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Novel π-conjugated donor–acceptor chromophores, based on the strong electron-donating tetrathiafulvalene moiety and different electron-withdrawing acceptors, exhibit large second-order optical nonlinearities. The effect of increasing the length of the polyenic spacer and the influence of the nature of the acceptor moiety on the NLO properties have been studied by using the electric field-induced second-harmonic generation (EFISH) technique as well as by semiempirical and ab initio theoretical calculations. A charge-transfer band has been observed in the absorption spectra of these D-π-A compounds that undergoes an hypsochromic shift when increasing the number of vinylenic spacer units connecting both donor and acceptor moieties. The degree of the intramolecular charge transfer from the donor to the acceptor has also been analyzed by means of Raman spectroscopy.

Introduction

Donor (D)–acceptor (A) substituted organic molecules with large second-order nonlinear optical (NLO) properties have been the subject of considerable research efforts due to their potential applications in areas such as optical modulation, molecular switching, optical memory, and frequency doubling.1,2 Although organic molecules are not as robust as inorganics, they have received a great deal of interest in the nonlinear optics field given that they offer many advantages over traditional inorganic crystals: (i) organic materials present high electronic susceptibilities (χ(2)) through high molecular hyperpolarizability (β) and fast response time; (ii) they are cheaper to produce and (iii) easier to fabricate; (iv) they are compatible with existing semiconductor technology; and (v) their structures can be tailored in myriad ways allowing to finely tune NLO properties for desired applications.

A key objective in the development of materials for nonlinear optical applications is to find highly active chromophores with large second-order polarizabilities β. The first hyperpolarizability and, hence, the second-order NLO response is related to an electronic intramolecular charge transfer (ICT) excitation between the ground and excited states of the molecule. Both theoretical and experimental studies have shown that large hyperpolarizabilities generally arise from a combination of a strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path. Thus, a variety of donor–acceptor chromophores...
acceptor organic molecules containing different acceptor units such as nitro, nitrite, sulfonyl, polycyanovinyl, 4-methylidenediethylythio barbituric acid, phosphonate, 1,3-bis(dicyano methylid)indan, 3-dicyanovinyl-2,3-dihydrobenzo thiophen-2-yldien-1,1-dioxide, pyridinium salts or diazonium salts and donor units such as dialkylamines, alkoxaryl groups, ferrocene, guanidyl, phosphoranimidyl, azulene or the 1,3-dithiole ring have been previously reported (Chart 1).

In this context, we reported in 1997 the first NLO materials containing the TTF unit as the donor moiety in D-π-A systems. Although TTF and its derivatives were originally prepared as strong electron-donor molecules for the development of electrically conducting materials, during recent years they have shown new and


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Chart 1

in some cases little exploited possibilities. Our investigations have confirmed that TTF derivatives can display efficient NLO responses, the combination of
The key step in the general reaction scheme involves the reaction of monolithio-TTF (generated from TTF and lithium disopropylamide) with the commercially available N,N-dimethylaminocrotonaldehyde (7) to yield 5b and with 5-(N,N-diethylamino)-4-pentendial (8)27 to obtain 5c by following Jutz's procedure,28 which has been recently extended to several organolithium systems by Friendl, Yang, and Marder.29 All-trans vinylalcohols amides were used in all cases as starting materials, and only all-trans vinylalcohols were obtained according to the coupling constants observed in the 1H NMR spectra.

As previously stated, we reported the synthesis of the first NLO materials containing the TTF unit as the donor moiety and diacyan methylene as the acceptor group (1a,b).20 Now we have extended these series to 1c by incorporating another vinylene unit between the donor and acceptor moieties. This compound was obtained in 60% yield from 5c by Knoevenagel condensation with malonitrile under basic conditions (Scheme 1). Due to the presence of the conjugated nitrile group in 1c, bands at 2230 and 2219 cm\(^{-1}\) can be observed in the FT-IR spectra and two signals at ca. 115 ppm are present in the 13C NMR spectra.

