neighboring molecules interact through van der Waals forces (Figure 2, b). Each bromide anion forms weak bonds with the four nearest phosphonium cations and occupies holes between the columns.

The efficiency of phosphonium salt **6** as a new building block for olefination reactions was tested by reacting it with a variety of carbonyl-containing compounds under a range of experimental conditions.

Initial efforts focused on the Wittig olefination using 4-nitrobenzaldehyde and *t*BuOK as a base in anhydrous tetrahydrofuran (THF) at reflux. Under these conditions, the *E*/*Z* mixture of isomers was easily separated by column chromatography on silica gel using dichloromethane as the eluent in excellent yield (97 %). Furthermore, the *E* isomer was obtained as the major product in 75:25 ratio. To achieve a better selectivity for the *E*/*Z* isomers, different conditions were explored by changing the solvent, base, and temperature (Table 1).

Table 1. Conditions used for the Wittig olefination reaction with **6** and 4-nitrobenzaldehyde.[a]

Entry	Solvent	Base	Temp. [°C]	Yield [%]	*E*/*Z* [%]
1	toluene	*t*BuOK	reflux	97	75:25
2	toluene	LiHDMS	reflux	93	63:37
3	DMF	*t*BuOK	r.t	94	65:35
4	DMF	NaH	r.t	90	82:18
5	DMF	LiHDMS	r.t	93	65:35

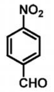
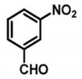
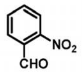
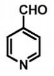
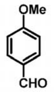
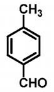
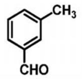
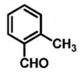
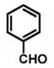
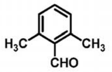
[a] Reagents and conditions: **6** (1 mmol), 4-nitrobenzaldehyde (1.5 mmol), base (1.5 mmol), time 5 h, argon atmosphere.

The best *E*/*Z* ratio was obtained by using NaH (Table 1, entry 4) as base in anhydrous *N*,*N*-dimethylformamide (DMF) at room temperature. The reaction product was obtained in very good yield (90 %) with a *E*/*Z* ratio of 82:18. However, NaH was not appropriate for other substrates. When the reaction was carried out at room temperature with LiHDMS (Table 1, entry 5) or *t*BuOK (Table 1, entry 3) very good yields were obtained, albeit with significantly poorer *E*/*Z* ratios. Therefore, the former conditions (toluene, *t*BuOK, reflux) were chosen for the study with a variety of aldehydes (Table 2).

The scope of the new building block for olefination reactions was tested with a range of aromatic aldehydes bearing electron-withdrawing or electron-donating groups in different positions, aliphatic aldehydes, and ketones (Table 2). The products were isolated as a mixture of both the *Z* and *E* isomers, and the respective ratios were determined by ^{1}H NMR spectroscopic analysis.[16]

All compounds were formed in excellent yields (over 90 %). The *E*/*Z* isomeric ratios of the Wittig products were almost unaffected by the electronic nature of the substituent. However, as expected, the Wittig olefination reaction was strongly influenced by the position of the substituent on the aromatic ring. Thus, for instance, the use of 3,5-dimethylbenzaldehyde (Table 2, entry 10) afforded an *E*/*Z* isomeric ratio for **16** of 99:1 due to the strong steric hindrance of the two methyl groups in the *ortho*-position. This ratio decreased to 80:20 when only one methyl group was present *ortho* to the carbonyl group (Table 2, entry 8), and to 55:45 when benzaldehyde was used (Table 2, entry 9). Attempts to carry out the reaction with ketones (acetophenone and benzophenone) met with failure. The presence of a strong base in the former case and the lower reactivity and steric hindrance in the latter, could account for these experimental findings.

Table 2. Starting aromatic aldehydes and compounds prepared by olefination reaction with phosphonium salt **6**[a] and their λ_{max} values.

