Pergamon

Tetrahedron 58 (2002) 7463–7475

TETRAHEDRON

Synthesis and properties of push–pull chromophores for second-order nonlinear optics derived from π-extended tetrathiafulvalenes (TTFs)

Manuel Otero,[a] Mª Ángeles Herranz,[a] Carlos Seoane,[a] Nazario Martín,[a,*] Javier Garín,[b] Jesús Orduna,[b] Rafael Alcalá[c] and Belén Villacampa[c]

[a]Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense de Madrid, Avenida Complutense 22, E-28040 Madrid, Spain
[b]Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain
[c]Departamento de Física de la Materia Condensada, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

Received 14 March 2002; revised 6 June 2002; accepted 10 July 2002

Abstract—Novel π-extended tetrathiafulvalene (exTTF) derivatives connected to a *p*-nitrophenyl electron-accepting unit through a π-conjugated oligoenic spacer (**14a–c–16a–c**) show good second-order optical nonlinearities. The effect of the conjugation length of the oligoenic spacer and the presence of a thiophene ring in the π-conjugated bridge (**20a–c**) have been theoretically (PM3) and/or experimentally (EFISH technique) studied. The redox properties of the novel compounds have been investigated by cyclic voltammetry (CV) and the CV data reveal the good donor ability of the exTTF unit. Although the energy of the intramolecular charge-transfer (ICT) band displayed by these compounds and their redox potentials are fairly insensitive to the nature of the conjugated spacer linking the donor and the acceptor moieties, an increase in their second order nonlinear optical responses is observed on increasing the conjugation lengths. Compounds **20a–c** bearing a thiophene ring show a remarkable thermal stability with decomposition temperatures over 400°C. A new series of D-π-A compounds (**23a–c**) bearing a 1,3-dithiol-2-ylidene donor unit has also been synthesized and studied. © 2002 Elsevier Science Ltd. All rights reserved.

---

1. Introduction

The synthesis of molecular and polymeric materials exhibiting nonlinear optical (NLO) properties is currently a major task in chemistry due to their applications in the domain of opto-electronics and photonics.[1] Molecular NLO-phores are traditionally constituted by electron donor and acceptor moieties covalently connected through a conjugated bridge, and a wide variety of π-conjugated and homo- and heterobridges have been investigated.[2] In this regard, Marder has shown that bond length alternation, i.e. the average difference in length between single and double bonds in the molecule, is the relevant parameter in the optimization of the hyperpolarizability of molecules.[3]

Another important aspect in the design of molecules exhibiting NLO properties has been directed to the synthesis of systems where the loss of aromaticity in the ground state is compensated by a gain in aromaticity in the charge separated form.[4] Finally, a good thermal and chemical stability as well as low optical loss (high transparency) are important requirements for molecular organic materials to be incorporated into more practical nonlinear optical polymers.[1]

In the search of new NLO-phores, during the last years, we have reported the synthesis and second order NLO properties of push–pull tetrathiafulvalenes (TTFs) connected through an oligoenic bridge to different acceptor moieties (**1–3**).[5] In these systems, the degree of intramolecular charge transfer from the donor to the acceptor has been recently analyzed by means of Raman spectroscopy.[6]

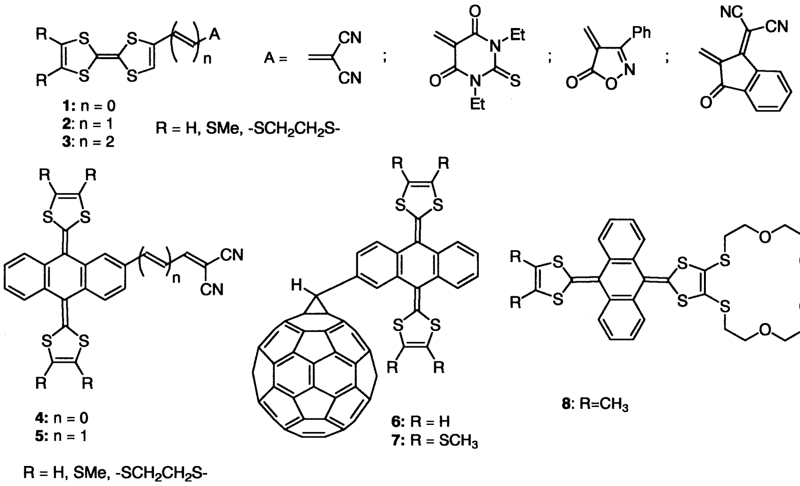
TTF and its derivatives are nonaromatic (14 π electrons) planar π-electron-donor molecules which are easily oxidized to form reversibly the radical cation and dication species.[7] Both species are thermodynamically very stable due to the aromatic character (six π-electrons) of the resulting 1,3-dithiolium cation. Therefore, TTFs fulfill the requirement of gain in aromaticity in the oxidized state. In addition, these TTF-phores show a good degree of thermal stability as evidenced by the decomposition temperatures around 200°C.[6]

The effect of methyl substituents in the TTF moiety and the nature of the conjugated bridge on the NLO properties have also been recently studied.[8]

Keywords: D-π-A compounds; 1,3-dithiol-2-ylidene; π-extended tetrathiafulvalene (exTTF); nonlinear optics (NLO); electrochemistry.

* Corresponding author. Tel.: +34-91-394-4227; fax: +34-91-394-4103; e-mail: nazmar@quim.ucm.es

PII: S0040-4020(02)00803-7



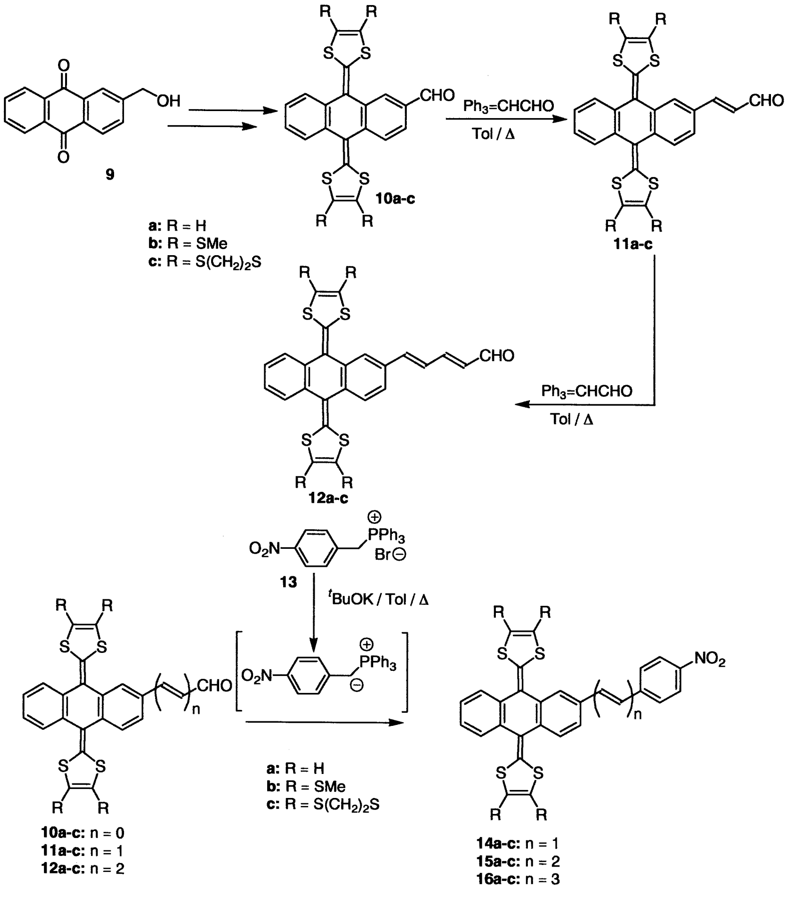
1: n = 0
2: n = 1
3: n = 2
4: n = 0
5: n = 1
6: R = H
7: R = SCH$_3$
8: R=CH$_3$

π-Extended TTFs (exTTFs) with quinonoid structures (**4**, **5**) have been much less studied as NLO-phores despite their good hyperpolarizabilities ($\mu\beta$=230–550×10^{-48} esu) and excellent thermal stabilities with decomposition temperatures close to 300°C.[9]

Quinonoid π-extended TTFs are an important class of modified TTFs which, in contrast to the parent TTF, undergo a two-electron oxidation to form the dication species at potential values close to that of TTF.[10] exTTFs have been successfully used as donor units in the preparation of charge transfer (CT) complexes with high electrical conductivities (σ_{rt}=60 S cm^{-1}).[11]

More recently, exTTFs have been studied in the preparation of photovoltaic systems (**6**,**7**)[12] and in chemical sensors and redox-switchable ligands (**8**).[13]

In this paper, we describe the synthesis of new series of exTTF-containing molecules in which a *p*-nitrophenyl group has been used as the acceptor component in these push–pull systems. Thus, we have systematically modified the length of the oligoenic spacer connecting both donor and acceptor moieties. In addition, we have studied the effect of the substituents on the 1,3-dithiole rings of the exTTF unit, as well as the presence of a thiophene ring in the π-extended bridge. A series of D-π-A compounds endowed with a



Scheme 1.

differently substituted 1,3-dithiole ring as donor unit has been synthesized in order to compare its NLO-response with that of the related exTTF systems.

2. Results and discussion

2.1. Synthesis

The preparation of the novel exTTF-π-A (**14a–c–16a–c**) was carried out in a multistep synthetic procedure from the formyl-free compound **10**,[14] which was in turn obtained from commercially available 2-hydroxymethyl-9,10-anthraquinone (**9**). Higher vinylogues **11** and **12** were prepared from **10** by reaction with triphenylphosphoranylideneacetaldehyde in refluxing toluene as shown in Scheme 1.

The target push–pull molecules (**14a–c–16a–c**) were synthesized by Wittig reaction from the respective formyl-exTTFs (**10–12**) by reaction with the carbanion of (4-nitrobenzyl)triphenylphosphonium bromide (**13**) generated in the presence of potassium *tert*-butoxide (see Section 4). Compounds **14a–c–16a–c** were obtained as stable solids in good yields (61–97%).