As noted above, following these first examples of TTF-containing D-\(\pi\)-A systems, we have extended these series to new acceptor moieties. Marder has proposed a model that correlates the molecular hyperpolarizability value \(\beta\) with the degree of charge separation in the ground state.30 This research group has shown how stilbenes or diphenylpolyenes endowed with donor and acceptor groups exhibit a loss of aromaticity in these moieties, which produces a deficient contribution of resonance forms with charge separation. To solve this problem, new acceptor moieties have been designed having a topology that allows a gain in aromaticity in the charge-separated state. These acceptor groups, frequently used in the design of D-\(\pi\)-A systems for NLO, are the 3-phenyl-5-isoxazolone and the N,N-dimethylthiobarbituric acid.7 Thus, we have chosen these groups to combine them with the TTF moiety in order to extend the study of the NLO properties of TTF derivatives. The syntheses of these new series of compounds (2a-c, 3a-c) have been carried out by Knoevenagel condensation between formyl-TTFs (5a-c) and the corresponding N,N-dimethylthiobarbituric acid (9) and 3-phenyl-5-isoxazolone (10), respectively. Best results have been obtained by simply refluxing stoichiometric amounts of both reagents in ethanol, while the mixture was protected from light and oxygen (Scheme 2). The attempted use of different catalysts, such as ethylenediammonium diacetate or piperidine, invariably led to decomposition products.

Attempts to obtain compound 3a invariably led to a mixture of decomposition products while derivatives 3b,c have been obtained in 72 and 69% yield, respectively. The structure of these compounds has been confirmed by their spectroscopic and analytical data. The signals corresponding to the ethylenic protons in the 1H NMR spectra

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with $J = 13$ to $15$ Hz indicate an all-trans configuration for the double bonds.

Other acceptor groups that have been successfully used for the synthesis of effective NLO materials are 3-(dicyanomethylen)indan-1-one (11) and 1,3-bis(dicyanomethylene)indan (12). Thus, we have prepared compounds 4a–c by refluxing stoichiometric amounts of both formyl-TTFs (5a–c) and 3-dicyanovinylindan-1-one (11) in acetic anhydride while the mixture was protected from light and oxygen (Scheme 3).

Derivatives 4a–c were obtained as stable crystalline solids in moderate yields (45–52%). Their structure was confirmed by the spectroscopic and analytical data. Their FT-IR spectra exhibit bands at 2215 and 1700 cm$^{-1}$ corresponding to the nitrile and carbonyl groups respectively. Interestingly, when a similar reaction was carried out using 1,3-bis(dicyanomethylene)indan as the acceptor moiety, highly insoluble dark materials were obtained. As a consequence of the strong donor ability of the TTF moiety and the strong acceptor character of the 1,3-bis(dicyanomethylene)indan system, formation of a charge-transfer complex in solution between the two molecules has to be taken into consideration. In fact, Batsanov et al. have reported that TTF and 1,3-bis(dicyanomethylene)indan form a 1:1 complex exhibiting semiconducting properties. This fact strongly suggests that after combination of the TTF derivative with the tetracyano derivative of the indandione, a concurrence between the two reaction takes place, and the faster electron transfer process yields mainly the corresponding charge-transfer complexes.

**Electrochemistry.** The electrochemical properties of the new TTF-based NLO chromophores 1–4 have been determined by cyclic voltammetry. The results indicate that these compounds exhibit reversible one-electron redox processes with well-defined redox potentials. The oxidation potentials are typically higher than those of TTF, suggesting a stronger electron-withdrawing character of the dicyanomethylene group. The reduction potentials are also shifted, indicating a stronger electron-donating character of the TTF moiety. These characteristics make these chromophores promising candidates for various NLO applications.
studied by cyclic voltammetry at room temperature in dichloromethane solutions, using glassy carbon as the working electrode, SCE as reference, and tetra-n-butylammonium perchlorate as the supporting electrolyte. The corresponding data are collected in Table 1 along with the redox potentials of the unsubstituted tetrathiafulvalene (TTF) used as reference.

