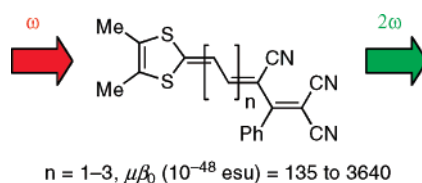# JOC Article

Synthesis, Structure, and Optical Properties of 1,4-Dithiafulvene-Based Nonlinear Optic-phores

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n = 1–3, $\mu\beta_0$ (10^{-48} esu) = 135 to 3640

Polyenic nonlinear optic (NLO)-phores with a proaromatic 1,4-dithiafulvene electron donor and the little explored 1,1,3-tricyano-2-phenylpropene acceptor have been synthesized. Their configurational and conformational features, ground state polarization, and linear and nonlinear optical properties have been determined experimentally and theoretically, and the results are compared to those of tetrathiafulvalene-related derivatives. The newly prepared compounds show close to optimal bond length alternation values for maximizing the first molecular hyperpolarizability, and one of them displays the highest $\mu\beta_0$ value ever reported for a dithiafulvene-based NLO-phore. The first example of a dithiafulvenylmethylene transfer reaction is also reported.

Introduction

Organic electrooptic materials are currently being investigated for their use in photonic devices and optical information processing.[1] Conjugated donor−acceptor (D−π−A) systems constitute the widest class of organic compounds studied for their nonlinear optical (NLO) properties,[2] and it is well known that the first molecular hyperpolarizability (β), which characterizes the molecular NLO efficiency, depends on the strength of the D and A groups and on the length and nature of the conjugated path.[3] The interplay between these parameters determines the ground state polarization of the NLO-phores and the bond length alternation (BLA) along the chain,[4] the latter parameter being especially useful in the establishment of structure/NLO property relationships, which have eventually led to attain huge β values.[5]

Many of the reported NLO-phores have aromatic electron donors, like *N,N*-dialkylanilines, or aromatic spacers, like phenylene and thienylene, but it was soon recognized that molecules with aromatic ground states undergo a decrease in their resonance energy upon intramolecular charge transfer (ICT) excitation, since the corresponding excited states have an increased quinoid (and usually zwitterionic) character. Marder et al. suggested that this detrimental effect on the ICT process and hence, on the second-order NLO response, could be

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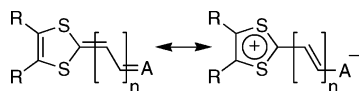(2) (a) Marder, S. R. *Chem. Commun.* **2006**, 131−134. (b) Suponitsky, K. Yu.; Timofeeva, T. V.; Antipin, M. Yu. *Russ. Chem. Rev.* **2006**, *75*, 457−496.
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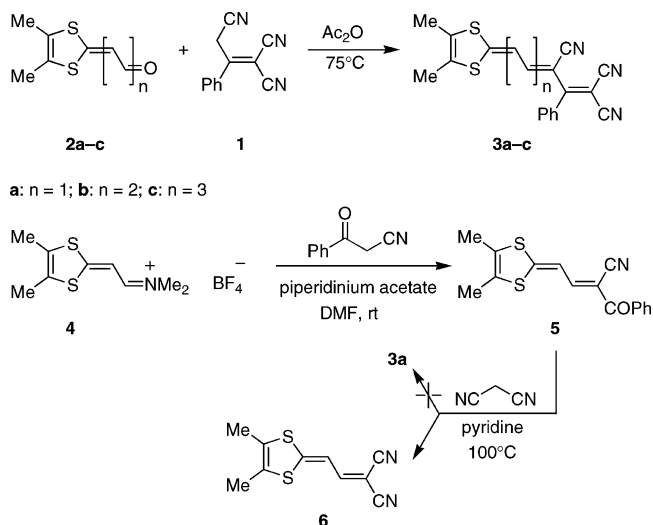
compensated for by the introduction of subunits gaining aromaticity (proaromatic) on charge separation, and this strategy has been widely applied to proaromatic acceptors,[5a,6] although the beneficial effect of proaromatic donors[7] and spacers[7c,8] on β has also been confirmed. Thus, it is not surprising that 1,4-dithiafulvenes (2-methylene-1,3-dithioles), which are proaromatic due to the electronic sextet of the 1,3-dithiolium cation limiting form, have attracted much attention as NLO-donors[7b,8,9] since they were first explored to that end.[10]