Entry	Starting compound	Compound[b] *E*:*Z* (%)	Yield[c] (%)	λ_{max} (CH_2Cl_2) (log ε)
1		**7** (75:25)	97	473 (4.10)
2		**8** (70:30)	92	439 (4.27)
3		**9** (70:30)	92	431 (4.27)
4		**10** (75:25)	94	459 (4.24)
5		**11** (80:20)	95	436 (4.48)
6		**12** (70:30)	93	436 (4.49)
7		**13** (75:25)	96	436 (4.47)
8		**14** (80:20)	95	437(4.44)
9		**15** (55:45)	98	436 (4.47)
10		**16** (99:1)	90	435 (4.53)
11		**17** (73:27)	93	432 (4.25)

[a] Reagents and conditions: **6** (1 mmol), aldehyde (1.5 mmol), *t*BuOK (1.5 mmol), 110 °C, 5 h, under argon. [b] Ratios were determined by ^{1}H NMR spectroscopic analysis. [c] Isolated yield after column chromatography.

The electronic spectra of compounds **7**–**17** as well as starting phosphonium salt **6** show a strong band at low energy values corresponding to a charge transfer (CT) process from the donor moiety (exTTF) to the acceptor aryl moiety.[5,17] As expected, the vinyl group facilitates the electronic communication between the exTTF and aryl moieties, and the position of the CT band depends on the substituent on the aryl unit. Thus, whereas this band appears around λ_{max} (CH_2Cl_2) = 430 nm, the presence of a nitro group in the *para* position shifts this value to λ_{max} (CH_2Cl_2) = 473 nm. These findings could be accounted for by the stronger electron-accepting ability of the *p*-nitrobenzene unit compared to the other substituents (Table 2). On the other hand, changes in the polarity of the solvent had a significant influence on the position of the low energy wavelength band. Thus, for compound **11** and **15** [λ_{max} = 439 (toluene); 436 (dichloromethane); 432 (acetonitrile) nm] a slight hypsochromic effect was observed with increasing solvent polarity. This effect was more clearly observed for compound **7** bearing the *p*-nitro group [λ_{max}: 480 (toluene); 473 (dichloromethane); 458 (acetonitrile) nm], thus confirming the solvatochromic effect and the electronic communication between the electroactive moieties (Figure 3).

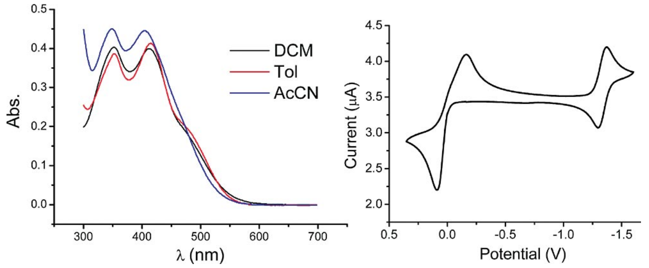


Figure 3. Electronic spectra (left) and cyclic voltammogram (right) of **7**. A hypsochromic effect is observed in the electronic spectra, whereas in the CV the oxidation wave of the exTTF is significantly shifted by the presence of a *p*-nitro substituent.

This electronic interaction has also been confirmed by means of a cyclic voltammetry study. The redox potentials of the novel exTTF derivatives **6**, **7**, **10**, **11**, and **15** have been determined by cyclic voltammetry at room temperature in acetonitrile solutions, using glassy carbon as the working electrode, Ag/Ag+ as reference, and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The redox potential values are collected in Table S2 of the Supporting Information, together with that of phosphonate **6** for comparison purposes. It is important to note that the electrochemically irreversible oxidation wave of the exTTF (around 100 mV) does not allow a precise comparison between the studied compounds. However, the presence of the *p*-nitro group in **7** significantly shifts cathodically the oxidation wave due to its electron-withdrawing effect. Furthermore, the reduction wave of the nitro group is observed at around 1335 mV. Interestingly, compound **6** shows, in addition to the expected oxidation wave at 170 mV, a second oxidation wave at around 420 mV that can be reasonably assigned to the oxidation of the bromide counterion of the phosphonium salt.[18]

Conclusions

We have described the synthesis of a valuable new building block of exTTF and determined its elusive structure by X-ray analysis. Its efficiency in the Wittig olefination reaction has been successfully demonstrated with a number of aromatic aldehydes under basic conditions, affording the respective products in excellent yields. The reaction is affected very little by the electronic nature of the substituents on the benzene ring of benzaldehyde, however, it is strongly impacted by the position of the substituent on the ring due to steric hindrance; this can result in *E*/*Z* ratios ranging from 55:45 up to 99:1. This new building block is easily prepared in excellent yield and significantly improves the previous methods reported so far to obtain exTTF derivatives. Furthermore, this approach paves the way for the construction of more sophisticated electroactive structures – involving the very useful exTTF donor moiety – in supramolecular chemistry and molecular electronics.