All the voltammograms show two reversible one-electron oxidation waves corresponding to the TTF moiety, and one irreversible reduction wave, corresponding to the acceptor moiety. In all cases the oxidation potential values are shifted toward more positive values in comparison with unsubstituted TTF measured under the same experimental conditions, which is consistent with an increase in the oxidation potential produced by the presence of the acceptor moieties. The general trend is that this shift is bigger as the length of the spacer decreases indicating a stronger interaction between the donor and acceptor groups when they are closer.

Concerning the cathodic region of these voltammograms, the diethylthiobarbituric acid moiety shows the best electron acceptor properties, whereas derivatives 1, 3, and 4 present similar reduction potentials.

**UV−vis, IR, and Raman Spectroscopy.** The lowest energy absorption bands in electronic spectra observed for compounds 1−4 are given in Table 2. These bands (Figure 1) can be assigned to an intramolecular charge transfer (ICT) process and are subject to two general trends: (i) a red shift of the lowest energy absorption band is observed when increasing the acceptor ability of the acceptor moiety. The more red-shifted values of \( \lambda_{\text{max}} \) for derivatives 4 in comparison with that of derivatives 2 are an exception to this rule. (ii) The ICT band upshifts when the length of the oligoenic spacer is increased. This fact suggests that the extension of the charge transfer is reduced due to the inclusion of extra vinylenic double bonds in the spacer unit.

To analyze these experimental observations, we have carried out an IR and Raman spectroscopy study on these systems.

The Raman spectra of compounds 1−4 are shown in Figures 2 and 3, respectively. In view of the B3LYP32/6-31G** vibrational eigenvectors plotted in Figure 4, the
Raman line around 1585–1540 cm\(^{-1}\) can be assigned to a \(v(C=C)\) stretching mode of the vinylenic spacer coupled to some extent with a \(v(C=C)\) stretching of the TTF donor unit, whereas the line near 1495–1470 cm\(^{-1}\) arises from a \(v(C=C)\) stretching vibration mainly located on the TTF group, which extends toward the vinylenic spacer.

The two Raman lines undergo an upshift with increasing length of the \(d\)-spacer: 1544 and 1469 cm\(^{-1}\) (1a), 1579 and 1461 cm\(^{-1}\) (1b), and 1584 and 1493 cm\(^{-1}\) (1c) for the series of the dicyanomethylene acceptor group and 1543 and 1462 cm\(^{-1}\) (2a), 1576 and 1459 cm\(^{-1}\) (2b), and 1575 and 1483 cm\(^{-1}\) (2c) for the series of the \(N,N'\)-diethylthiobarbituric acid acceptor group.

Matsuzaki et al. have reported a Raman study of some mixed-valent and charge-transfer salts of TTF to determine either the formal charge or the degree of charge transfer, \(\rho\), of the molecule or ion that forms the one-dimensional stack.\(^{34-36}\) The plot of the Raman frequencies of the TTF salts vs \(\rho\) gives a straight line, and the formal charges of TTF estimated from the empirical relation agree well with those obtained from neutron and X-ray scatterings. The so-called \(v_3\) mode of TTF (associated to the stretching vibration of the central C=C bond) is measured at 1516 cm\(^{-1}\) in the neutral molecule (\(\rho = 0\)) and at 1420 cm\(^{-1}\) in the monocation (\(\rho = 1\)), and it shows the largest frequency shift with increasing \(\rho\) (ca. 100 cm\(^{-1}\)), thus giving the most reliable estimation of the formal charge or degree of charge transfer.