Furthermore, and given the success of polycyano acceptors, such as tricyanovinyl[11] or derivatives of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF),[12] which have given rise to NLO-phores with very high β values, it is surprising that 1,1,3-tricyano-2-phenylpropene (**1**),[13] structurally related to TCF, has received only scant attention in this field.[14]

In this paper we describe the synthesis of NLO-phores **3**, comprising a dithiafulvene donor and acceptor **1**, and report their structural, electrochemical, and linear and nonlinear optical properties, which have been studied both experimentally and theoretically. Moreover, systems **8**, where a tetrathiafulvalene (TTF) donor replaces the dithiafulvene moiety, have also been synthesized with the intention of comparing the influence that these structurally related donors have on the optical properties of the corresponding D−π−A compounds. This also allows us

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SCHEME 1

a: n = 1; **b**: n = 2; **c**: n = 3

to study the effect of linking a conjugated moiety to different positions of the 1,3-dithiol-2-ylidene ring and, ultimately, to compare the electron donor abilities of dithiafulvenes and TTFs.

Results and Discussion

Synthesis. The target dithiafulvene-based merocyanines **3a**−**c** were prepared by Knoevenagel reaction of the corresponding aldehydes **2a**−**c**[15] with **1** in acetic anhydride (Scheme 1). It is noteworthy that the reaction of **2a** (taken as a model compound) with **1** takes place much more slowly when piperidine/EtOH is used instead of Ac$_2$O. The fact that most Knoevenagel reactions of **1** are carried out in the latter solvent[14] points to an activation of the corresponding aldehydes via their highly electrophilic *O*-acetyloxonium derivatives.

On the other hand, the reaction of iminium salt **4**,[16] which is also expected to behave as an activated equivalent of the parent aldehyde **2a**, with **1** under a variety of conditions only led to recovery of the starting materials. In order to check the electrophilicity of salt **4**, it was treated with benzoylacetonitrile, and compound **5** was indeed obtained in high yield (Scheme 1). It was then thought that its reaction with malononitrile could give rise to **3a** but, to our surprise, compound **6**, identified by comparison with an authentic sample,[17] was the only obtained product. To the best of our knowledge, this constitutes the first example of a "dithiafulvenylmethylene transfer" reaction, which belongs to the more general class of transalkenylation reactions, which have some precedents in the literature[18] and seem to
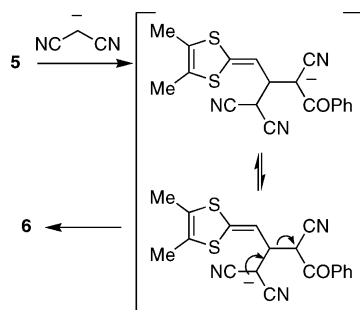
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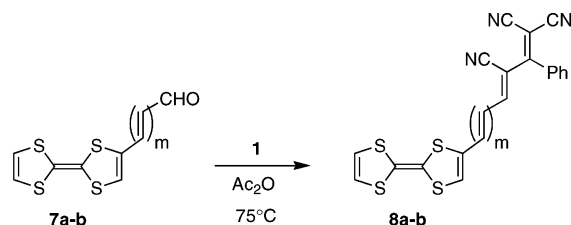
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SCHEME 2

proceed through a Michael/retrograde Michael sequence (Scheme 2). It should be noted that it is not easy to predict the position of these equilibria, since examples are known where either the stronger or the weaker carbon acid is the leaving group and, in the present case, both species have similar pK_a values.[19]
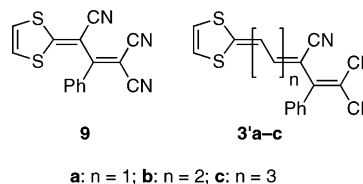
In order to compare their electrochemical and optical properties with those of compounds **3**, TTF derived merocyanines **8a,b** were chosen as model compounds and were prepared from formyl-TTF derivatives **7a,b**[20] using conditions similar to those described above (eq 1).

