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The First Tetrathiafulvalene Derivatives Exhibiting Second-Order NLO Properties

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Abstract: The second order NLO properties of push-pull TTF derivatives have been studied for the first time. The effect of modifying both the acceptor and the donor moieties on the $\mu\beta$ values has been studied by experimental (EFISH) and theoretical techniques.

1. Introduction

The design and synthesis of novel organic materials exhibiting nonlinear optical (NLO) properties is currently a very active research field because of their applications in photonic components.[1-3] The presence of electron-donor and electron-acceptor moieties in the molecule, bonded through a π-conjugated spacer has been identified as the main molecular feature in the search for high molecular hyperpolarizability (β).[4-6] Bond lengh alternation in the polyene connective segment linking both donor and acceptor fragments has also a striking influence on the β values.[7] A variety of hyperpolarizable donor-acceptor organic molecules containing different acceptor units[1-6] such as nitro, cyano, sulfonyl, polycyanovinyl[8-13] or diazonium salts[14] and donor units[1-6] mainly dialkylamines, alkoxyaryl groups, ferrocene or the 1,3-dithiole ring[9-13] have been previously reported.

In spite of the different types of chromophores used, more study is needed for the development of more efficient donors, acceptors and conjugating moieties for NLO compounds.[15-18]

Although TTF derivatives[19] are the most widely used donors in the preparation of organic conductors[20-21] and some extended derivatives have been studied for third order NLO,[22-24] their possible role as active chromophores for second order nonlinear optics has not yet been tested.[25] This is surprising given the current interest in the emerging area of multi-property materials.

In order to evaluate the ability of TTF for second harmonic generation we have investigated the NLO properties of a series of derivatives where the TTF moiety is linked to acceptor carbonyl or dicyanovinyl groups through ethylenic spacers.

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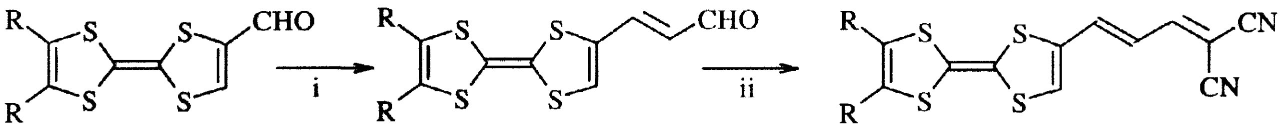
2. Results and discussion

The synthesis of the novel TTF-based donor-π-acceptors is shown in the Scheme. The starting formyl-TTF derivatives **1a**[26] and **1b**[27,28] were obtained as previously described. The α,β-unsaturated aldehydes (**2**) were prepared[27] from **1** by Wittig reactions with triphenylphosphoranylideneacetaldehyde. Compounds **3** were obtained from the respective aldehydes (**2**) by Knoevenagel condensation with malononitrile under basic conditions.



1a: R= H
1b: 2R = $(SCH_2)_2$

2a: R= H
2b: 2R = $(SCH_2)_2$

3a: R= H
3b: 2R = $(SCH_2)_2$

Reagents: i) Ph_3P= CHCHO; C_6H_6; Δ; ii) $CH_2(CN)_2$; $NH_4^+ AcO^-/AcOH$; Tol /Δ

The electrochemical properties of the novel compounds were determined by cyclic voltammetry at room temperature and the data are collected in Table 1. All the voltammograms show the presence of two reversible one-electron oxidation waves corresponding to the formation of the cation-radical and dication of the TTF moiety. On the reduction side, the dicyanovinyl group gives rise to an irreversible wave at a high negative value, thus indicating its moderate electron-acceptor character (Table 1).

Table 1
UV-Vis and Redox Potentials for the TTF-containing Compounds Prepared

Compound	λ_{max}[a]	$E^{1/2}_{1ox}$[b]	$E^{1/2}_{2ox}$[b]	E^{1}_{red}[b]
2a	486	0.53	0.82	-
2b	469	0.59	0.91	-
3a	633	0.54	0.84	-0.87
3b	612	0.59	0.90	-0.84

[a] In nm, dioxane (**2a**, **2b**) or $CHCl_3$ (**3a**, **3b**) as solvent; [b] In Volts; SCE *vs* Pt; CH_2Cl_2 as solvent; $Bu_4N^+ClO_4^-$; 200 mV/s.