The \(v_3\) mode of the TTF moiety correlates with the Raman line near 1495–1470 cm\(^{-1}\) of our NLO chromophores. Under the assumption of general applicability of the linear relation \(v_3\) vs \(\rho\) proposed by these authors, the degree of intramolecular charge transfer can be estimated to be approximately 0.48 (1a), 0.37 (1b), and 0.25 (1c) for the series of the dicyanomethylene acceptor group and 0.57 (2a), 0.59 (2b), and 0.35 (2c) for the series of the \(N,N'\)-diethylthiobarbituric acid acceptor group. Thus, the values of \(\rho\) are found to be larger for the \(2a-c\) than for the \(1a-c\) compounds. These Raman results are in full agreement with the better electron acceptor properties of the diethylthiobarbituric acid as compared with the dicyanomethylene group. This Raman spectroscopy study reveals that of the six NLO-phores studied, 2b displays the more effective intramolecular charge transfer. The increasing weight of the zwitterionic canonical structure (where an electron is fully transferred from the donor to the acceptor) in the stabilization of the electronic ground state could justify the high positive \(E^{1/2}_{1/2,\alpha}\) and \(E^{2}_{1/2,\alpha}\) values of 2b (see Table 1).

In accordance with the trend of variation of the oxidation potentials on the chemical structure of these TTF-based NLO-phores, we observe that the Raman \(v_3\) mode of the TTF moiety upshifts in frequency as the...
length of the $\pi$-bridge becomes longer, thus suggesting that the intramolecular charge transfer is less effective with increasing number of vinylenic units in the $\pi$-spacer.

The presence in push–pull molecules of a highly delocalized $\pi$-system gives rise to Raman spectra of a rather simple appearance: usually two to four lines with overwhelmingly strong activity dominate the whole spectrum. On the other hand, the electron-acceptor group withdraws electronic charge from the donor through the conjugated spacer, giving rise to a relevant molecular dipole moment roughly coincident with the chain axis of the molecule. For this reason, the shorter the chain length the stronger the bond polarization and more efficient the activation in the IR of the normal modes associated to the intramolecular charge transfer. On the contrary, the intensities of the few Raman bands experimentally observed continuously increase as the length of the spacer becomes longer, due to the increasing polarizability of the $\pi$-conjugated skeleton.

It has already been suggested the existence of a critical chain length in the class of the push–pull polyenes shown above in which the interaction between donor and acceptor groups is inhibited. For chains with a length longer than the critical value, the bond polarization is confined within a few bonds close to the polar end groups, whereas the bonds in the middle of the $\pi$-bridge are practically apolar and still keep a strongly alternating polyene-like structure.

We observe that the frequencies of the infrared absorption bands due to the $\nu(C=N)$ stretching modes also increase with increasing the length of the $\pi$-spacer: 2212 and 2217 cm$^{-1}$ (1a), 2221 cm$^{-1}$ (1b), and 2220 and 2229 cm$^{-1}$ (1c) (see Figure 5). This finding has a straightforward explanation: as the chain length of the spacer becomes shorter (and more electronic charge is transferred from the donor to the acceptor end groups), the loss of triple bond character of the cyano groups (since the C≡N groups enter in the resonant stabilization of the zwitterionic form of the molecule) is more pronounced.

It has been suggested on the basis of a one-dimensional model for the class of disubstituted D–$\pi$–A molecules, that the intramolecular charge transfer, $\Delta q$, from the donor to the acceptor end groups goes down roughly as $1/L$ (where $L$ is the molecular length) and that the corresponding $L\Delta q$ contribution to the total dipole moment vary relatively slowly with length along a given series of chromophores with the same pair of donor and acceptor. The length dependence of $\beta$ for such molecules is dominated by that of $\gamma/\alpha$ of the corresponding unsubstituted $\pi$-conjugated bridge (where $\gamma$ and $\alpha$ are the third-order and linear polarizabilities, respectively) or roughly quadratic ($L^2$) as found experimentally (since $\alpha \approx L^3$ and $\gamma \approx L^5$).