In is worth mentioning that this reaction was carried out using different bases (*n*-BuLi/THF, EtONa/EtOH). However, the best results were obtained with *t*-BuOK in refluxing toluene since the use of high temperatures allowed to obtain the all-*trans* compounds as the only reaction product.

The structure of the obtained compounds was confirmed by analytical and spectroscopic (FT-IR, ^{1}H NMR, ^{13}C NMR, MS, UV–Vis) methods. Thus, the NO_2 group was observed in the FT-IR spectra as two bands at around 1508 and 1338 cm^{-1}. The ^{1}H NMR spectra of compounds bearing only one vinyl group (**14a–c**) show the vinyl protons as doublets at around 7.3 and 7.1 ppm with coupling constants of J=16.1–16.8 Hz. Compounds **15a–c** bearing two vinyl groups show the vinyl protons as two doublets with coupling constants of J=15.4–14.8 and 10.4–10.0 Hz. More complex spectra were observed for **16a–c** due to the overlapping signals. However, coupling constants of J=15.7–15.0 and 10.3–9.7 Hz were observed (see Section 4). These coupling constant values (J=16.8–14.9 Hz) clearly confirm the formation of *trans* stereoisomers.

In addition, the 1,3-dithiole protons in compounds (**14a–16a**) appear as a singlet at δ 6.3 ppm (4H), and when the dithiole ring bears SMe and $S(CH_2)_2S$ substituents, these are observed as singlets at δ~2.4 ppm (12H) and 3.3 ppm (8H), respectively. This assignment is in good agreement with that previously reported for related TTF derivatives.[8]

The UV–Vis spectra of compounds **14a–c–16a–c** show a low energy intramolecular charge-transfer (ICT) band which appears as a clear shoulder in the visible region, similarly to that observed for the formyl-containing precursors (**10–12**). The UV–Vis spectra of the electroactive *p*-nitrotoluene and exTTF (**24**) have been also included in Fig. 1 for comparison purposes. In these systems (**14–16**), the ICT band remains nearly unaltered without showing a clear bathochromic shift in comparison with the respective aldehydes (**10–12**). The same behavior was observed for the differently substituted exTTFs (see Fig. 1). This behavior is in contrast to that previously observed for other stronger acceptors such as the dicyanovinylene group for which a bathochromic shift of around 100 nm was observed when compared to the related aldehydes.[8]

Enhancement of thermal stability in molecules **14a–c–16a–c** can in principle be achieved by introducing (hetero)aromatic structures along the conjugation path of the molecules. Therefore, we carried out the synthesis of a new series of exTTF-π-A molecules (**20a–c**) incorporating a thiophene ring in the conjugated bridge.

The synthesis of compounds **20a–c** was carried out as depicted in Scheme 2. The phosphonium salts (**17a–c**)[15] were prepared from 2-hydroxymethyl-exTTF which was obtained in a three steps synthesis from 2-hydroxymethyl-9,10-anthraquinone by following the procedure developed in our laboratory.[16] After isolation, compounds **17a–c** were rapidly reacted with potassium *tert*-butoxide in refluxing toluene to form the Wittig ylide (**18**) which reacted with 5-(2-*p*-nitrophenylvinyl)-2-thiophenecarbaldehyde (**19**) to lead to the push–pull molecules **20a–c** which were obtained in low to moderate yield (9–57%) due to the decomposition of the starting salt.

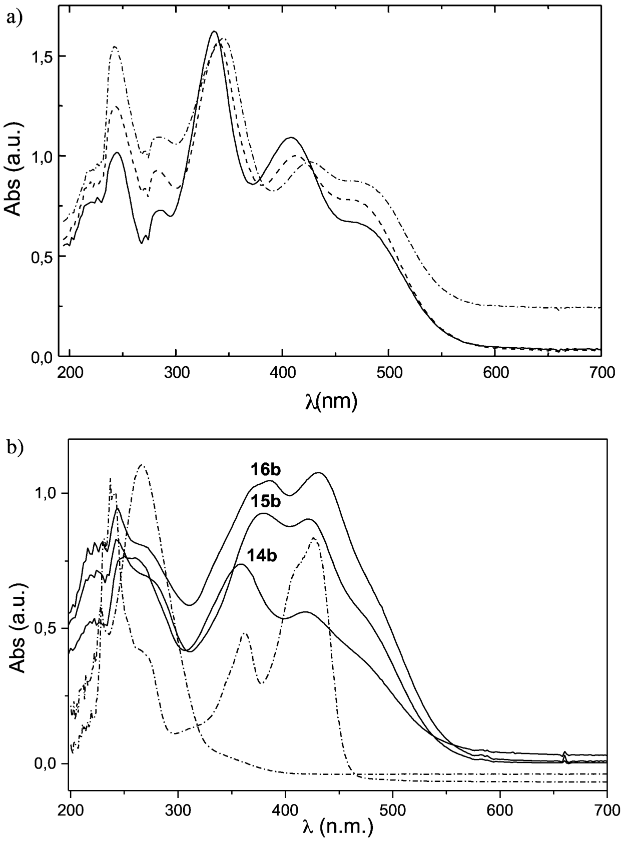
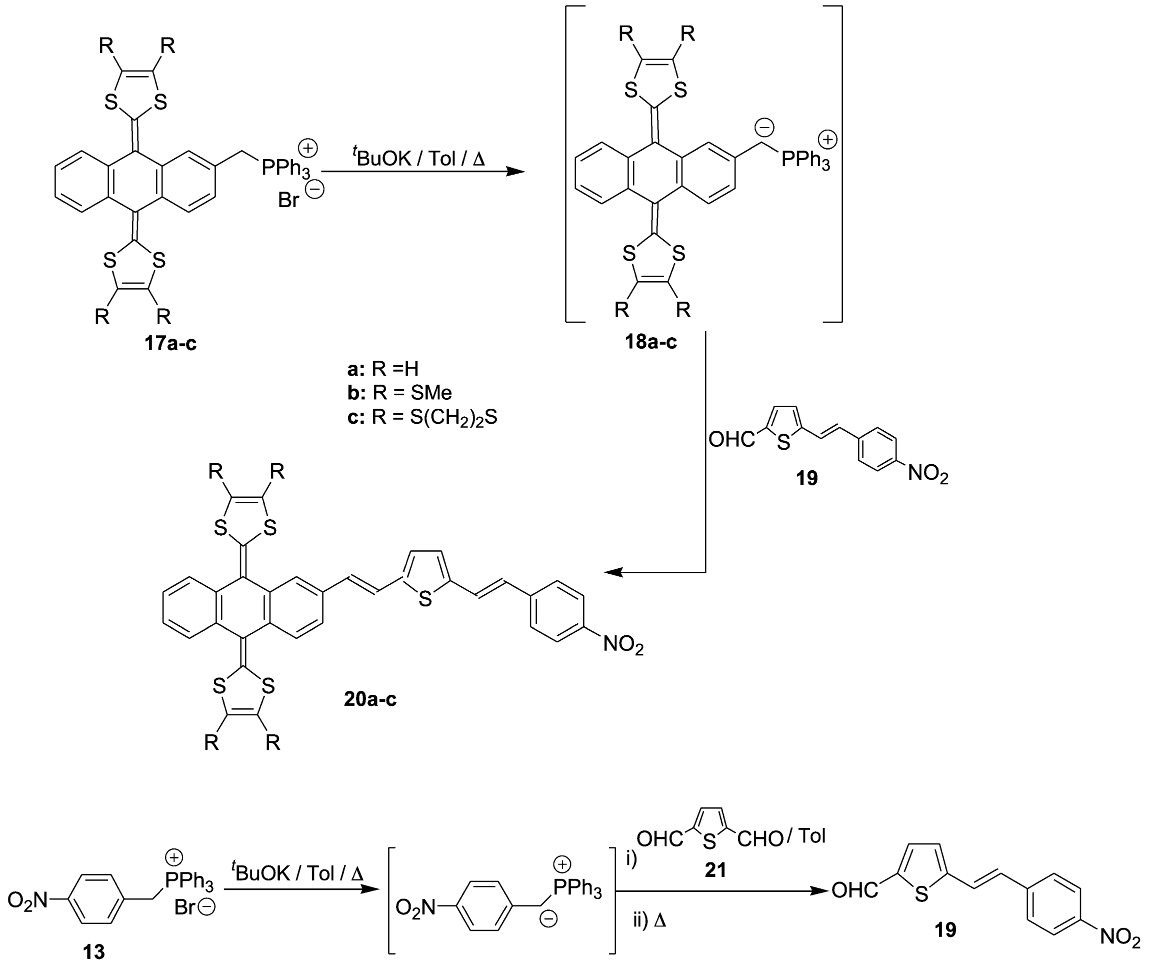


Figure 1. (a) UV–Vis spectra of compounds **12a** (—), **12b** (- - -) and **12c** (-·-·-). (b) UV–Vis spectra fof **14b** (—), **15b** (—), **16b** (—), *p*-nitrotoluene (-·-·-) and exTTF (**24**) (- - -).



Scheme 2.

2-Formylthiophene derivative **19** was in turn obtained by treatment of phosphonium bromide **13** with potassium *tert*-butoxide to form the intermediate ylide, which reacted with commercially available 2,5-diformylthiophene (**21**) in stoichiometric amounts (1:1) to form compound **19** in 70% yield.

It is worth mentioning that phosphonium salts **17a–c** are important building blocks for the construction of more sophisticated donor–acceptor systems provided the synthetic versatility of the Wittig reaction with a wide variety of eletroactive systems endowed with carbonyl groups.

The ^1H NMR spectroscopic data confirm, similarly to compounds **14–16**, the formation of the all-*trans* isomers as the only isolated compounds according to the observed coupling constants (~16 Hz) for these systems (**20a–c**). The electronic spectra of **20a–c** reveal the presence of a ICT band which is observed as a shoulder at around 500 nm overlapping with the π-extended aromatic system (Fig. 2).

As shown in Fig. 2, substitution on the 1,3-dithiole ring in **20a–c** has not a significant effect on the λ_{max} values.