Experimental Section

Methyltriphenylphosphonium-exTTF Bromide (6): To a suspension of 2-hydroxymethyl-exTTF (**5**; 150 mg, 0.126 mmol) in toluene (20 mL), triphenylphosphane hydrobromide (252 mg, 0.72 mmol) was added and the reaction mixture was stirred at reflux for 5 h. The solvent was partially removed under vacuum, then hexane was added, resulting in a precipitate. The precipitate was filtered and washed with a mixture of hexane/diethyl ether (7:3) to afford **6** (70 mg, 0.10 mmol, 84% yield) as an orange solid. ^{1}H NMR (300 MHz, [D$_7$]DMF): δ = 8.17–8.16 (m, 3 H, Ar), 8.09–7.99 (m, 12 H), 7.89–7.83 (m, 2 H), 7.71–7.68 (m, 2 H, Ar), 7.58–7.55 (m, 2 H, Ar), 7.19 (m, 1 H, Ar), 6.99 (s, 2 H, dithiole), 6.93 (d, *J* = 6.7 Hz, 1 H, dithiole), 6.75 (d, *J* = 6.7 Hz, 1 H, dithiole), 5.68 (t, *J* = 15 Hz, 1 H, CH$_2$), 5.47 (t, *J* = 15 Hz, 1 H, CH$_2$) ppm. ^{13}C NMR (75 MHz, [D$_7$]DMF): δ = 138.6, 138.5, 138.4, 136.3, 136.0, 136.02, 135.9, 135.8, 135.7, 135.6, 135.2, 135.0, 131.1, 130.9, 130.2, 130.1, 129.5, 128.8, 127.3, 127.2, 127.0, 126.9, 126.8, 126.7, 126.1, 126.0, 125.9, 125.6, 125.5, 121.1, 121.0, 120.7, 119.4, 118.8, 118.7, 118.6, 118.3 ppm. FTIR (KBr): ṽ = 3005, 1585, 1543, 1512, 1485, 1452, 1437, 1394, 1319, 1283, 1190, 1161, 1111, 1028, 995, 924, 891, 866, 796, 735, 719, 690, 652, 633 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 439 (4.49), 425 (4.45), 372 (4.29) nnm. HRMS (MALDI): calcd. for $C_{39}H_{28}BrPS_4$ 733.9995; found 734.0013.

When the preparation of **6** was carried out with a larger amount of 2-hydroxymethyl-exTTF (**5**; 1 g, 2.44 mmol), compound **6** was obtained in a similar yield (80%).

CCDC-854063 contains the supplementary crystallographic data for compound **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of 7–17: To a solution of phosphonium salt **6** (1 mmol) and the corresponding aldehyde (1.5 mmol) in anhydrous toluene heated to reflux under argon atmosphere, potassium *tert*-butoxide (1.5 mmol) was slowly added. After 5 h, the mixture was cooled to room temperature, then water and CHCl$_3$ were added. The combined organic phases were washed with water and dried with MgSO$_4$. After evaporation of the solvent, the mixture was purified by flash column chromatography (SiO$_2$; hexane/CH$_2$Cl$_2$, 1:1).

Compound 7 (*E* Isomer): ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 8.24 (d, *J* = 8.8 Hz, 2 H, ArH), 7.92 (d, *J* = 1.7 Hz, 1 H, ArH), 7.77–7.70 (m, 5 H, ArH), 7.52 (dd, *J* = 8.1, *J'* = 1.7 Hz, 1 H, Ar), 7.41–7.32 (m, 3 H, ArH, vinyl), 7.24 (d, *J* = 16.3 Hz, 1 H, vinyl), 6.40 (s, 4 H, dithiole) ppm. ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ = 147.1, 144.3, 137.3, 137.0, 136.3, 136.1, 135.6, 135.5, 134.4, 133.2, 127.3, 126.7, 126.6, 126.5, 125.9, 125.4, 125.3, 125.2, 124.4, 123.8, 122.0, 117.8, 117.7, 117.4 ppm. FTIR (neat): ṽ = 3022, 1543, 1508, 1456, 1419, 1338, 1259, 1107, 1026, 951, 866, 843, 802, 756, 690, 634 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 473 (4.10), 413 (4.42), 352 (4.43) nm. HRMS (MALDI): calcd. for $C_{28}H_{17}NO_2S_4$ 527.0137; found 527.0148.