It has also been hypothesized that the ground-state polarization and bond length alternation (BLA) (i.e., the difference between average length of carbon–carbon double and single bonds in a polyenic chain) are useful parameters to consider when establishing structure-property relationships for NLO molecules. BLA varies from negative values for the neutral polyene structure, through zero for the polar cyanine-like structure, to positive values for the highly polar zwitterionic polyene structure. Also, as BLA changes from negative to positive values, the ground-state dipole moment, $\mu$, increases, and at the same time, $\beta$ initially increases, reaches a maximum, and begins to decrease, crossing through zero at BLA = 0 Å, and ultimately becomes negative when BLA is positive. This dependence of $\beta$ on the ground-state polarization and BLA for a series of donor–acceptor disubstituted polyenes has been experimentally demonstrated. The B3LYP/6-31G** geometry optimizations performed for compounds 1a–c indicate that BLA amounts nearly the same negative value for the three compounds (ca. $-0.064$ Å), and these results are therefore consistent with the observed positive $\beta$ values. Thus, the trend of variation of $\beta$ along the series of compounds studied in this work seems to be mainly determined by the quadratic dependence on $L$.

Second-Order Nonlinear Optical Properties. The $\mu\beta$ values of compounds 1–4 measured using the EFISH technique are gathered in Table 2 along with the $\mu\beta(0)$ values calculated assuming a two-level model (compounds 1a and 4a were not measured due to their instability under the EFISH conditions). In comparison, the relevant application parameter $\mu\beta(0)$ for the classical NLO dye DR1 is ca. $600 \times 10^{-48}$ esu. It can be seen that the nonlinear optical activity is larger for compounds containing better acceptors and that $\mu\beta$ values increase with increasing the length of the ethylenic spacer.

Thermal stability is also an important criterion for technological applications. These compounds show a good degree of thermal stability as evidenced by the decomposition temperatures of compounds 2a (194 °C), 2b (195 °C), and 2c (206 °C).

To gain further understanding of the NLO behavior of these compounds, we have performed theoretical calculations starting with the Finite Field (FF) PM3 method.
molecular geometries, we have performed optimizations in the ground state and a small 0.11 Å, which should be related to a poor charge transfer 

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but underestimates largely the activity of compounds 

4

and values. 

It is noteworthy that in the case of compounds 

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which has proved to be very accurate in the prediction of the NLO properties of TTF-derived chromophores at a minimal computational cost.43 These calculations predicted the s-cis conformation of the bond linking the TTF core to the ethylenic spacer as the most stable one, and the FF procedure afforded the results gathered in Table 3. It can be seen that FF-PM3 provides an adequate description of the NLO properties of compounds 1 and 2 but underestimates largely the activity of compounds 3 and 4. It is noteworthy that in the case of compounds 3, the less stable E isomers are predicted to display larger \( \mu \) values.

In an attempt to obtain a better agreement between the observed and calculated \( \mu \) values, we have performed ab initio calculations using the coupled perturbed Hartree–Fock (CPHF) method and the medium-size 6-31G* basis set.44 Although ab initio calculations differ from PM3 in the prediction of the s-trans conformation of the bond linking the TTF moiety to the ethylenic spacer, the calculated \( \mu \) values displayed in Table 3 are analogous to FF-PM3 ones and are unable to explain the NLO response of compounds 3 and 4. Furthermore, while it has been reported that diffuse functions are necessary to obtain accurate hyperpolarizabilities,45 the use of the 6-31+G* basis set incorporating diffuse functions on heavy atoms causes the prediction of increased \( \mu \) values but does not modify the predicted trends in NLO activity (Table 3).

A possible explanation to poor property prediction displayed by semiempirical and Hartree–Fock methods can be found in the used ground-state geometries that are a consequence of the low charge transfer predicted by these methods. Thus, the calculated bond lengths in the ethylenic spacers are 1.45–1.46 Å for single C–C bonds and 1.33–1.34 Å for double C=C bonds, being nearly identical to those of unsubstituted polyenes and corresponding to a bond length alternation (BLA) of 0.11 Å, which should be related to a poor charge transfer in the ground state and a small \( \beta \) value. To obtain better molecular geometries, we have performed optimizations using the B3P86/6-31G* model chemistry that has been successfully applied to TTF derivatives48 and provides better C–S bond lengths than the commonly used B3LYP functional.49 The geometries calculated in this way display distances of 1.42–1.43 and 1.36–1.37 Å for single and double C–C bonds, respectively, corresponding to a BLA of ca. 0.06 Å that is near the optimum value in the search for large hyperpolarizabilities. Unfortunately, DFT methods are unable to predict accurately hyperpolarizabilities due to an incomplete screening of the external electric field,50 and consequently, we decided to calculate HF hyperpolarizabilities on DFT geometries. The effect of the geometry on the calculated \( \mu \) values of 4c is depicted in Figure 6. The DFT geometry gives rise to enhanced \( \mu \) and \( \beta \) values and causes a redirection of the \( \mu \) vector due to the increased charge transfer from TTF to the acceptor moiety in the ground state.