Compounds **20a–c** exhibit a remarkable thermal stability with melting points over 400°C. Therefore, these molecules are appealing systems for further incorporation into poled polymers in the search of NLO materials.

In order to compare the push–pull systems bearing the exTTF donors with other known and efficient donor chromophores as the 1,3-dithiol-2-ylidene moiety, we have carried out the synthesis of compounds **23a–c**. These compounds were easily prepared by two consecutive Wittig–Horner and Wittig olefination reactions as shown in Scheme 3.

Thus, compounds **22a–c** were obtained by reaction of 2,5-diformylthiophene **21** with the respective phosphonate

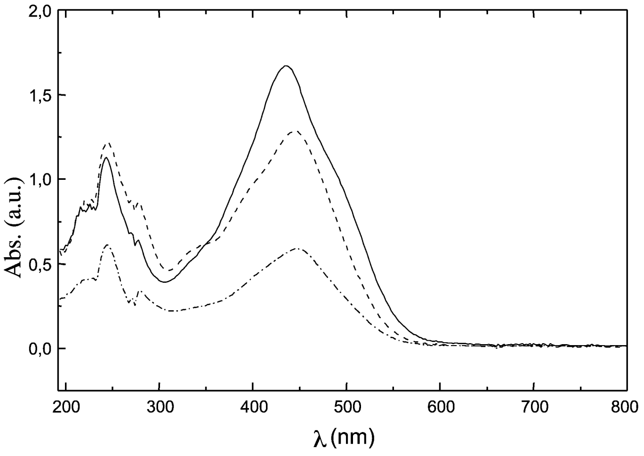
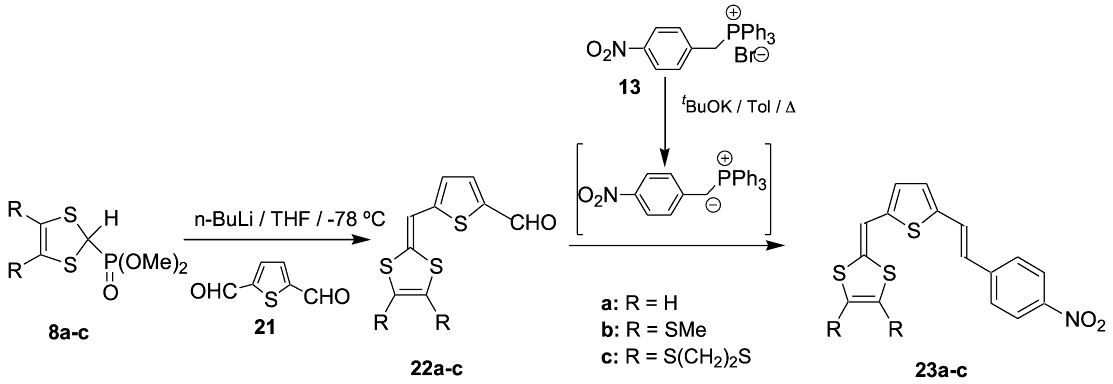


Figure 2. UV–Vis spectra for **20a** (—), **20b** (- - -) and **20c** (-·-·-).



Scheme 3.

under basic conditions according to the procedure previously reported in the literature.[17] Further olefination reaction of **22a–c** with 4-nitrobenzyl(triphenyl) phosphonium bromide (**13**) afforded compounds **23a–c** in high yields (65–98%).

The ^1H NMR spectra of **23a–c** clearly confirm the presence of the all-*trans* isomers as the only product formed in the olefination reaction (J=16.5 Hz).

The UV–Vis spectra of compounds **23a–c** show a low energy ICT band in the visible region (λ_{max}=490 nm in CH_2Cl_2) as a consequence of the stronger electron-accepting character of the *p*-nitrophenyl chromophore, in comparison with the carbonyl group. A slightly negative solvatochromism was observed for compound **23b** [CH_3CN (ε: 35.94) 478 nm; EtOH (ε: 24.55) 482; CH_2Cl_2 (ε: 8.93) 490] in agreement with other related structures.[17,18] Nevertheless, in our case, the observed solvatochromism could stem from the difference in refractive indices of solvents.

Compounds **23a–c** showed decomposition temperatures in the range 190–260°C which are remarkably lower than those observed for the related exTTF derivatives (**20a–c**) (>400°C), thus proving the additional thermal stabilization provided by the exTTF units.

2.2. Electrochemistry

The redox properties of the novel compounds obtained have been determined by cyclic voltammetry (CV) at room temperature in methylene dichloride solutions, using glassy carbon as the working electrode, SCE as reference, and tetra-*n*-butylammonium perchlorate as the supporting electrolyte. The respective data are collected in Table 1 along with the redox potentials of compound **13** and the parent unsubstituted exTTF donor (**24**).

The voltammograms of exTTF derivatives **14–16** and **20** show the presence of two one-electron reduction waves corresponding to the reduction of the *p*-nitrophenyl group similarly to that found for the reference compound **13** (see Table 1). It is worth mentioning that the first reduction potential of compounds **16a–c** appears at slightly less negative values (anodically shifted) than those of compounds **14** and **15**, which can be attributed to the longer distance to the exTTF donor unit.

The first reduction potential of aldehydes **12a–c** appear at more negative values than those containing the *p*-nitrophenyl group (**14–16**), which indicates the poorer electron–acceptor character of the carbonyl group.

On the oxidation side, all the exTTF systems show only one oxidation wave involving two electrons to form the dication species, similarly to that observed for the reference exTTF (**24**).[11,19] The oxidation potential values are lower for the unsubstituted exTTF moiety (compounds **12a**, **14a**, **15a**, **16a**, **20a**). As expected, substitution on the 1,3-dithiole rings of the exTTF units with the SMe and $S(CH_2)_2S$ groups leads to more positive values and, therefore, to poorer electron donors.[19]

Interestingly, compounds **23a–c** bearing the 1,3-dithiole ring as electron donor unit exhibit more positive oxidation potential values, thus confirming their poorer electron donor ability related to the exTTF unit (see Table 1 and Fig. 3).

The electrochemical redox behavior of **20b** was studied at different temperatures and the voltammograms are shown

Table 1. Redox properties of novel push–pull molecules (**12**, **14**, **15**, **16**, **20**, **23**)

Compounds	E^{1}_{red}[a]	E^{2}_{red}[a]	$E^{1}_{\mathrm{ox(a.p.)}}$[a]	$E_{\mathrm{ox(c.p.)}}$[a]
12a	−1.37	–	0.45	0.04
12b	−1.35	–	0.60	0.24
12c	−1.37	–	0.54	0.30
14a	−1.01	−1.49	0.51	0.13
14b	−1.00	−1.44	0.62	0.43
14c	−1.02	−1.47	0.64	0.38
15a	−1.01	−1.37	0.45	0.20
15b	−1.00	−1.42	0.62	0.43
15c	−0.97	−1.43	0.65	0.40
16a	−0.97	−1.37	0.47	0.19
16b	−0.93	−1.41	0.65	0.37
16c	−0.94	−1.39	0.66	0.35
20a	−1.06	−1.47	0.48	−0.07
20b	−1.05	−1.45	0.60	0.21
20c	−1.07	−1.46	0.57	0.16
23a	−1.10	−1.62	0.65	0.43
23b	−1.11	−1.61	0.73	0.53
23c	−1.08	−1.52	0.71	0.57
13	−1.00	−1.57	–	–
24	–	–	0.45	−0.03

[a] V vs SCE; $Bu_4N^+ClO_4^-$ as supporting electrolyte; CH_2Cl_2 as solvent; 200 mV/s; a.p. anodic peak; c.p. cathodic peak; **24**: 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene.

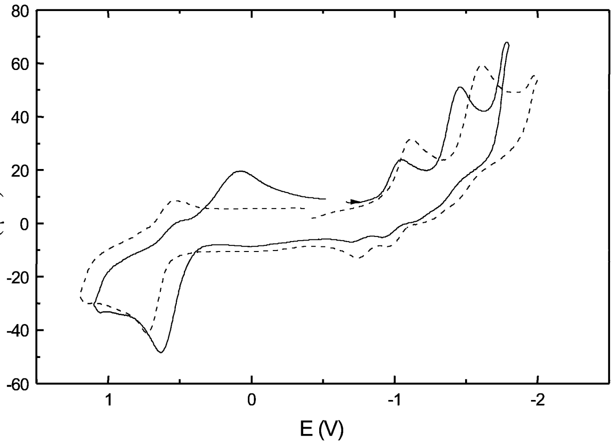


Figure 3. Cyclic voltammograms of compounds **20b** (—) and **23b** (- - -).

in Fig. 4. The oxidation potential values are anodically shifted with decreasing the temperature [$E_{\text{ox}(35°\text{C})}$=0.58 V; $E_{\text{ox(rt)}}$= 0.60 V; $E_{\text{ox}(0°\text{C})}$=0.60 V; $E_{\text{ox}(-78°\text{C})}$=0.64 V] which indicates the higher difficulty in the formation of the dication species. A more remarkable effect is the reduction from the dication to the neutral form, which undergoes a drastic shift to lower potentials when lowering the temperature [$E_{\text{red}(35°\text{C})}$=0.32 V; $E_{\text{red(rt)}}$=0.21 V; $E_{\text{red}(0°\text{C})}$=0.17 V; $E_{\text{red}(-78°\text{C})}$=0.02 V] becoming a more electrochemically irreversible system. This behavior has been previously observed and indicates the high stability of the formed dications.[19,20]

2.3. Theoretical calculations and NLO properties

In order to gain a better understanding of the geometrical and electronic properties of the compounds synthesized as well as on the observed ICT band, which is a prerequisite to the attainment of high β values,[21–23] theoretical calculations were performed.