The UV-Vis absorptions of the novel compounds were measured in the same solvent used for EFISH measurements. The lowest energy absorption bands are shown in Table 1. Replacement of the carbonyl group in **2a,b** by the dicyanovinyl group in **3a,b** produces a large bathochromic shift (140-150 nm) due to the stronger acceptor character of the cyano groups. On the other hand, introduction of the ethylenedithio group on the TTF ring results in a slight hypsochromic shift (~20 nm) of the λ_{max} position (Table 1) in sharp contrast with the effect observed in dithiafulvenyl chromophores.[9-13]

The charge transfer nature of this band, which is a prerequisite to the attainment of high β values,[29-31] has been studied by quantum-chemical methods. Calculations started with a previous geometry optimization using both semiempirical (AM1 or PM3)[32] and *ab initio*[33] (HF/3-21G*) methods that lead to a planar structure for compounds **2a** and **3a**. Similar results were obtained when semiempirical calculations were applied to **2b** and **3b** whereas the optimized geometries at *ab initio* level presented a boat-like shape with bending angles of 18° and 6.6° at the sulfur atoms of the TTF core (Figure 1) thus resembling the X-ray structure of unsubstituted EDT-TTF.[34] Polarization functions on sulfur atoms included in the 3-21G* basis set are thus responsible for the prediction of such a bent geometry that parallels results for BEDT-TTF using the 6-31G** basis set.[35]

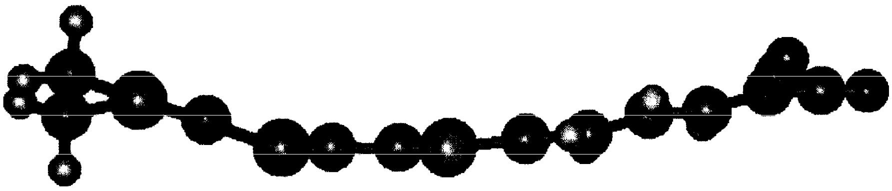


Figure 1. Side view of compound **3b** optimized at HF/3-21G* level.

While the geometries predicted by semiempirical and *ab initio* methods differ, there is a complete agreement in the predicted HOMO and LUMO topologies. The HOMO is located on the TTF donor fragment, and the LUMO is mainly spread on the acceptor moiety (Figure 2) while sulfur atoms in the ethylenedithio moiety present in compounds **2b** and **3b** have only a very small contribution to the HOMO. It can be seen that there is an overlap between the molecular HOMO and LUMO which is necessary for obtaining large second order responses.[29]

We have also calculated the orbital energies taking advantage of the usefulness of hybrid density functional theory methods to predict HOMO-LUMO energy differences.[36] The HOMO-LUMO gaps calculated by single point B3LYP[37]/6-31G* calculations on geometries optimized at the HF/3-21G* level (2.58 eV = 481 nm for **2a**, 2.62 eV = 474 nm for **2b**, 1.99 eV = 623 nm for **3a**, and 2.02 eV = 613 nm for **3b**) are in excellent agreement with the above reported experimental values (see Table 1). It is notable that this type of calculation predicts the otherwise unexpected hypsochromic shift caused by the ethylenedithio group in **2b** and **3b**.

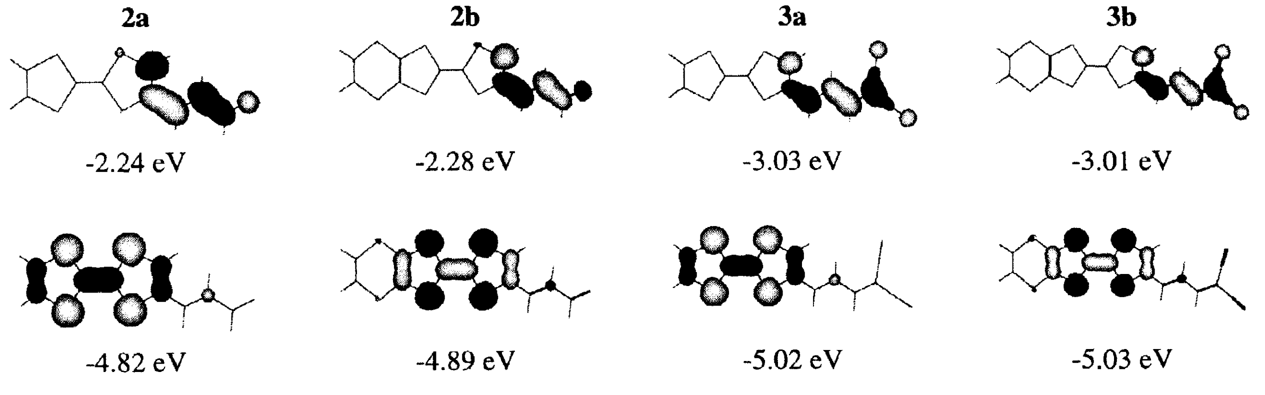


Figure 2. LUMO (top) and HOMO (bottom) topologies and calculated energies (B3LYP/6-31G*//HF/3-21G*).