Compound 7 (*Z* Isomer): ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 8.12 (d, *J* = 8.8 Hz, 2 H, ArH), 7.72–7.65 (m, 2 H, ArH), 7.61 (d, *J* = 8.1 Hz, 1 H, ArH), 7.51–7.48 (m, 3 H, ArH), 7.33–7.30 (m, 2 H, ArH), 7.19 (dd, J = 8.1, 1.7 Hz, 1 H, ArH), 6.89 (d, J = 12.1 Hz, 1 H, vinyl), 6.72 (d, J = 12.1 Hz, 1 H, vinyl), 6.38 (s, 2 H, dithiole), 6.32 (d, J = 6.8 Hz, 1 H, dithiole), 6.21 (d, J = 6.8 Hz, 1 H, dithiole) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 146.9, 144.9, 136.9, 136.8, 135.9, 135.5, 135.4, 135.2, 134.5, 133.9, 130.4, 128.7, 126.9, 126.5, 126.4, 125.6, 125.5, 125.4, 125.3, 124.1, 121.9, 121.8, 117.8, 117.7, 117.3 ppm. FTIR (neat): $\tilde{\nu}$ = 3020, 1545, 1508, 1456, 1410, 1335, 1259, 1100, 955, 864, 756, 693, 650, 635 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 473 (4.10), 413 (4.42), 352 (4.43) nm. HRMS (MALDI): calcd. for $C_{28}H_{17}NO_2S_4$ 527.0137; found 527.0133.

Compound 8 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (t, J = 1.8 Hz, 1 H, ArH), 8.18 (t, J = 1.8 Hz, 1 H, ArH), 8.10 (m, 1 H, ArH), 8.04 (m, 1 H, ArH), 7.98–7.12 (m, 20 H, ArH, vinyl), 6.80 (d, J = 12.0 Hz, 1 H, vinyl), 6.65 (d, J = 12.0 Hz, 1 H, vinyl), 6.33–6.14 (m, 8 H, dithiole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 148.7, 139.9, 136.4, 136.2, 136.0, 135.6, 135.2, 133.9, 133.8, 132.9, 132.2, 131.5, 129.5, 129.4, 127.8, 126.3, 126.1, 125.4, 125.3, 125.2, 125.0, 124.9, 124.7, 124.1, 123.1, 122.0, 121.9, 121.7, 121.0, 117.4, 117.3, 117.0, 116.9 ppm. FTIR (neat): $\tilde{\nu}$ = 3020, 1547, 1510, 1456, 1420, 1341, 1259, 1105, 951, 866, 843, 756, 690, 650, 634 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 439 (4.27), 313 (4.36) nm. HRMS (MALDI): calcd. for $C_{28}H_{17}NO_2S_4$ 527.0137; found 527.0107.

Compound 9 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (m, 1 H, ArH), 8.19 (m, 1 H, ArH), 8.10 (m, 1 H, ArH), 8.04 (m, 1 H, ArH), 7.89–7.13 (m, 20 H, ArH, vinyl), 6.81 (d, J = 12.0 Hz, 1 H, vinyl), 6.66 (d, J = 12.0 Hz, 1 H, vinyl), 6.39–6.14 (m, 8 H, dithiole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 148.6, 139.2, 136.3, 136.1, 136.0, 135.9, 135.6, 135.2, 134.9, 133.9, 133.7, 132.9, 132.2, 131.5, 129.5, 129.3, 127.8, 126.3, 126.0, 125.9, 125.4, 125.2, 125.1, 124.9, 124.8, 124.6, 124.1, 123.1, 121.9, 121.8, 121.7, 121.6, 120.9, 117.4, 117.3, 117.2, 117.1, 116.9, 116.8 ppm. FTIR (neat): $\tilde{\nu}$ = 3050, 1547, 1510, 1456, 1341, 1256, 1110, 867, 756, 690, 634 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 431 (4.27), 325 (4.25) nm. HRMS (MALDI): calcd. for $C_{28}H_{17}NO_2S_4$ 527.0137; found 527.0109.