The calculation of the hyperpolarizabilities using quantum chemical calculations is usually performed on isolated molecules in the gas phase and at a fixed conformation and hence are not expected to reproduce quantitatively the experimental EFISH values obtained in solution. Furthermore, the ab initio models employing large basis sets that are usually required to obtain accurate results can not be used on large molecules like those presented in this paper due to their large computational cost. Having this in mind, we have performed semiempirical calculations using the PM3 hamiltonian and the Time-Dependent Hartree–Fock (TDHF) approximation since this method has proved to reproduce successfully the trends in the NLO response of tetrathiafulvalene chromophores.[5b–c,8,24]

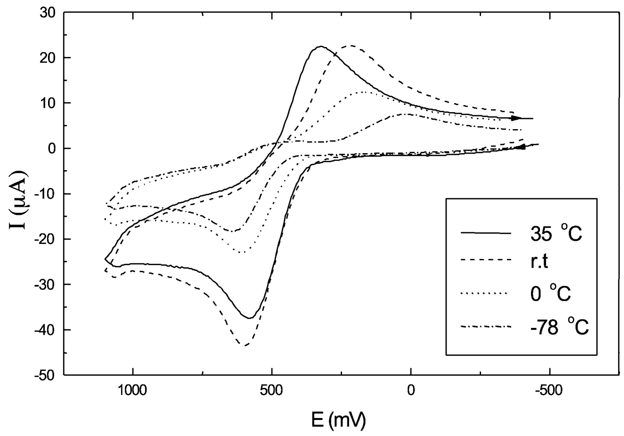


Figure 4. Cyclic voltammograms of compound **20b** at different temperatures.

Two possible conformations (A and B) were considered for the calculations of the geometry of compounds **14–16** (Fig. 5).

Theoretical calculations predict in all cases studied practically the same heats of formation for both conformations (A, B). The difference (0.1 kcal/mol) between their heats of formation indicates that both conformations should be possible and, therefore, the calculations of the NLO properties were carried out on both conformers (A and B).

The molecular geometry of conformation A for compound **16a** is shown in the Fig. 5. As expected, the exTTF donor unit shows a highly distorted geometry out of planarity due to the strong steric interactions between the 1,3-dithiole rings and the *peri* hydrogens. To avoid these interactions, the molecule adopts a butterfly shape with the central ring upward and the dithiole rings pointing downward. This geometry is in full agreement with that calculated for other related systems[19] as well as that determined by X-ray crystallography.[11] It has been reported that the PM3 method provides a good description, even better than ab initio HF/6-31G* calculations, for the molecular structure of extended TTFs with a minimal computational cost.[19] A planar geometry was determined for the conjugated oligoenic spacer and *p*-nitrophenyl moiety (Fig. 5).

The electronic structure of **14–16** shows that the HOMO is located on the exTTF donor fragment, and the LUMO is mainly spread on the *p*-nitrophenyl acceptor moiety and the oligoenic spacer (Fig. 5). It can be seen that there is an overlap between the HOMO and LUMO which is an important requirement to obtain large second order NLO responses.[21]

The $\mu\beta$ values of the exTTF derivatives (**14–16**) were measured using the EFISH technique[22] and the values are presented in Table 2, along with the $\mu\beta(0)$ values calculated assuming a two-level model (compounds **20a–c** were not measured due to their instability under EFISH conditions). In order to minimize possible resonance effects which would enhance the NLO response, measurements were performed at a fundamental wavelength of 1.907 nm. For the sake of comparison, the $\mu\beta(0)$ of DANS is 363×10^{-48} esu ($CHCl_3$).

As shown in Table 2, while semiempirical calculations overestimate the experimental NLO response, the calculated $\mu\beta$ values follow the same trend than that observed experimentally with the only exception of compound **15b** which displays an unexpectedly high NLO response.

The NLO response increases with increasing the π-conjugation between both donor and acceptor moieties.

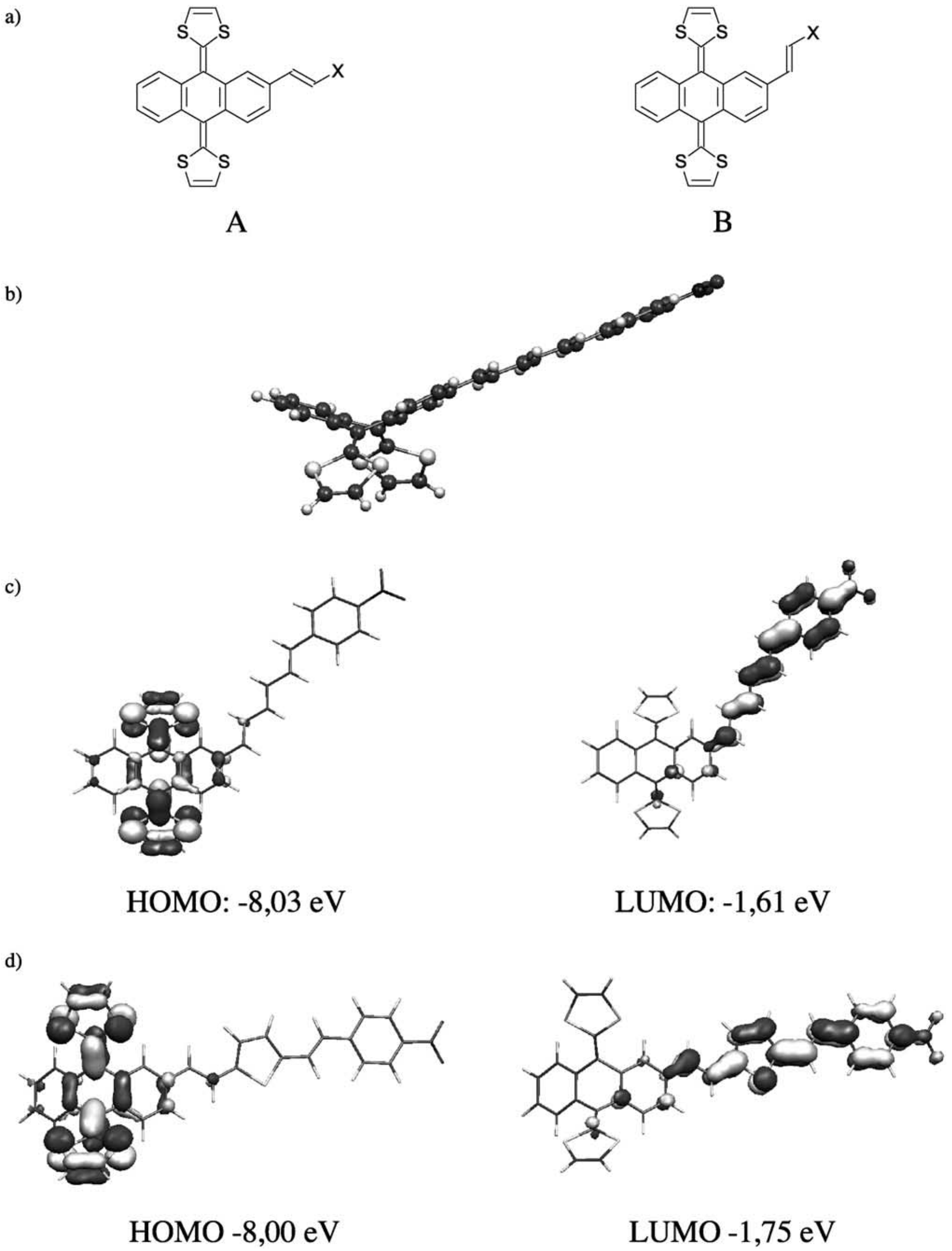


Figure 5. (a) Two possible conformations (A and B) for compounds **14**–**16a**–**c** and **20**. (b) Calculated molecular geometry (PM3) of compound **16a**. (c) HOMO–LUMO orbitals for compound **16a**. (d) HOMO–LUMO orbitals for compound **20a**.

However, a most interesting result is that alkylthio substituents on the 1,3-dithiole ring significantly increase the $\mu\beta$ values.

It is also worthy to note that the NLO responses of compounds **14a**, **15a** and **16a** are very similar to those of analogous chromophores containing a tetrathiafulvalene linked to the *p*-nitrophenyl acceptor.[8]

The geometry calculated (PM3) for compound **20a** was quite similar to that found for compounds **14**–**16**. Interestingly, a planar geometry is observed for the benzene-π-acceptor moiety, thus supporting the good NLO response. As expected, the HOMO is located on the exTTF unit and the LUMO on the acceptor and vinyl-thiophene fragment (see Fig. 5).

Although we were not able to measure the experimental $\mu\beta$ values for **20a**–**c**, the calculated values predict a good NLO response, similar to that of compounds **16a**–**c** bearing three vinyl units. These values are remarkably higher than those of the related systems bearing the 1,3-dithiol-2-ylidene as the donor unit in **23a**–**c** (Table 2).

Thermal stability is an important criterion for technological applications. In this regard, compounds **20a**–**c** show an outstanding thermal stability (decomposition temperatures >400°C) and, therefore, these could be interesting systems for further applications.

The $\mu\beta$ values determined experimentally for **23a**–**c** show the same trend observed for compounds **20a**–**c** for the substitution pattern on the 1,3-dithiole ring. Thus, the NLO

Table 2. λ_{max} values and calculated and experimental NLO properties of novel systems

Compounds	λ_{max} (nm)[a]	$\mu\beta_{exp}$[a,b]	$\mu\beta(0)_{exp}$[a,b]	PM3 Conf. A		PM3 Conf. B	
				μ[c]	$\mu\beta(0)$[b]	μ[c]	$\mu\beta(0)$[b]
14a	~480 (sh)	180	140	6.74	290	6.73	288
14b	~480 (sh)	212	163	7.22	361	7.20	354
14c	~480 (sh)	205	155	7.38	367	7.40	359
15a	~480 (sh)	230	180	6.78	382	6.78	382
15b	~480 (sh)	360	277	7.29	466	7.25	452
15c	~480 (sh)	255	191	7.43	468	7.32	432
16a	~490 (sh)	324	247	6.87	485	6.85	484
16b	~490 (sh)	350	270	7.35	568	7.30	554
16c	~490 (sh)	331	250	7.54	578	7.54	567
20a	~500 (sh)	–	–	7.18	537	–	–
20b	~500 (sh)	–	–	7.90	667	–	–
20c	~500 (sh)	–	–	7.97	649	–	–
23a	490	315	219	6.44	397	–	–
23b	490	470	323	6.69	443	–	–
23c	490	370	266	6.78	481	–	–

[a] In CH_2Cl_2.
[b] In 10^{-48} esu units.
[c] In Debye.

response increases with the presence of alkylthio substituents on the 1,3-dithiole ring (Table 2). In contrast to the exTTF derivatives, PM3 method did not lead to a good correlation with experimental $\mu\beta$ values, since they predict an *anti* conformation of the vinyl group with the sulfur atom of the thiophene ring, which is in contrast to the experimental geometries determined by X-ray crystallography.[25]

Therefore, and for comparison purposes, we calculated the $\mu\beta(0)$ value for **23a–c** using the more reliable conformation with a *syn* geometry. The calculated values show a similar correlation with those experimental values found for the exTTF derivatives (Table 2).