\( \mu \) values calculated using HF/6-31G*/B3P86/6-31G* are gathered in Table 3, it can be seen that while most of them are somewhat overestimated with respect to the experimental values, this model chemistry yields the best correlation of all the described calculations. The results obtained for compounds 3 must be commented on separately. While all the theoretical methods

### Table 3. Experimental and Calculated NLO Properties of Compounds 1–4

<table>
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<tr>
<th></th>
<th>( \mu ) (0)</th>
<th>FF-PM3</th>
<th>HF/6-31G*/HF/6-31G*</th>
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<td></td>
<td>( \mu_\alpha )</td>
<td>( \mu_\beta )</td>
<td>( \mu_\gamma )</td>
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\( \mu_\alpha \) Dipole moments in debye, hyperpolarizabilities in \((10^{-30} \text{ esu})\) and \( \mu_\beta \) in \((10^{-48} \text{ esu})\). b Measured in chloroform at 1907 nm. c Measured in dichloromethane at 1907 nm.
which the donor TTF unit is connected to different acceptor moieties through an oligoenic spacer of variable length. The CV measurements reveal an amphoteric behavior showing two reversible oxidation waves corresponding to the formation of the radical cation and dication species of the TTF moiety and an irreversible reduction wave corresponding to the electron-accepting moiety.

The barbituric acid derivatives (2a–c) showed stronger electron-acceptor properties than the remaining acceptors, as judged from their reduction potential values. All the D–π–A systems showed an intramolecular charge transfer band in their electronic spectra which is strongly influenced by the acceptor ability of the acceptor moiety as well as by the length of the oligoenic spacer. Thus, a red shift of the lowest energy absorption band was observed when increasing the acceptor strength. However, a most interesting observation was the hypsochromic shift when increasing the length of the oligoenic spacer. This fact, which at present has not a clear explanation, has been analyzed by UV–vis and Raman spectroscopy. In particular, we have found that the characteristic Raman-active νπ transition of the TTF moiety (identified on the basis of B3LYP/6-31G* force field quantum chemical calculations) undergoes an upshift with increasing length of the π-spacer, thus suggesting a less effective intramolecular charge transfer as derived from previous empirical relations.

The differences in the NLO behavior of the E and Z isomers of compounds 3 are displayed in Figure 7. It can be seen that while the βHOMO value calculated for 3c (E) is smaller than that of the Z isomer, the better alignment of the μ and β vectors renders the former more active in the EFISH measurements.

The topologies and energies of molecular orbitals have been studied by means of the B3P86/6-31G* model chemistry. The HOMO–LUMO energy gaps calculated in this way, from 1.68 to 2.20 eV, account for this transition as being responsible for the lowest energy absorption in every case. Furthermore, a recent TD-DFT study on compounds 2a–c correctly reproduces the hypsochromic effect observed on lengthening the ethylenic spacer. The charge-transfer character of the HOMO–LUMO transition is demonstrated by the topology of these orbitals (see Figure 8).