Compound 10 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.58 (d, J = 1.7 Hz, 1 H, ArH), 8.49 (d, J = 1.7 Hz, 1 H, ArH), 7.91–7.17 (m, 4 H, ArH, vinyl), 7.11 (d, J = 16.0 Hz, 1 H, vinyl), 6.85 (d, J = 12.0 Hz, 1 H, vinyl), 6.61 (d, J = 12.0 Hz, 1 H, vinyl), 6.37–6.26 (m, 8 H, dithiole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 149.1, 145.9, 145.6, 136.7, 136.2, 135.0, 135.2, 135.1, 134.3, 133.7, 133.5, 133.3, 132.1, 132.0, 131.9, 128.5, 128.4, 126.1, 126.0, 125.5, 125.4, 124.9, 123.4, 121.8, 121.7, 121.0, 117.4, 117.3, 117.2, 117.1, 117.0, 116.9 ppm. FTIR (neat): $\tilde{\nu}$ = 3050, 2925, 2852, 1549, 1513, 1421, 1347, 1252, 1115, 868, 843, 757, 690, 651, 633 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 459 (4.24), 379 (4.41) nm. HRMS (MALDI): calcd. for $C_{27}H_{17}NS_4$ 483.0244; found 483.0189.

Compound 11 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 1.7 Hz, 1 H, ArH), 7.73–7.66 (m, 4 H, ArH), 7.57–7.54 (m, 3 H, ArH), 7.49 (d, J = 8.6 Hz, 2 H, ArH), 7.40 (dd, J = 8.6, 1.7 Hz, 1 H, ArH), 7.32–7.24 (m, 6 H, ArH), 7.21 (dd, J = 8.6, 1.7, 1 H Hz, ArH), 7.12 (d, J = 16.0 Hz, 1 H, vinyl), 7.02 (d, J = 16.0 Hz, 1 H, vinyl), 6.90 (d, J = 8.6 Hz, 2 H, ArH), 6.80 (d, J = 8.6 Hz, 2 H, ArH), 6.60 (d, J = 12.0 Hz, 1 H, vinyl), 6.55 (d, J = 12.0 Hz, 1 H, vinyl), 6.34–6.31 (m, 4 H, dithiole), 6.30–6.19 (m, 4 H, dithiole), 3.85 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 158.5, 135.7, 135.6, 135.4, 135.3, 135.2, 134.7, 134.3, 133.9, 132.3, 132.2, 131.5, 130.5, 130.2, 130.1, 129.9, 129.6, 128.8, 128.6, 128.4, 127.7, 126.4, 126.1, 126.0, 125.9, 125.5, 125.2, 124.9, 122.6, 122.2, 122.1, 117.3, 117.2, 117.1, 117.0, 55.3, 55.2 ppm. FTIR (neat): $\tilde{\nu}$ = 2924, 2852, 1511, 1421, 1152, 915, 843, 758, 691, 636 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 436 (4.48), 378 (4.56), 328 (4.57) nm. HRMS (FAB): calcd. for $C_{29}H_{20}OS_4$ 512.0397; found 512.0378.

Compound 12 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 1.7 Hz, 1 H, ArH), 7.73–7.65 (m, 4 H, ArH), 7.56–7.53 (m, 3 H, ArH), 7.44–6.99 (sm, 18 H, ArH, vinyl), 6.32–6.19 (m, 8 H, dithiole), 2.47 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3, 137.2, 135.7, 135.6, 135.5, 135.4, 135.3, 134.3, 131.3, 130.0, 129.9, 129.8, 128.9, 128.6, 128.4, 128.2, 127.6, 127.2, 126.3, 126.0, 125.9, 125.5, 125.3, 124.9, 124.8, 124.2, 123.8, 122.9, 122.2, 122.1, 117.3, 117.2, 117.1, 116.9, 21.2 ppm. FTIR (neat): $\tilde{\nu}$ = 2924, 2852, 1508, 1383, 1211, 1029, 956, 766 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 436 (4.49), 376 (4.45), 319 (4.52) nm. HRMS (MALDI): calcd. for $C_{29}H_{20}S_4$ 496.0442; found 496.0437.