3. Summary and conclusions

In summary, we describe the synthesis of novel π-extended TTF derivatives in which the exTTF unit is connected to a *p*-nitrophenyl acceptor through different bridges (**14–16**). A systematic study has been carried out on the length of the oligoenic spacer as well as on the substitution on the exTTF moiety. The electrochemical study reveals the good donor character of the π-extended TTF unit and the effect of the alkylthio substituents on the donor ability.

In order to improve the thermal properties of these compounds, a thiophene ring has been inserted in the conjugated oligoenic spacer. Theoretical calculations (PM3) predict a good NLO response for these molecules (**20a–c**) which exhibit a remarkable thermal stability with decomposition temperatures over 400°C.

A new series of D-π-A systems bearing a 1,3-dithiol-2-ylidene donor connected to the same *p*-nitrophenyl group as acceptor NLO-phore has been synthesized. Although a comparison of the experimental $\mu\beta(0)$ values of compounds **20a–c** and **23a–c** has not been possible, the latter also show good NLO responses.

All the D-π-A systems prepared show the presence of a low energy intramolecular charge-transfer band (ICT) in their electronic spectra which is nearly independent of the donor ability of the donor moiety and the length of the oligoenic spacer.

In agreement with their nature, the studied compounds (**14a–c–16a–c**, **23a–c**) showed second order NLO responses that were measured by using the EFISH technique. Therefore, π-extended TTFs are interesting NLO-phores which exhibit good $\mu\beta$ values and thermal stabilities for further practical applications. Work is in progress to optimize the NLO response by using other stronger acceptors as well as to embody them into polymeric systems.

4. Experimental

All melting points were measured with a Gallenkamp apparatus and are uncorrected. IR spectra were recorded either as KBr pellets or as films with NaCl plates with a Perkin–Elmer 257 spectrometer. UV–Vis spectra were recorded with a Perkin–Elmer Lambda 3 instrument. ^{13}C- and ^{1}H NMR spectra were recorded with a Varian VXR-300 spectrometer (300 and 75 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts are given as δ values (int. Standard: TMS). Fourier Transform Infrared absorption (FT-IR) measurements were made with a Perkin–Elmer Model 1760 X spectrometer. All spectra were collected using a resolution of 2 cm^{-1}, and the mean of 50 scans was obtained. Interference from atmospheric water vapor was minimized by purging the instrument for 10–15 min with dry argon before beginning data collection. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. MS were recorded with a Hewlett–Packard HP5989A spectrometer. Cyclic voltammograms were recorded on a potentiostat/galvanostat Versastat EG&G PAR, equipped with a software electrochemical analysis Model 250 by using a GCE (glassy carbon) as working electrode, SCE as reference electrode, $Bu_4N^+ClO_4$ as supporting electrolyte, dichloromethane as solvent, and at a scan rate of 200 mV/s. 2-Hydroxymethyl-9,10-anthraquinone, 2,5-diformylthiophene and (4-nitrobenzyl)triphenylphosphonium bromide are commercially available and were used without further purification. EFISH measurements were taken with a nonlinear optics spectrometer from SOPRA. The fundamental light at 1.907 μm was the first Stokes peak of a hydrogen Raman cell pumped by the 1.064 μm light from a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns, pulse). That light was passed through a linear polariser and focused on the EFISH cell. The polarising dc voltage (parallel to the light polarization) used in this cell was 6 kV. The output light from the cell was passed through an interference filter to select the second harmonic light (0.954 μm) which was finally detected with a R642 photomultiplier from Hamamatsu. Static $\mu\beta(0)$ values were deduced from the experimental values using a two-level dispersion model.

Molecular orbital calculations for compounds **14–16a–c** were carried out using the version PC-GAMESS 6.0[26] of the GAMESS program.[27]

4.1. Synthesis of starting aldehydes

Aldehydes **10a–c**[14] and **11a–c**[9] were prepared by following the procedures previously reported in the literature. Aldehydes **12a–c** were prepared according to the following general procedure:

A solution of (tiphenylphosphoranylidene)acetaldehyde (0.9 mmol) and the corresponding carbonyl compound (**11a–c**) (0.3 mmol) in toluene, was refluxed under argon atmosphere for 16 h. The solvent was removed under reduced pressure, and the crude material washed with water (50 mL) and extracted with methylene dichloride (3×50 mL). The organic extracts were dried, and the solvent was removed under reduced pressure. The resulting mixture was purified by silica gel chromatography using methylene dichloride as eluent.

4.1.1. 2-(4-Formyl-1,3-butadienyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (12a). Yield 65%; mp 190–193°C (dec.); FT-IR (KBr) 1670, 1655, 1618, 1585, 1545, 1500, 1452, 1287, 1151, 1119, 1012, 987, 800, 756, 646, 615 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.64 (d, 1H, J=8.0 Hz), 7.86 (d, 1H, J=1.5 Hz), 7.74–7.64 (m, 3H), 7.57–7.54 (m, 1H), 7.43 (dd, 1H, J_1=8.1 Hz, J_2=1.5 Hz), 7.35–7.29 (m, 2H), 7.08–7.03 (m, 2H), 6.36–6.33 (m, 4H), 6.30 (dd, 1H, J_1=15.1 Hz, J_2=9.1 Hz); ^{13}C NMR (50 MHz, CDCl$_3$) δ 167.7, 152.2, 142.2, 139.2, 136.7, 136.0, 135.1, 133.1, 132.4, 131.4, 130.9 (2C), 128.8 (2C), 126.1, 126.0, 125.4, 124.9, 123.8, 121.6, 121.5, 117.4, 117.3, 116.9, 114.0; MS (m/z) 460 (M$^+$, 100); UV–Vis (CH$_2$Cl$_2$) λ_{max} (log ε) 460 (4.19), 408 (4.40), 336 (4.57), 286 (4.22), 244 (4.37) nm.

4.1.2. 2-(4-Formyl-1,3-butadienyl)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (12b). Yield 34%; mp 185–187°C; FT-IR (KBr) 2924, 2852, 1676, 1657, 1612, 1597, 1562, 1547, 1529, 1510, 1493, 1444, 1412, 1394, 1319, 1275, 1262, 1151, 1117, 1012, 981, 769, 756 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.63 (d, 1H, J=8.1 Hz), 7.75–7.70 (m, 1H), 7.67 (s, 1H), 7.63–7.53 (m, 3H), 7.45 (d, 1H, J=8.4 Hz), 7.36–7.32 (m, 2H), 7.07–7.04 (m, 2H), 6.32 (dd, 1H, J_1=15.1 Hz, J_2=8.1 Hz), 2.40 (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.8, 151.9, 141.8, 135.9, 135.3, 134.3, 133.5, 132.6, 132.4, 131.9, 131.8, 130.9 (2C), 128.8 (2C), 126.8, 126.5, 126.4, 126.1, 125.9, 125.8, 125.4, 125.3, 124.4, 123.0, 19.2 (2C), 19.1 (2C); MS (m/z) 644 (M$^+$, 100); UV–Vis (CH$_2$Cl$_2$) λ_{max} (log ε) 462 (4.22), 412 (4.32), 340 (4.52), 284 (4.29), 244 (4.44) nm.

4.1.3. 2-(4-Formyl-1,3-butadienyl)-9,10-bis(4,5-ethylendithio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (12c). Yield 35%; mp 190–192°C (dec.); FT-IR (KBr) 2924, 2854, 1728, 1672, 1618, 1599, 1508, 1460, 1379, 1277, 1121, 1074, 1040, 1007, 980, 754, 706, 679, 611 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.64 (d, 1H, J=7.9 Hz), 7.74–7.69 (m, 1H), 7.63 (s, 1H), 7.56–7.48 (m, 3H), 7.44 (dd, 1H, J_1=8.0 Hz, J_2=1.5 Hz), 7.37–7.32 (m, 2H), 6.37–6.28 (m, 2H), 6.32 (dd, 1H, J_1=15.2 Hz, J_2=8.0 Hz), 3.31 (s, 8H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 167.7, 151.9, 141.8, 135.9, 135.3, 134.4, 133.6, 132.4, 131.7, 130.9 (2C), 130.6, 128.8 (2C), 126.5, 126.4, 126.0, 125.6, 125.5, 124.4, 123.4, 111.3, 111.2, 111.0, 110.7, 29.6 (2C); MS ((m/z)) 640 (M$^+$, 67); UV–Vis (CH$_2$Cl$_2$) λ_{max} (log ε) 468 (4.38), 426 (4.44), 344 (4.70), 286 (4.51), 242 (4.69) nm.

4.2. Synthesis of donor-π-acceptor compounds (14–16a–c)

A toluene solution of (4-nitrobenzyl)triphenylphosphonium bromide (268 mg, 0.56 mmol) and potassium *tert*-butoxide (149 mg, 1.33 mmol) was heated to reflux under argon atmosphere. After 30 min, a solution of the corresponding aldehyde (**10–12a–c**) (0.22 mmol) was added and refluxed for 16 h. The solvent was removed under reduced pressure and the residue washed with water and extracted with methylene dichloride. The organic extract was dried, and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane/methylene dichloride (1:1) as eluent.