Experimental Section

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. 13C and 1H NMR spectra were recorded with a Varian VXR-300 spectrometer (300 and 75 MHz for 1H and 13C, 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. Fourier transform Raman (FT-Raman) spectra were recorded using a Bruker FRA106/S apparatus with a germanium photoresistor operating at liquid nitrogen temperatures as the near-infrared...
detector. Radiation of 1064 nm from a Nd:YAG laser was used for Raman excitation with the operating power adjusted to 100 mW. Light reflected and scattered off the samples was filtered to remove that elastically scattered and then passed through a Michelson interferometer in a backscattering arrangement. Samples were analyzed as pure solids in sealed capillaries. One thousand scans were added to increase the signal-to-noise ratio. Spectra were plotted after baseline correction to remove the flavin resonance bands by the samples in the near infrared region. Elemental analyses were performed with a Perkin-Elmer CHN 2400 apparatus. MS were recorded with a Hewlett-Packard HP5899A spectrometer. 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 is focused with a linear polarizer and focused on the EFISH cell. The polarization 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 μ(0) values were deduced from the experimental values using a two-level dispersion model. Cyclic voltammograms were recorded on a potentiostat/galvanostat Versastat EG & G PAR, equipped with a software electrochemical analysis software Model 250 by using a GCE (glassy carbon) as working electrode, SCE as reference electrode, Bu4NClO4 as supporting electrolyte, dichromatemethane as solvent, and at a scan rate of 200 mV/s. Tetrathiafulvalene (TTF), N,N-diethylthiobarbituric acid, 3-phenyl-5-isoxazolone and 1,3-indandione are commercially available and were used without further purification. Ethanol and tetrahydrofuran were dried with sodium and were distilled before use. Theoretical calculations were performed with the gaussian 94 and Gaussian 9863 programs. Geometry optimizations were performed on isolated entities using the default convergence criteria, and harmonic vibrational frequencies and molecular hyperpolarizabilities were calculated analytically using the CPHF procedure. Semiempirical FF-PM3 calculations were performed using MOPAC 6.0.4

(E)-3-[Tetraphiafulvalenyl]acyraldehyde (5b). Under argon atmosphere, at −78 °C, 0.73 mL (1.09 mmol) of a 1.5 M solution of lithium diisopropylamide (LDA) in tetrahydrofuran/heptane was added to a solution of 204 mg (1 mmol) of TTF in 10 mL of dry THF. Then, 99 mg (1 mmol) of 3-(dimethylamino)-acrolein (7) was added and the reaction was allowed to reach room temperature overnight. Afterward, the mixture was poured over a 2 M aqueous solution of hydrochloric acid. The organic layer was extracted with diethyl ether and dried over sodium sulfate. After vacuum elimination of the solvent, the residue was obtained as a red solid (<40% yield). 

Afterward, the mixture was poured over a 2 M aqueous solution of hydrochloric acid. The organic layer was extracted with diethyl ether and dried over sodium sulfate. After vacuum elimination of the solvent, the residue was obtained as a red solid (<40% yield).
Synthesis of TTF Derivatives 3b,c. General Procedure. A 161 mg (1 mmol) sample of 3-phenyl-5-isoxazolone (10) was added to a solution of 1 mmol of the corresponding formyl-TTF derivative (5a–c) in 15 mL of dry ethanol. The solution was refluxed under argon atmosphere with exclusion of light for 2 h. After this time, the precipitated solid was filtered, washed thoroughly with ethanol, and purified by flash chromatography (hexane/dichloromethane) to afford derivatives 3b,c as red solids.

3-Phenyl-4-(3-tetrathiafulvalenyl-2-propenyliden)-5-isoxazolone (3b). By following the above general procedure and using (E)-3-(tetraphthiafulvalenyl)acrylaldehyde (5b) as the reagent, derivative 3b was obtained in a 72% yield: mp 214–216 °C; 1H NMR (DMSO-66) δ 7.72 (d, J = 14.7 Hz, 1H), 7.68–7.57 (m, 5H), 7.35 (s, 1H), 7.29 (d, J = 14.4 Hz, 1H), 6.79 (m, 2H), 5.90 (dd, J = 14.7 Hz, J′ = 11.7 Hz, 1H); 13C NMR (DMSO-d6, 75 MHz) δ 169.1, 164.9, 161.9, 149.9, 141.7, 135.7, 135.0, 131.0, 129.2, 128.5, 128.2, 127.1, 123.8, 120.3, 120.1, 115.9, 114.8, 104.8; FTIR (KBr, cm−1) 3066, 1750, 1606, 1574, 1523, 1490, 1385, 1196, 1165, 1104; UV–vis (CH2Cl2) λmax (nm) 658, 408, 320; MS (rel intensity) 427 (M+), 412 (M+−1) 306, 230. Anal. Calcd for C23H12N2O2S4: C, 60.00; H, 2.63; N, 6.09. Found: C, 59.76; H, 2.32; N, 6.45. 