Compound 13 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 1.7 Hz, 1 H, ArH), 7.73–7.53 (m, 7 H, ArH), 7.44–6.99 (sm, 18 H, ArH, vinyl), 6.32–6.19 (m, 8 H, dithiole), 2.40 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2 (2), 137.3, 135.8, 135.8, 135.6, 135.3, 135.2, 134.7, 131.3, 130.0, 129.9, 129.8, 128.9, 128.6, 128.4, 128.2, 127.6, 127.2, 126.3, 126.0, 125.9, 125.5, 125.3, 124.9, 124.8, 124.2, 123.8, 122.9, 122.2, 122.1, 117.3, 117.2, 117.1, 116.9, 21.4 ppm. FTIR (neat): $\tilde{\nu}$ = 2929, 2854, 1596, 1507, 1335, 1210, 1025, 956, 765 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 436 (4.47), 376 (4.37), 318 (4.50) nm. HRMS (ESI): calcd. for $C_{29}H_{20}S_4$ 496.0442; found 496.0447.

Compound 14 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 1.7 Hz, 1 H, ArH), 7.73–7.62 (m, 7 H, ArH), 7.51–7.03 (sm, 18 H, ArH, vinyl), 6.32–6.17 (m, 8 H, dithiole), 2.47 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.4, 135.9, 135.7, 135.5, 135.4, 135.3, 134.8, 130.5, 130.4, 130.2, 129.9, 129.7, 129.5, 127.6, 127.0, 126.7, 126.2, 126.0, 125.9, 125.6, 125.3, 125.0, 124.7, 124.3, 123.0, 122.3, 122.2, 117.3, 117.2, 117.1, 116.8, 19.9 ppm. FTIR (neat): $\tilde{\nu}$ = 2925, 2855, 1594, 1509, 1330, 1209, 1031, 957, 763 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 437 (4.44), 376 (4.35), 315 (4.39) nm. HRMS (ESI): calcd. for $C_{29}H_{20}S_4$ 496.0442; found 496.0448.

Compound 15 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86–7.83 (m, 1 H, ArH), 7.70–7.67 (m, 3 H, ArH), 7.55–7.52 (m, 2 H, ArH), 7.50–7.15 (sm, 20 H, ArH, vinyl), 6.31–6.15 (m, 8 H, dithiole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.4, 135.8, 135.6, 135.3, 135.2, 135.0, 134.7, 134.1, 130.5, 130.1, 129.2, 128.7, 128.6, 128.4, 127.6, 126.8, 126.5, 126.2, 125.9, 125.8, 125.5, 125.3, 124.9, 124.8, 124.2, 122.8, 122.1, 122.0, 117.2, 117.1, 116.9 ppm. FTIR (neat): $\tilde{\nu}$ = 3043, 2852, 1541, 1508, 1195, 1165, 964, 846, 801, 758, 691, 650, 634 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 436 (4.47), 378 (4.40), 313 (4.52) nm. HRMS (MALDI): calcd. for $C_{28}H_{18}S_4$ 482.0286; found 482.0303.

Compound 16 (*E* Isomer): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.89 (d, J = 1.6 Hz, 1 H, ArH), 7.75–7.71 (m, 3 H, ArH), 7.45 (dd, J = 8.10, 1.6 Hz, 1 H, ArH), 7.36–7.33 (m, 2 H, ArH), 7.24 (d, J = 16.8 Hz, 1 H, vinyl), 7.10 (m, 3 H, ArH), 6.71 (d, J = 16.8 Hz, 1 H, vinyl), 6.38 (s, 4 H, dithiole), 2.42 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 139.1, 138.5, 138.3, 138.0, 137.9, 137.6, 137.8, 137.5, 136.8, 135.8, 130.1, 129.6, 128.9, 128.4, 128.3, 127.6, 127.3, 126.4, 124.82, 119.7, 119.5, 119.4, 23.2 ppm. FTIR (neat): $\tilde{\nu}$ = 2941, 2854, 1543, 1510, 1197, 1167, 964, 871, 756 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 435 (4.53), 373 (4.43), 303 (4.51) nm. HRMS (MALDI): calcd. for $C_{30}H_{22}S_4$ 510.0599; found 510.0603.