4.2.1. 2-(2-*p*-Nitrophenylvinyl)-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (14a). Yield 75%; mp 206–208°C (dec.); FT-IR (KBr) 1591, 1543, 1508, 1456, 1419, 1338, 1259, 1107, 1026, 951, 866, 843, 802, 756, 690, 650, 634 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.23 (d, 2H, J=8.5 Hz), 7.90 (s, 1H), 7.74–7.70 (m, 3H), 7.66 (d, 2H, J=8.5 Hz), 7.45 (d, 1H, J=7.6 Hz), 7.34–7.29 (m, 2H), 7.31 (d, 1H, J=16.2 Hz), 7.18 (d, 1H, J=16.2 Hz), 6.34 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 146.6, 143.9, 136.6, 136.3, 136.2, 136.0, 135.9, 135.4, 135.2, 135.1, 133.7, 133.0, 126.8 (2C), 126.1 (2C), 125.4, 124.9 (2C), 124.2 (2C), 123.3, 121.8, 121.7, 117.4, 117.3, 117.2, 116.9; MS (m/z) 527 (M$^+$, 5), 497 (M$^+$−30, 100); UV–Vis (CH$_2$Cl$_2$) λ_{max} (log ε) ~480 (sh), 410 (4.31), 352 (4.34), 234 (4.33) nm. Anal. calcd for $C_{28}H_{17}S_4NO_2\cdot CH_2Cl_2\cdot C_6H_{14}$ (%): C 60.16, H 4.76, N 2.00, S 18.35. Found (%): C 60.39, H 4.51, N 2.24, S 18.57.

4.2.2. 2-(2-*p*-Nitrophenylvinyl)-9,10-bis(4,5-dimethyl-thio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (14b). Yield 97%; mp 242–245°C (dec.); FT-IR (KBr) 2922, 2852, 1629, 1591, 1560, 1512, 1491, 1458, 1450, 1419, 1381, 1338, 1281, 1109, 966, 835, 771, 746, 694, 682, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, 2H, J=8.8 Hz), 7.71 (s, 1H), 7.68 (d, 2H, J=8.8 Hz), 7.60–7.56 (m, 2H), 7.58 (d, 1H, J=8.5 Hz), 7.49 (dd, 1H, J_1=8.5 Hz, J_2=1.5 Hz), 7.36–7.31 (m, 2H), 7.32 (d, 1H, J=16.1 Hz, CH), 7.19 (d, 1H, J=16.1 Hz), 2.42–2.39 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.8, 143.7, 135.2, 135.0, 134.4, 134.2, 132.7, 132.0, 131.6, 130.6, 129.8, 127.4, 126.9, 126.6, 126.5, 126.4, 126.1, 125.9, 125.7, 125.4, 125.3, 125.0, 124.2, 124.1, 124.0, 123.8, 123.3, 123.1, 19.3 (4C); MS (m/z) 711 (M^+, 25), 681 (M^+-30, 12); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~480 (sh), 416 (4.48), 356 (4.62), 234 (4.64) nm.

4.2.3. 2-(2-*p*-Nitrophenylvinyl)-9,10-bis(4,5-ethylendi-thio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (14c). Yield 61%; mp 208–210°C (dec.); FT-IR (KBr) 2924, 2852, 1630, 1593, 1562, 1547, 1510, 1450, 1338, 1279, 1109, 852, 756, 694, 634 cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, 2H, J=8.8 Hz), 7.72–7.64 (m, 3H), 7.59–7.44 (m, 4H), 7.40–7.28 (m, 2H), 7.32 (d, 1H, J=16.8 Hz), 7.18 (d, 1H, J=16.8 Hz), 3.31 (s, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.8, 144.0, 143.8, 135.3, 135.1, 134.6, 134.4, 134.3, 132.8, 130.7, 130.4, 130.0, 128.7, 127.0, 126.6, 126.5, 126.0, 125.5, 125.0, 124.2, 124.1, 124.0, 123.7, 123.6, 111.2, 111.1, 111.0, 110.7, 29.6 (4C); MS (m/z) 707 (M^+, 99); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~480 (sh), 432 (4.44), 358 (4.56), 248 (4.63) nm. Anal. calcd for $C_{32}H_{21}S_8NO_2$ (%): C 54.3, H 3.0, N 2.0. Found (%): C 55.2, H 3.5, N 2.2.

4.2.4. 2-(4-*p*-Nitrophenyl-1,3-butadienyl)-9,10-bis(1,3-di-thiol-2-ylidene)-9,10-dihydroanthracene (15a). Yield 64%; mp 190–192°C (dec.); FT-IR (KBr) 1583, 1543, 1508, 1450, 1338, 1275, 1181, 1107, 984, 852, 812, 758, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, 2H, J=8.6 Hz), 7.82 (s, 1H), 7.73–7.64 (m, 3H), 7.56 (d, 2H, J=8.6 Hz), 7.37 (d, 1H, J=8.0 Hz), 7.33–7.29 (m, 2H), 7.15 (dd, 1H, J_1=15.2 Hz, J_2=10.4 Hz), 7.02 (dd, 1H, J_1=14.8 Hz, J_2=10.4 Hz), 6.85 (d, 1H, J=14.8 Hz), 6.73 (d, 1H, J=15.2 Hz), 6.33 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.5, 144.0, 136.0, 135.9, 135.5, 135.2, 135.1, 134.2, 133.9, 130.6, 130.0, 129.8, 128.2, 127.9, 127.5, 126.6, 126.1, 126.0, 125.3, 124.9, 124.6, 124.3, 124.2, 123.0, 122.0, 121.9, 117.4, 117.3, 117.2, 117.0; MS (m/z) 553 (M^+, 100), 523 (M^+-30, 11); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~480 (sh), 418 (4.55), 378 (4.53), 238 (4.44) nm.

4.2.5. 2-(4-*p*-Nitrophenyl-1,3-butadienyl)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15b). Yield 95%; mp 170–173°C (dec.); FT-IR (KBr) 2920, 2852, 1637, 1585, 1560, 1508, 1490, 1450, 1419, 1337, 1279, 1109, 987, 854, 756, 611 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 2H, J=8.8 Hz), 7.64 (s, 1H), 7.60–7.54 (m, 5H), 7.41 (d, 1H, J=8.1 Hz), 7.36–7.29 (m, 2H), 7.16 (dd, 1H, J_1=15.0 Hz, J_2=10.0 Hz), 7.03 (dd, 1H, J_1=15.4 Hz, J_2=10.0 Hz), 6.85 (d, 1H, J=15.0 Hz), 6.76 (d, 1H, J=15.4 Hz), 2.41 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.6, 143.8, 135.5, 135.1, 134.8, 134.6, 134.4, 133.7, 132.3, 132.1, 131.7, 131.4, 130.4, 128.6, 128.3, 127.5, 126.6, 126.5, 126.4, 126.0, 125.8, 125.4, 125.3, 125.1, 124.6, 124.2, 124.1, 123.7, 123.5, 123.3, 19.2 (2C), 19.0 (2C); MS (m/z) 737 (M^+, 39), 707 (M^+-30, 46); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~480 (sh), 454 (4.43), 420 (4.58), 378 (4.59), 240 (4.54) nm. Anal. calcd for $C_{34}H_{27}S_8NO_2$ (%): C 55.3, H 3.7, N 1.9. Found (%): C 56.0, H 4.3, N 2.2.

4.2.6. 2-(4-*p*-Nitrophenyl-1,3-butadienyl)-9,10-bis(4,5-ethylendithio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15c). Yield 80%; mp 196–198°C (dec.); FT-IR (KBr) 2924, 2852, 1589, 1508, 1458, 1337, 1279, 1109, 981, 852, 756, 744, 604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 1H, J=8.8 Hz), 8.21 (d, 1H, J=8.8 Hz), 7.72 (s, 1H), 7.70 (d, 1H, J=8.8 Hz), 7.57 (d, 1H, J=8.8 Hz), 7.61–7.49 (m, 3H), 7.40 (dd, 1H, J_1=7.9 Hz, J_2=1.5 Hz), 7.38–7.30 (m, 2H), 7.15 (dd, 1H, J_1=15.1 Hz, J_2=10.3 Hz), 7.03 (dd, 1H, J_1=15.1 Hz, J_2=10.3 Hz), 6.85 (d, 1H, J=15.1 Hz), 6.76 (d, 1H, J=15.1 Hz), 3.32 (s, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.6, 144.4, 135.5, 135.2, 134.8, 134.6, 134.5, 133.8, 130.8, 130.6, 130.4, 129.7, 128.8, 128.7, 127.4, 126.4, 126.0, 125.6, 124.5, 124.2, 124.0, 123.9, 123.8, 123.7, 123.6, 123.5, 111.2, 111.1, 111.0, 110.7, 29.7 (2C), 29.6 (2C); MS (m/z) 733 (M^+, 25); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~480 (sh), 452 (4.29), 428 (4.37), 376 (4.50), 244 (4.49) nm.

4.2.7. 2-(6-*p*-Nitrophenyl-1,3,5-hexatrienyl)-9,10-bis(1,3-di-thiol-2-ylidene)-9,10-dihydroanthracene (16a). Yield 65%; mp 268–270°C (dec.); FT-IR (KBr) 1635, 1578, 1558, 1541, 1508, 1458, 1419, 1338, 1257, 1109, 997, 976, 860, 800, 744, 692, 636, 611 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 2H, J=8.8 Hz), 7.79 (s, 1H), 7.75–7.64 (m, 5H), 7.35 (d, 1H, J=8.8 Hz), 7.34–7.25 (m, 2H), 7.06 (dd, 1H, J_1=15.7 Hz, J_2=10.3 Hz), 6.96 (dd, 1H, J_1=15.0 Hz, J_2=10.3 Hz), 6.77–6.51 (m, 4H), 6.33 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.2, 136.9, 136.1, 135.8, 135.2, 134.5, 133.7, 132.5, 132.3, 131.3, 130.6, 130.1, 129.8, 129.7, 129.3, 128.8, 128.7, 128.6, 127.5, 126.6, 126.0, 124.9, 124.3, 124.1, 123.9, 123.8, 123.5, 117.3 (2C), 117.0 (2C); MS (m/z) 579 (M^+, 100), 549 (M^+-30, 56); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~490 (sh), 426 (4.59), 398 (4.53), 240 (4.46) nm.