a: m = 0; **b**: m = 1

General Structural Aspects. Given the nonsymmetrical nature of **1**, its Knoevenagel reactions with aldehydes can give rise to (*E*)- and/or (*Z*)-isomers around the newly formed C=C bond. As far as we know, this issue has only once been addressed in the literature[14b] indicating an "all-*E*-configuration", a statement which contradicts the depicted structure in that paper (this seems to be a nomenclature error rather than a structural misassignment). Moreover, the PhC—C(CN) single bond of the acceptor moiety can adopt an s-*cis* or s-*trans* conformation. We herein provide full structural (configurational and conformational) information of the target compounds, based on X-ray diffraction data of compound **9** (the first derivative of acceptor **1** to be characterized by this technique), ^{1}H NMR data of compounds **3** and **8**, and theoretical calculations carried out on **8** and model compounds **3′**, where the methyl substituents have been replaced by hydrogen atoms for the sake of simplicity.

Crystal Structure of 9. Compound **9**, recently reported by us,[21] can be considered the simplest derivative of the dithiafulvene-based family **3a–c**. Single crystals of **9** were grown from CDCl$_3$ solution, and X-ray analysis shows that the molecule is completely planar, except for the phenyl ring which is orthogonal to the dithiolylidenetricyanopropene moiety, which is exactly

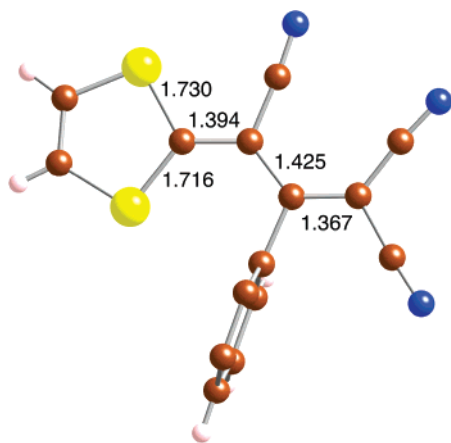(19) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

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9   **3′a–c**

a: n = 1; **b**: n = 2; **c**: n = 3

on the mirror plane of the *P*2$_1$/*m* space group in the crystallographic structure.

Inspection of Figure 1 shows that C—C bond lengths along the polyenic spacer display a low degree of alternation, which is more marked near the acceptor end. As expected, the lengthening of the S$_2$C=C bond is accompanied by a shortening of the adjacent C—S bonds (averaged length, 1.723 Å). In fact, this length is shorter than the corresponding ones in other structures featuring 1,3-dithiolylidene and dicyanomethylene moieties conjugated through oligoenic[17,22] or (hetero)aromatic spacers.[9b] These features, together with the fact that the mean alternation between single- and double-bond lengths (BLA) in all-*trans* polyenes is ca. 0.11 Å, point to a high degree of push—pull character for compound **9**. It is also noteworthy that previous theoretical calculations on this compound predicted[21] that the less polar (μ = 6.09 D) s-*cis* conformation is slightly more stable (by ca. 1 kcal/mol) than the s-*trans* conformation in the gas phase. No doubt, the crystalline environment favors the highly polar (μ = 11.99 D) geometry experimentally found.