$\mu\beta$ values of TTF derivatives (**2**) were measured using the electric-field-induced second harmonic generation (EFISH)[30] technique at 1,378 nm in dioxane as solvent. In order to minimize possible resonance effects which would enhance the nonlinear response, measurements of dicyanovinyl containing compounds (**3**) were performed at a fundamental wavelength of 1,907 nm.

As shown in Table 2, the substitution of formyl by dicyanovinyl as the acceptor group results in higher $\mu\beta$ values. The presence of the ethylenedithio substituent on the TTF ring leads to an enhancement of the nonlinear response, in agreement with previous observations in dithiafulvenyl type donors.[10] A most interesting result is that ethylenedithio derivatives **2b** and **3b** show an increase in $\mu\beta$ values together with an hypsochromic shift when compared to compounds **2a** and **3a** respectively, thus overcoming the well-known transparency-nonlinear efficiency trade-off.

Table 2

Calculated and Experimental Second Order Polarizabilities.

	FF-AM1			**FF-PM3**			**CPHF/6-31G***			**Experimental**	
Compound	μ[a]	β_{vec}[b]	$\mu\beta_o$[c]	μ[a]	β_{vec}[b]	$\mu\beta_o$[c]	μ[a]	β_{vec}[b]	$\mu\beta_o$[c]	$\mu\beta$[c]	$\mu\beta_o$[c,d]
2a	3.8	24.8	95	3.1	10.9	34	4.4	7.8	35	80[e]	35
2b	5.4	36.0	195	4.4	16.7	73	4.8	6.9	33	95[e]	45
3a	5.6	74.6	420	5.0	35.0	175	7.7	24.9	190	470[f]	234
3b	7.3	94.6	686	6.3	43.4	275	8.0	20.2	161	560[f]	295

[a] In Debye; [b] In $\cdot 10^{-30}$ esu units; [c] In $\cdot 10^{-48}$ esu units; [d] Values obtained from a two-level dispersion model; [e] Measured in dioxane at 1,378 nm; [f] Measured in $CHCl_3$ at 1,907 nm.

We have also performed theoretical calculations of the static hyperpolarizability* using the coupled semiempirical and *ab initio* procedures included in MOPAC (Finite Field) and Gaussian 94 (Coupled Pertubed Hartree-Fock), respectively, in order to compare with the experimental $\mu\beta_0$ values obtained from a two-level dispersion model[31] and evaluate the predictive power of these methods for this new family of chromophores (Table 2).

Both semiempirical and *ab initio* methods predict qualitatively the large enhancement in $\mu\beta_0$ values when passing from compounds **2** to **3** while the increased hyperpolarizabilty caused by the ethylenedithio group is only predicted by the semiempirical methods. Thus both AM1 and PM3 are useful in predicting trends in hyperpolarizability, but the quantitative values obtained from AM1 calculations are largely overestimated and the PM3[38] method provides more precise results. It is also noteworthy that PM3 calculations are also quantitatively more precise than the more expensive *ab initio* methods. An analogous result was also observed when these methods were employed to calculate bond distances in TTF derivatives[39] and confirms the good parameterisation of PM3 for this type of compounds.

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* Definitions described in ref [29] have been used. Thus, the vector conponent of the static hyperpolarizability is defined as follows: $\beta_{vec} = (\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z)/|\mu|$ with $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$; $\beta_y = \beta_{yxx} + \beta_{yyy} + \beta_{yzz}$ and $\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$.

3. Conclusions

To conclude, second order nonlinear optical activity has been observed in TTF-containing chromophores for the first time and the studied compounds show high $\mu\beta$ values. Theoretical calculations have been performed to study the UV spectra and the second order NLO properties of the studied compounds. The PM3 calculated static hyperpolarizabilities are in good agreement with the experimental values indicating that this method may be used to predict the NLO properties of novel TTF-derived chromophores.

The inclusion of the ethylenedithio group as a substituent in the TTF core causes an enhancement of the NLO properties together with an hypsochromic shift thus constituting an exception to the commonly assumed transparency-nonlinear efficiency trade-off. Substitution on the TTF ring, which allows the tunning of its donating ability, together with the possibility of forming organized TTF-based materials, greatly enhances the usefulness of these chromophores and paves the way to new multi-property materials. Work along these directions is in progress.

4 Experimental

General.