4.2.8. 2-(6-*p*-Nitrophenyl-1,3,5-hexatrienyl)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (16b). Yield 77%; mp 220–222°C (dec.); FT-IR (KBr) 2923, 2854, 1637, 1593, 1577, 1508, 1452, 1419, 1338, 1272, 1178, 1107, 995, 956, 850, 752, 692, 638 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, 2H, J=8.8 Hz), 7.61 (d, 1H, J=1.5 Hz), 7.60–7.50 (m, 5H), 7.38 (dd, 1H, J_1=7.9 Hz, J_2=1.5 Hz), 7.35–7.30 (m, 2H), 7.07 (dd, 1H, J_1=15.6 Hz, J_2=10.1 Hz), 6.97 (dd, 1H, J_1=15.6 Hz, J_2=10.0 Hz), 6.77–6.55 (m, 4H), 2.41 (s, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.5, 143.9, 136.6, 135.1, 134.5, 134.4, 134.3, 133.6, 132.9, 132.5, 131.5, 131.4, 130.9, 130.7, 130.6, 130.1, 129.7, 129.3, 129.0, 128.8, 128.7, 127.5, 126.6, 126.4, 125.8, 125.5, 125.4, 124.3, 124.1, 123.9, 123.8, 123.5, 19.3 (2C), 19.1 (2C); MS (m/z) 763 (M^+, 6), 733 (M^+-30, 8); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~490 (sh), 428 (4.53), 382 (4.51), 242 (4.47) nm.

4.2.9. 2-(6-*p*-Nitrophenyl-1,3,5-hexatrienyl)-9,10-bis(4,5-ethylendithio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (16c). Yield 63%; mp 190–192°C (dec.); FT-IR (KBr) 2924, 2852, 1508, 1456, 1337, 1284, 1109, 995, 850, 746, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, 2H, J=8.8 Hz), 7.58–7.45 (m, 6H), 7.39–7.28 (m, 3H), 7.06 (dd, 1H, J_1=15.4 Hz, J_2=9.7 Hz), 6.96 (dd, 1H,

J_1=15.4 Hz, J_2=10.1 Hz), 6.78–6.50 (m, 4H), 3.31 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 146.9, 144.4, 142.9, 137.1, 135.5, 134.9, 134.7, 134.6, 134.1, 133.2, 132.8, 131.3, 131.1, 130.5, 129.5, 129.2, 129.1, 127.9, 127.0, 126.9, 126.3, 126.0, 124.7, 124.5, 124.4, 124.2, 123.9, 111.5, 111.4 (2C), 111.1, 30.8, 30.1, 30.0, 29.3; MS (*m/z*) 759 (M^+, 14); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~490 (sh), 434 (4.44), 382 (4.47), 240 (4.46) nm. Anal. calcd for $C_{36}H_{25}S_8NO_2$ (%): C 56.9, H 3.3, N 1.8. Found (%): C 57.3, H 4.0, N 2.1.

4.2.10. Synthesis of 5-(2-*p*-nitrophenylvinyl)-2-thiophenecarbaldehyde (19). (4-nitrobenzyl)triphenylphosphonium bromide **13** (341 mg, 0.71 mmol) and potassium *tert*-butoxide (79 mg, 0.71 mmol) were dissolved in toluene under argon atmosphere and the reaction was vigorously stirred at room temperature for one hour. After this time, a toluene solution of 2,5-thiophenedicarbaldehyde **21** (100 mg, 0.71 mmol) was added. After 5 h, the reaction was heated to reflux for 10 h. The solvent was removed under reduced pressure and the residue washed with water and extracted with methylene dichloride. The organic layer was dried and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane/methylene dichloride (3:1) as eluent.

Yield 70%; mp 191–192°C; FT-IR (KBr) 1659, 1584, 1508, 1491, 1448, 1387, 1338, 1263, 1227, 1194, 1105, 1049, 951, 868, 833, 806, 775, 746, 687, 669, 631 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.23 (d, 2H, *J*=8.9 Hz), 7.99 (d, 1H, *J*=3.9 Hz), 7.88 (d, 2H, *J*=8.9 Hz), 7.80 (d, 1H, *J*=16.4 Hz), 7.51 (d, 1H, *J*=3.9 Hz), 7.41 (d, 1H, *J*=16.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 150.4, 146.9, 142.9, 142.6, 138.9. 130.1, 129.3, 128.0 (2C), 125.8, 124.2 (2C); MS (*m/z*) 259 (M^+, 5), 229 (M^+−30, 100); UV–Vis (CH_2Cl_2) λ_{max} (log ε) 382 (7.25), 240 (4.05) nm. Anal. calcd for $C_{13}H_9SNO_3$ (%): C 60.2, H 3.5, N 5.4, S 12.4. Found (%): C 60.0, H 3.8, N 5.3, S 12.0.

4.3. Synthesis of donor-π-acceptor compounds (20a–c)

The corresponding salt of π-extended TTF (**17a–c**) (0.22 mmol) and potassium *tert*-butoxide (54 mg, 0.48 mmol) were dissolved in toluene and heated to reflux. After 1 h, a solution of compound **19** in toluene was added and the reaction was heated to reflux for 12 h. The solvent was removed under reduced pressure and the resulting mixture washed with water and extracted with methylene dichloride. The organic layer was dried and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane/methylene dichloride (5:1) as eluent.

4.3.1. 2-{2-[5-(2-*p*-Nitrophenylvinyl)-2-thienyl]vinyl}-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (20a). Yield 57%; mp >400°C; FT-IR (KBr) 1544, 1508, 1450, 1419, 1337, 1109, 1047, 1030, 945, 862, 825, 800, 758, 746, 636, 604 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, 2H, *J*=8.9 Hz), 7.85 (d, 1H, *J*=1.5 Hz), 7.84 (d, 2H, *J*=8.9 Hz), 7.74 (d, 1H, *J*=16.0 Hz), 7.67–7.62 (m, 3H), 7.57 (dd, 1H, J_1=8.2 Hz, J_2=1.5 Hz), 7.51 (d, 1H, *J*=16.0 Hz), 7.39–7.33 (m, 2H), 7.29 (d, 1H, *J*=3.9 Hz), 7.24 (d, 1H, *J*=3.9 Hz), 7.09 (d, 1H, *J*=15.4 Hz), 7.04 (d, 1H, *J*=15.4 Hz), 6.79–6.73 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.9, 146.9, 1445, 144.1, 142.3, 141.6, 137.9, 137.8, 136.1, 135.4, 135.2, 135.0, 131.0, 129.3, 129.2, 129.1, 128.7, 128.0, 127.9, 127.5, 127.2, 126.6, 126.0, 125.6, 125.3, 125.0, 123.9, 123.4, 123.0, 121.3, 119.2, 119.1, 119.0, 118.9; MS (*m/z*) (%) 635 (M^+, 100), 605 (M^+−30, 85); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~500 (sh), 434 (4.72), 244 (4.55) nm. Anal. calcd for $C_{34}H_{21}S_5NO_2$ (%): C 64.2, H 3.3, N 2.2. Found (%): C 63.9, H 4.0, N 1.6.

4.3.2. 2-{2-[5-(2-*p*-Nitrophenylvinyl)-2-thienyl]vinyl}-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (20b). Yield 11%; mp >400°C; FT-IR (KBr) 1589, 1514, 1497, 1452, 1419, 1337, 1313, 1281, 1109, 945, 827, 754 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, 2H, *J*=8.9 Hz), 7.84 (d, 2H, *J*=8.9 Hz), 7.74 (d, 1H, *J*=16.1 Hz), 7.69 (s, 1H), 7.67–7.50 (m, 4H), 7.47–7.34 (m, 3H), 7.30 (d, 1H, *J*=3.8 Hz), 7.26 (d, 1H, *J*=3.8 Hz), 7.09 (d, 1H, *J*=16.1 Hz), 7.08 (d, 1H, *J*=16.1 Hz), 2.43 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 143.7, 143.5, 140.7, 135.1, 134.7, 134.5, 134.4, 134.2, 134.0, 131.4 (2C), 131.2, 129.4, 129.1, 127.5, 126.6, 126.5, 126.3, 126.2, 125.9, 125.8, 125.7, 125.4 (2C), 125.2, 124.3, 124.2, 123.5, 123.3, 121.9, 120.5, 120.1, 119.7, 19.1 (4C); MS (*m/z*) (%) 819 (M^+, 100), 789 (M^+−30, 3); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~500 (sh), 440 (4.72), 246 (4.70) nm. Anal. calcd for $C_{38}H_{29}S_9NO_2$ (%): C 55.6, H 3.6, N 1.7. Found (%): C 54.9, H 4.1, N 1.5.

4.3.3. 2-{2-[5-(2-*p*-Nitrophenylvinyl)-2-thienyl]vinyl}-9,10-bis(4,5-ethylendithio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (20c). Yield 9%; mp >400°C; FT-IR (KBr) 1589, 1508, 1452, 1419, 1337, 1109, 945, 862, 795, 754, 739, 725, 712, 685, 669, 615 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, 2H, *J*=8.9 Hz), 7.80 (d, 2H, *J*=8.9 Hz), 7.70 (d, 1H, *J*=15.9 Hz), 7.62 (s, 1H), 7.57–7.45 (m, 4H), 7.43–7.31 (m, 3H), 7.26 (d, 1H, *J*=3.7 Hz), 7.23 (d, 1H, *J*=3.7 Hz), 7.06 (d, 2H, *J*=15.9 Hz), 3.32 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 143.8, 143.5, 140.7, 140.3, 135.2, 134.7, 134.5, 134.4, 134.2, 130.1, 129.4, 129.0, 127.5, 126.5 (3C), 126.4, 126.2, 126.0, 125.7, 125.6, 125.5, 124.4, 124.2 (2C), 123.9, 123.8, 123.4, 121.9, 111.0 (2C), 110.6 (2C), 29.7 (2C), 29.6 (2C); MS (*m/z*) (%) 815 (M^+, 100), 785 (M^+−30); UV–Vis (CH_2Cl_2) λ_{max} (log ε) ~500 (sh), 448 (4.38), 280 (4.14), 244 (4.40) nm.