Synthesis of TTF Derivatives 4a–c. General Procedure. A 194 mg (1 mmol) sample of dicyanomethyleneindan-dione (11)9 was added to a solution of 1 mmol of the corresponding formyl-TTF derivative (5a–c) in 15 mL of acetic anhydride. The solution was refluxed under argon atmosphere with exclusion of light for 2 h. After this time, the precipitated solid was filtered, washed thoroughly with ethanol, and purified by flash chromatography (hexane/dichloromethane) to afford derivatives 4a–c as red solids.

3-Dicyanomethylen-2-(tetrathiafulvalenylmethylidene)-1-indanone (4a). By following the above general procedure and using formyl-TTF (5a) as the reagent, derivative 4a was obtained in a 52% yield: mp ≥ 300 °C; 1H NMR (DMSO-d6, 300 MHz) δ 8.69 (d, 1H), 8.22 (s, 1H), 7.93 (d, 1H), 7.78 (m, 2H), 7.66 (d, 1H), 6.41 (d, 1H), 6.36 (d, 1H); 13C NMR (DMSO-d6, 75 MHz) δ 176.3, 169.6, 147.1, 135.5, 131.2, 129.4, 127.1, 123.8, 121.3, 120.7, 113.7, 110.8, 109.5, 108.5, 107.9, 106.8, 104.7, 104.5, 103.2; FTIR (KBr, cm−1) 2214, 1701, 1589, 1541, 1471, 1456, 1375, 1342; UV–vis (CH2Cl2) λmax (nm) 798, 390, 310, 230. Anal. Calcd for C31H12N2O2S: C, 55.89; H, 1.98; N, 6.87. Found: C, 56.49; H, 2.24; N, 7.51.

3-Dicyanomethylen-2-(3-tetrathiafulvalenyl-2-propenylidene)-1-indanone (4b). By following the above general procedure and using (E)-3-(tetrathiafulvalenyl)acrylaldehyde (5b) as the reagent, derivative 4b was obtained in a 47% yield: mp > 300 °C; 1H NMR (DMSO-d6, 300 MHz) δ 8.51 (d, 1H), 8.19 (d, 1H), 7.96 (m, 2H), 7.89 (d, 1H), 7.78 (m, 1H), 7.74 (s, 1H), 7.55 (d, 1H), 6.80 (s, 2H); FTIR (KBr, cm−1) 2218, 1697, 1591, 1569, 1541, 1481, 1456, 1359, 1342; UV–vis (CH2Cl2) λmax (nm) 726, 428, 308, 218. Anal. Calcd for C23H12N2O2S: C, 58.07; H, 2.32; N, 6.45. Found: C, 58.62; H, 2.59; N, 7.02.

3-Dicyanomethylen-2-(5-tetrathiafulvalenyl-2,4-pentadienylidene)-1-indanone (4c). By following the above general procedure and using 5-(tetrathiafulvalenyl)penta-2,4-dienal (5c) as the reagent, derivative 4c was obtained in a 45% yield: mp > 300 °C; FTIR (KBr, cm−1) 2212, 1697, 1575, 1522, 1483, 1458, 1379, 1340; UV–vis (CH2Cl2) λmax (nm) 690, 458, 300, 222; MS m/z (rel intensity) 466 (M+, 100). Anal. Calcd for C24H12N2O2S: C, 60.00; H, 2.63; N, 6.09. Found: C, 60.55; H, 2.32; N, 6.71.

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Supporting Information Available: B3P86/6-31G* geometries (Cartesian coordinates) and energies (atomic units) of compounds 1a–c, 2a–c, 3b,c, and 4b,c. This material is available free of charge via the Internet at http://pubs.acs.org. J O010717K