Compound 17 (*E*+*Z* Isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.62 (m, 10 H, ArH), 7.35–7.21 (m, 4 H, ArH), 6.45–6.23 (m, 12 H, dithiole, vinyl), 2.21–0.81 (sm, 30 H, aliphatic) ppm. ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ = 136.3, 136.2, 135.9, 135.7, 135.6, 134.1, 132.3, 129.7, 128.6, 127.0, 126.3, 125.9, 125.4, 125.3, 125.2, 123.9, 122.6, 117.7, 117.6, 33.5, 32.3, 32.2, 30.4, 30.0, 29.8, 29.6, 29.5, 29.3, 23.0, 14.2 ppm. FTIR (neat): $\tilde{\nu}$ = 2941, 2857, 1508, 1457, 1375, 1195, 1165, 964, 871, 756 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (logε) = 432 (4.25), 368 (4.09) nm. HRMS (MALDI): calcd. for C$_{29}$H$_{28}$S$_4$ 504.1068; found 504.1087.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, X-ray structure, and crystal data.

Acknowledgments

Financial support by the Ministerio de Economía y Competitividad of Spain (project number CTQ2011-24652), Consolider-Ingenio (CSD 2007-00010), and Comunidad de Madrid (CAM) (MADRISOLAR-2 project S2009/PPQ-1533) is acknowledged.

---

[1] a) F. Wudl, G. M. Smith, E. J. Hufnagel, *J. Chem. Soc. C* **1970**, 1453; b) S. Hünig, G. Kiesslich, D. Schentzow, R. Zahradnik, P. Carsky, *Int. J. Sulfur Chem. Part C* **1971**, *6*, 109; c) *TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene* (Eds.: J. Yamada, T. Sugimoto), Kodansha–Springer, Berlin, **2004**.

[2] a) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372; b) D. Canevet, M. Sallé, G. Zhang, D. Zhang, D. Zhu, *Chem. Commun.* **2009**, 2245–2269.

[3] a) Y. Yamashita, Y. Kobayashi, T. Miyashi, *Angew. Chem.* **1989**, *101*, 1090; b) 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; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1450; c) N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, *J. Org. Chem.* **1998**, *63*, 1268.

[4] a) M. R. Bryce, *J. Mater. Chem.* **1995**, *5*, 1481; b) C. A. Christensen, A. S. Batsanov, M. R. Bryce, *J. Am. Chem. Soc.* **2006**, *128*, 10484.

[5] a) R. Andreu, A. I. de Lucas, J. Garín, N. Martín, J. S. Orduna, L. Sánchez, C. Seoane, *Synth. Met.* **1997**, *86*, 1817; 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; c) M. Otero, M. A. Herranz, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, *Tetrahedron* **2002**, *58*, 7463.

[6] a) M. R. Bryce, A. S. Batsanov, T. Finn, T. K. Hansen, J. A. K. Howard, M. Kamenjicki, I. K. Lednev, S. A. Asher, *Chem. Commun.* **2000**, 295; b) N. Godbert, A. S. Batsanov, M. R. Bryce, J. A. K. Howard, *J. Org. Chem.* **2001**, *66*, 713.

[7] a) N. Martín, L. Sánchez, M. A. Herranz, B. Illescas, D. M. Guldi, *Acc. Chem. Res.* **2007**, *40*, 1015; b) S. Wenger, P.-A. Bouit, Q. Chen, J. Teuscher, D. Di Censo, R. Humphry-Baker, J.-E. Moser, J. L. Delgado, N. Martin, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2010**, *132*, 5164; c) M. P. Eng, S. Shoaee, A. Molina-Ontoria, A. Gouloumis, N. Martín, J. R. Durrant, *Phys. Chem. Chem. Phys.* **2011**, *13*, 3721.