4.4. Synthesis of donor-π-acceptor compounds (23a–c)

A toluene solution of (4-nitrobenzyl)triphenylphosphonium bromide **13** (304 mg, 0.64 mmol) and potassium *tert*-butoxide (90 mg, 0.81 mmol) was heated to reflux. After 1 h, a solution of the corresponding aldehyde (**22a–c**) (0.25 mmol) in toluene was added and heated to reflux for 16 h. The reaction crude was washed with water and extracted with methylene dichloride. The organic layer was dried and the obtained solid was purified by silica gel chromatography using hexane/methylene dichloride (1:1) as eluent.

4.4.1. 2-(*E*-2-*p*-Nitrophenylvinyl)-5-(1,3-dithiol-2-ylidenemethyl)thiophene (23a). Yield 72%; mp 245–247°C (dec.); FT-IR (KBr) 1581, 1545, 1499, 1437, 1329, 1310, 1109, 947, 866, 673, 609 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.18 (d, 2H, J=9.0 Hz), 7.81 (d, 2H, J=9.0 Hz), 7.73 (d, 1H, J=16.5 Hz), 7.68 (d, 1H, J=3.8 Hz), 7.24 (d, 1H, J=3.8 Hz), 7.07 (s, 1H), 7.60 (d, 1H, J=16.5 Hz), 6.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.9, 139.4, 132.4, 132.2, 130.9, 128.8, 128.6, 128.4, 127.5, 126.2, 124.3, 124.2, 123.9, 123.5, 118.6, 118.5; MS (m/z) 345 (M$^+$, 100), 315 (M$^+$−30, 16); UV–Vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ε) 490 (4.31), 358 (3.95), 278 (3.93), 278 (3.93), 238 (3.95) nm. Anal. calcd for $C_{16}H_{11}S_3NO_2$ (%): C 55.6, H 3.2, N 4.1. Found (%): C 55.1, H 3.9, N 3.5.

4.4.2. 2-(*E*-2-*p*-Nitrophenylvinyl)-5-(4,5-dimethylthio-1,3-dithiol-2-ylidenemethyl)thiophene (23b). Yield 98%; mp 190–198°C (dec.); FT-IR (KBr) 1587, 1508, 1485, 1439, 1335, 1310, 1107, 943, 864, 825, 781, 746, 688, 609 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.21 (d, 2H, J=9.0 Hz), 7.57 (d, 2H, J=9.0 Hz), 7.38 (d, 1H, J=16.1 Hz), 7.10 (d, 1H, J=3.8 Hz), 6.90 (d, 1H, J=16.1 Hz), 6.79 (d, 1H, J=3.8 Hz), 6.70 (s, 1H), 2.50 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 146.3, 143.8, 141.4, 141.3, 140.3, 132.9, 129.2, 128.8, 126.3 (2C), 126.2, 124.7, 124.5, 124.2 (2C), 108.0, 19.2, 18.9; MS (m/z) 437 (M$^+$, 42), 407 (M$^+$−30, 100); UV–Vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ε) 490 (4.41), 360 (4.13), 270 (4.09), 242 (4.11) nm. Anal. calcd for $C_{18}H_{15}S_5NO_2$ (%): C 49.4, H 3.5, N 3.2. Found (%): C 50.1, H 4.1, N 3.2.

4.4.3. 2-(*E*-2-*p*-Nitrophenylvinyl)-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidenemethyl)thiophene (23c). Yield 65%; mp 258–260°C (dec.); FT-IR (KBr) 1583, 1545, 1500, 1439, 1425, 1375, 1333, 1306, 1180, 1107, 1051, 943, 858, 789, 744, 688, 631 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.19 (d, 2H, J=8.8 Hz), 7.82 (d, 2H, J=8.8 Hz), 7.74 (d, 1H, J=16.0 Hz), 7.29 (d, 1H, J=3.9 Hz), 7.13 (s, 1H), 7.08 (d, 1H, J=16.0 Hz), 6.94 (d, 1H, J=3.9 Hz), 3.44 (s, 4H); MS (m/z) 435 (M$^+$, 100), 405 (M$^+$−30, 22); UV–Vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ε) 490 (4.36), 368 (4.13), 266 (4.07), 248 (4.13) nm.

Acknowledgments

We thank DGICYT of Spain (Projects: PR BQU2000-0790, PB98-0818 and MAT99-1009-C02-02) and Gobierno de Aragón-Fondo Social Europeo (P009/2001) for financial support.

References

1. (a) In *Nonlinear Optical Properties of Organic Molecules and Crystal*. Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987. (b) In *Materials for Nonlinear Optics: Chemical Perspectives*. *ACS Symposium Series*, Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; American Chemical Society: Washington, DC, 1991. (c) Special issue on optical non-linearities in chemistry. Burland, D. M. Ed. *Chem. Rev.* **1994** 1–278. (d) Bosshard, C.; Sutter, K.; Pretre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*. Gordon & Breach: Basel, 1995. (e) In *Polymers for Second-Order Nonlinear Optics*. *ACS Symposium Series*, Lindsay, G. A., Singer, K. D., Eds.; American Chemical Society: Washington, DC, 1995; Vol. 601. (f) Kajzar, F.; Swalen, J. *Organic Thin Films for Waveguiding Nonlinear Optics*. Gordon & Breach: Amsterdam, 1996. (g) Miyata, S.; Sasabe, H. *Poled Polymers and Their Applications to SHG and EO Devices*. Gordon & Breach: Amsterdam, 1997. (h) Nalwa, H. S. *Nonlinear Optics of Organic Molecules and Polymers*. CRC: Boca Raton, FL, 1997. (i) Kuzyk, M. G.; Singer, K. D.; Twieg, R. J. *J. Opt. Soc. Am. B. Opt. Phys.* **1998**, *15*, 254.
2. For a review, see: Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175.
3. Marder, S. R.; Gorman, G. B.; Tiemann, B. G.; Cheng, L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 3006.
4. (a) Rao, V. P.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118. (b) Rao, V. P.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1993**, *34*, 1747. (c) Rao, V. P.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (d) Rao, V. P.; Jen, A. K. Y.; Cai, Y. *Chem. Commun.* **1996**, 1237. (e) Pauley, M. A.; Wang, C. H.; Jen, A. K. Y. *J. Chem. Phys.* **1995**, *102*, 6400.
5. (a) Andreu, R.; de Lucas, A. I.; Garín, J.; Martín, N.; Orduna, J.; Sánchez, L.; Seoane, C. *Synth. Met.* **1997**, *86*, 1817. (b) De Lucas, A. I.; Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B. *Tetrahedron* **1998**, *54*, 4655. (c) Garín, J.; Orduna, J.; Rupérez, J. I.; Alcalá, R.; Villacampa, B.; Sánchez, C.; Martín, N.; Segura, J. L.; González, M. *Tetrahedron Lett.* **1998**, *39*, 3577. (d) González, M.; Martín, N.; Segura, J. L.; Seoane, C.; Garín, J.; Orduna, J.; Sánchez, C.; Alcalá, R.; Villacampa, B. *Tetrahedron Lett.* **1999**, *40*, 8599.
6. González, M.; Segura, J. L.; Seoane, C.; Martín, N.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B.; Hernández, V.; López Navarrete, J. T. *J. Org. Chem.* **2001**, *66*, 8872.
7. For a recent review on TTFs, see: Segura, J. L.; Martín, N. *Angew. Chem. Int. Ed.* **2001**, *40*, 1372.
8. Bryce, M. R.; Green, A.; Moore, A. J.; Perepichka, D. F.; Batsanov, A. S.; Howard, J. A. K.; Ledoux-Rak, I.; González, M.; Martín, N.; Segura, J. L.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B. *Eur. J. Org. Chem.* **2001**, 1927.
9. Herranz, M. A.; Martín, N.; Sánchez, L.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B.; Sánchez, C. *Tetrahedron* **1998**, *54*, 11651.
10. For a recent review on quinonoid π-extended TTFs, see: Martín, N.; Ortí, E. *Handbook of Advanced Electronic and Photonic Materials and Devices*, Nalwa, H. S., Ed.; Academic: New York, 2001; Vol. 3, pp 245–265.
11. Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Karanlov, A. I. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1450.
12. Martín, N.; Sánchez, L.; Guldi, D. M. *Chem. Commun.* **2000**, 113.
13. (a) Godbert, N.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. *J. Org. Chem.* **2001**, *66*, 713. (b) Christensen, C. A.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. *J. Org. Chem.* **2001**, *66*, 3313. (c) Bryce, M. R.; Batsanov, A. S.; Finn, T.; Hansen, T. K.; Howard, J. A. K.; Kamenjicki, M.; Lednev, I. K.; Asher, S. A. *Chem. Commun.* **2000**, 295.
14. Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. *J. Org. Chem.* **1997**, *62*, 5690.
15. Pérez, I. PhD Dissertation, Universidad Complutense, 2002.

16. González, S. PhD Dissertation, Universidad Complutense, 2001.
17. De Lucas, A. I.; Martín, N.; Sánchez, L.; Seoane, C.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B. *Tetrahedron Lett.* **1997**, *38*, 6107.
18. Inove, S.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1997**, 1105.
19. Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268.
20. Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 157.
21. Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
22. Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.
23. Oudar, J. L.; Chemla, D. S. *J. Phys. Chem.* **1977**, *66*, 2664.
24. Garín, J.; Orduna, J.; Andreu, R. *Synth. Met.* **1999**, *102*, 1531.
25. (a) Roncali, J.; Rasmussen, L.; Thobie-Gautier, C.; Frère, P.; Brisset, H.; Sallé, M.; Becher, J.; Simonsen, O.; Hansen, T. K.; Benahmed-Gasmi, A.; Orduna, J.; Garín, J.; Jabault, M.; Gorgues, A. *Adv. Mater.* **1994**, *6*, 841. (b) De Lucas, A. I.; Martín, N.; de Miguel, P.; Seoane, C.; Albert, A.; Cano, F. H. *J. Mater. Chem.* **1995**, *5*, 1145.
26. Granovsky, A. http://www.classic.chem.msu.su/gran/gamess/index.html.
27. Schmidt, M. W.; Baldridge, K. K.; Boats, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.