All new compounds gave satisfactory microanalyses. Melting points were measured on a Büchi 510 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Varian Unity-300 or a Bruker ARX-300 spectrometer. IR spectra were recorded using a Perkin-Elmer FTIR 1600 spectrophotometer. Mass spectra (EI^+, 70 eV) were obtained on a VG Autospec EBE mass spectrometer. Accurate mass measurements were recorded at 10,000 resolution (peak width at 5% height) using perfluorokerosene as the reference compound. Cyclic voltammograms were measured using an EG&G PAR model 273 potentiostat. EFISH measurements were taken with a non-linear optics spectrometer from SOPRA S.A. The fundamental light source at 1.907 μm was the first Stokes peak of a hydrogen Raman cell pumped by the 1.064 μm light of a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns pulse). That light was passed through a linear polarized and focused on the EFISH cell. The polarized dc electric field (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. Optical absorption spectra were measured with a Hitachi U-3400 UV-VIS-NIR spectrophotometer. Molecular orbital calculations were performed on Intel® Pentium and Pentium Pro computers running under the Microsoft® Windows NT 4.0 Workstation operating system.

(*E*)-3-(Ethylenedithiotetrathiafulvalenyl)acrylaldehyde (2b). A solution of triphenylphosphoranylidene-acetaldehyde (304 mg, 1 mmol) and formyl-EDT-TTF (**1b**) (161 mg, 0.5 mmol) in benzene (20 mL) was refluxed under nitrogen for 3 h. After cooling, hexane (30 mL) was added, and the precipitated Ph_3PO was filtered. The solvent was evaporated and column chromatography of the residue (silicagel 70-230 mesh) using CH_2Cl_2/hexane (1:1) as eluent afforded compound **2b** as a violet solid (148 mg, 85% yield); mp 159-160°C. IR (Nujol mull) ν (cm^{-1}): 1660. ^{1}H-NMR ($CDCl_3$) δ: 9.58 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 15.5 Hz, 1H), 6.85 (s, 1H), 5.93 (dd, J_1 = 7.4 Hz, J_2 = 15.5 Hz, 1H), 3.28 (s, 4H). Accurate m/z: calcd. for $C_{11}H_8OS_6$: 347.8899; found: 347.8899.

Synthesis of TTFs derivatives 3a,b. A solution of the corresponding formyl-TTF (**2a** and **2b**) (0.86 mmol), malononitrile (3.30 mmol), ammonium acetate (0.06 g) and acetic acid (0.18 mL) in benzene (25 mL) was refluxed, under azeotropic removing of water, for 72 h. The solvent was evaporated and the final product was purified by flash chromatography by using hexane:ethyl acetate (5:1) as eluent.

4-(4',4'-dicyanobutadienyl)tetrathiafulvalene (3a). 75 % yield; mp 205-206°C (dec.). IR (KBr disk) ν (cm^{-1}): 2220 (CN), 1590, 1490, 1270, 1175, 860, 800, 645. ^{1}H-NMR (DMSO-d_6): 8.18 (d, 1 H, J=11.4 Hz), 7.75 (s, 1 H), 7.43 (d, 1 H, J= 14.4 Hz), 6.80 (d, 1 H, J=7.5 Hz), 6.78 (d, 1 H, J=7.5 Hz), 6.15 (dd, 1 H, J_1= 14.4, J_2=11.4 Hz). ^{13}C-NMR (DMSO-d_6): 158.2, 148.4, 137.8, 133.2, 129.0, 127.0, 126.7, 123.7, 119.2, 119.0, 118.7, 118.6. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 618 (3.80), 362 (4.45). Accurate m/z: calcd. for $C_{12}H_6N_2S_4$: 305.9413; found: 305.9424.

4-(4',4'-dicyanobutadienyl)ethilenedithiotetrathiafulvalene (3b). 93 % yield; mp 223 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2220 (CN), 1570, 1475, 1340, 1165, 960, 850, 770. ^{1}H-RMN (DMSO-d_6, 300 MHz) δ: 8.18 (1H, d, J=11.4 Hz), 7.76 (1H, s), 7.44 (1H, d, J=14.7 Hz), 6.19 (1H, dd, J_1= 14.7, J_2=11.4 Hz), 3.33 (4 H, s). ^{13}C-RMN (DMSO-d_6, 75 MHz) δ: 160.9, 139.9, 135.0, 133.2, 123.5, 119.2, 113.8, 111.9, 29.5. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 594 (3.79), 324 (4.34). Accurate m/z: calcd. for $C_{14}H_8N_2S_6$: 395.9012; found: 395.9002.

5. Acknowledgements

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