^{1}H NMR and BLA Studies. Full configurational and conformational assignment of compounds **3a–c** in solution was established by $^3J_{HH}$ coupling constants analysis and selective ge-1D NOESY experiments. $^3J_{HH}$ values along the polyenic chain allowed an unambiguous stereochemical assignment of the HC=CH bonds ((*E*)- configuration) and the HC—CH bonds (s-*trans*). The determination of the stereochemistry of the HC=C(CN) and the PhC—C(CN) bonds was possible thanks to the NOE between H$_{ortho}$ of the phenyl group and its nearest vinylic H atom. Thus, the C=C bond formed in the Knoevenagel reaction has (*Z*)-configuration, and all C—C single bonds along the polyenic chain are s-*trans*. Therefore, the geometry of compounds **3** in solution is that depicted in Scheme 1. Similar experiments conducted on compounds **8** established their stereochemistry as that shown in eq 1.

In the context of this work, coupling constants are especially interesting since the difference (ΔJ) between HC=CH and HC—CH coupling constants for vicinal protons (about 6 Hz for all-*trans* polyenes and nearly 0 Hz for cyanines) gives a clear indication of the ground state polarization of the studied compounds.[23] The measured $^3J_{HH}$ values (Table 1) indicate a reduced bond order for the formally double C=C bonds, together with a certain double bond character for the formally single C—C bonds along the chain. Average ΔJ values (0.6 Hz for **3b**, 1.6 Hz for **3c**, and 3.5 Hz for **8b**) show that compounds **3** are more polarized (less alternated) than compounds **8**, and that ground state polarization decreases on increasing the length of the spacer.

The structural features of compounds **3** are well reproduced by theoretical calculations on model compounds **3′**. Their molecular geometries were optimized at the B3P86/6-31G*

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FIGURE 1. Selected bond lengths for **9**.

TABLE 1. $^3J_{HH}$ Values along the Chain

compd	$^3J_{HH}$ (Hz)[a]
3a	12.9
3b	12.2, 12.8, 12.3
3c	12.0, 13.5, 11.9, 13.8, 12.2
8b	14.6, 11.1

[a] In CDCl$_3$. From donor to acceptor end.

TABLE 2. B3P86/6-31G* Values for C−S[a] and C−C[b] Bond Distances, BLA,[c] and Charge in the Dithiole Moiety

compd	C−S (Å)	C−C (Å)	BLA (Å)	charge (e)
3′a	1.753	1.373	0.031	+0.18
3′b	1.757	1.370	0.038	+0.14
3′c	1.759	1.368	0.041	+0.12

[a] Averaged values of the SC−S dithiole bonds. [b] S$_2$C=C bond. [c] Along the polyenic spacer.

TABLE 3. Cyclic Voltammetric Data[a] for Compounds 3 and 8

compd	E_{ox}	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$	E_{red}
3a	+1.25			−0.85, −1.12
3b	+0.85			−0.68
3c	+0.68			−0.57
8a[b]		+0.59	+0.91	−0.45
8b[b]		+0.52	+0.86	−0.38
TTF[b]		+0.38	+0.76	

[a] In volts, 10^{-3} M in CH$_2$Cl$_2$ vs Ag/AgCl, glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M Bu$_4$NPF$_6$, 100 mV s^{-1} scan rate. [b] In acetonitrile.

FIGURE 2. Cyclic voltammograms of **8a** (thick line) and **8b** (thin line).

TABLE 4. Experimental and Calculated[a] λ_{max} Values (nm)

compd	λ_{max} (CH$_2$Cl$_2$)	λ_{max} (DMSO)	λ_{max} (calcd)
3a	590	599, 555 (sh)	436[b]
3b	688	702, 645 (sh)	479[b]
3c	715	806, 726 (sh)	522[b]
8a	719	685	835
8b	708	673	843

[a] TD-DFT B3P86/6-31G*//B3P86/6-31G* level in the gas phase. [b] Calculated for the corresponding model compound **3′**.