[8] a) L. Sánchez, I. Pérez, N. Martín, D. M. Guldi, *Chem. Eur. J.* **2003**, *9*, 2457; b) F. Giacalone, L. L. Segura, N. Martín, D. M. Guldi, *J. Am. Chem. Soc.* **2004**, *126*, 5340; c) F. Giacalone, J. L. Segura, N. Martín, J. Ramey, D. M. Guldi, *Chem. Eur. J.* **2005**, *11*, 4819; d) C. Atienza, N. Martín, M. Wielopolski, N. Haworth, T. Clark, D. M. Guldi, *Chem. Commun.* **2006**, 3202; e) C. Atienza-Castellanos, M. Wielopolski, D. M. Guldi, C. van der Pol, M. R. Bryce, S. Filippone, N. Martín, *Chem. Commun.* **2007**, 5164; f) A. Molina-Ontoria, G. Fernandez, M. Wielopolski, C. Atienza, L. Sánchez, A. Gouloumis, T. Clark, N. Martín, D. M. Guldi, *J. Am. Chem. Soc.* **2009**, *131*, 12218; g) B. M. Illescas, J. Santos, M. Wielopolski, C. Atienza, N. Martín, D. M. Guldi, *Chem. Commun.* **2009**, 5374; h) D. M. Guldi, B. M. Illescas, C. Atienza, M. Wielopolski, N. Martín, *Chem. Soc. Rev.* **2009**, *38*, 1587; i) M. Wielopolski, J. Santos, B. M. Illescas, A. Ortiz, B. Insuasty, T. Bauer, T. Clark, D. M. Guldi, N. Martín, *Energy Environ. Sci.* **2011**, *4*, 765.

[9] X. Yang, G. Zhang, D. Zhang, D. Zhu, *Langmuir* **2010**, *26*, 11720.

[10] a) E. M. Pérez, L. Sánchez, G. Fernández, N. Martín, *J. Am. Chem. Soc.* **2006**, *128*, 7172; b) E. M. Pérez, N. Martín, *Chem. Soc. Rev.* **2008**, *37*, 1512; c) G. Fernández, E. M. Pérez, L. Sánchez, N. Martín, *Angew. Chem.* **2008**, *120*, 1110; *Angew. Chem. Int. Ed.* **2008**, *47*, 1094; d) E. M. Pérez, A. L. Capodilupo, G. Fernández, L. Sánchez, P. M. Viruela, R. Viruela, R. E. Orti, M. Bietti, N. Martín, *Chem. Commun.* **2008**, 4567; e) E. M. Pérez, N. Martín, *Pure Appl. Chem.* **2010**, *82*, 523.

[11] a) H. Isla, M. Gallego, E. M. Pérez, R. Viruela, E. Ortí, N. Martín, *J. Am. Chem. Soc.* **2010**, *132*, 1772; b) E. Huerta, H. Isla, E. M. Pérez, C. Bo, N. Martín, J. de Mendoza, *J. Am. Chem. Soc.* **2010**, *132*, 5351; c) D. Canevet, M. Gallego, H. Isla, A. de Juan, E. M. Pérez, N. Martín, *J. Am. Chem. Soc.* **2011**, *133*, 3184.

[12] B. Grimm, J. Santos, B. M. Illescas, A. Muñoz, D. M. Guldi, N. Martín, *J. Am. Chem. Soc.* **2010**, *132*, 17387.

[13] J. Santos, B. M. Illescas, N. Martín, J. Adrio, J. C. Carretero, R. Viruela, E. Ortí, F. Spänig, D. M. Guldi, *Chem. Eur. J.* **2011**, *17*, 2957.

[14] G. J. Marshallsay, M. R. Bryce, *J. Org. Chem.* **1994**, *59*, 6847.

[15] A. J. Moore, M. R. Bryce, *J. Chem. Soc. Perkin Trans. 1* **1991**, 157.

[16] Compound **7**, bearing the *p*-nitrophenylene moiety, has previously been reported although in a significant lower yield and without commenting on the *Z*/*E* isomeric ratio. See: M. Otero, M. A. Herranz, C. Seoane, N. Martín, J. Garıín, J. Orduna, R. Alcalá, B. Villacampa, *Tetrahedron* **2002**, *58*, 7463.

[17] a) M. Wielopolski, J. Santos, B. M. Illescas, A. Ortiz, B. Insuasty, T. Bauer, T. Clark, D. M. Guldi, N. Martín, *Energy Environ. Sci.* **2011**, *4*, 765; b) P.-A. Bouit, C. Villegas, J. L. Delgado, P. M. Viruela, R. Pou-Amérigo, E. Ortí, N. Martín, *Org. Lett.* **2011**, *13*, 604.

[18] G. D. Allen, M. C. Buzzeo, C. Villagrán, Ch. Hardacre, R. G. Compton, *J. Electroanal. Chem.* **2005**, *575*, 311.

Received: January 31, 2012