level, since this hybrid functional reproduces very well the geometry of 1,3-dithiole derivatives,[24] although calculated C−S bond lengths are usually 0.02 Å longer than those determined by X-ray diffraction.[8,17,24a] It can be seen (Table 2) that on lengthening the π-spacer, the increase in the SC−S bond lengths is accompanied by a shortening of the exocyclic S$_2$C=C bond and by an increase of the BLA parameter.
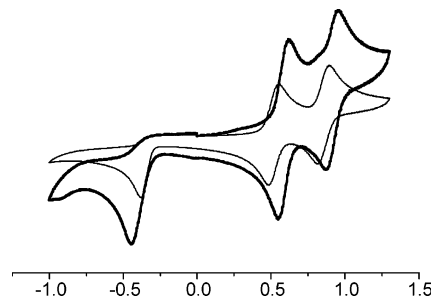
These facts, together with Mulliken population analysis, clearly show that charge transfer decreases as the length of the conjugated spacer increases. In other words, the contribution of the zwitterionic limiting form to the description of the ground state of compounds **3′** is higher for the shorter derivatives. Moreover, calculated gas phase BLA values are close to the optimal value (ca. 0.04 Å) which maximizes β.[1b]

Electrochemistry. The electrochemical properties of the new merocyanines were studied by cyclic voltammetry (Table 3).

The cyclic voltammograms of compounds **3** show one irreversible oxidation wave and one (or two, in the case of **3a**) irreversible reduction wave(s). On lengthening the polyenic chain there is a shift of the E_{ox} values toward less anodic potentials, together with a shift of the E_{red} values toward less

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cathodic potentials. This trend is mirrored by theoretical calculations, which show that calculated E_{HOMO} values increase with the length of the spacer (**3′a**: −6.55 eV; **3′b**: −6.31 eV; **3′c**: −6.12 eV), whereas calculated E_{LUMO} values decrease in the same order (**3′a**: −3.75 eV; **3′b**: −3.82 eV; **3′c**: −3.86 eV). These facts point to a decrease in the interaction between the donor and acceptor groups on lengthening the spacer.

Compounds **8** show two reversible oxidation waves corresponding to the TTF moiety and one irreversible reduction wave. In all cases the $E_{1/2}^{ox}$ values are shifted toward more positive values in comparison with TTF itself, due to the presence of the conjugated acceptor moiety. As expected from their E_{HOMO} values (**8a**: −5.76 eV; **8b**: −5.79 eV), the oxidation potentials of compounds **8** are lower than those of their dithiafulvene analogues **3**, and the dependence of the $E_{1/2}^{ox}$ and E_{red} values on the chain length is qualitatively the same as that found for compounds **3** (Figure 2).

Taken together, cyclovoltammetric data indicate that oxidation of the donor moiety (dithiafulvene or TTF) and reduction of the acceptor unit become increasingly easier on lengthening the π-spacer, indicating a smaller contribution of the charge-separated form to the ground state of the longer derivatives, in good agreement with the results of theoretical calculations.

UV−Vis Spectroscopy. The electronic absorption spectra of compounds **3** (Table 4) show a broad, low-energy ICT band and, as expected, the maxima values shift bathochromically with increasing number of conjugated double bonds. The marked

TABLE 5. Experimental[a] and Calculated[b,c] NLO Properties

	exptl		TD-DFT[d]				CPHF[e]		
compd	$\mu\beta^f$	$\mu\beta_0{}^f$	μ_g (D)	μ_e (D)	E (eV)	f	μ (D)	$\beta_{tot}{}^g$	$\mu\beta_0{}^f$
3a	240	135	14.52	20.28	2.84	0.9108	15.11	24.5	194
3b	2250	935	16.36	25.57	2.59	1.3411	16.50	80.7	979
3c	9680	3640	18.10	30.93	2.37	1.7408	17.73	177.1	2531
8a	600	220	11.31	28.71	1.49	0.1465	11.68	43.9	292
8b	1350	520	12.68	34.80	1.47	0.1999	12.87	83.3	653

[a] In CH_2Cl_2, at 1907 nm. [b] On B3P86/6-31G* geometries. [c] Calculations carried out on compounds **3'** instead of **3**. [d] B3P86/6-31G* level. [e] CPHF/6-31G* level. [f] In 10^{-48} esu. Experimental accuracy: ±10%, except for **3a** and **8a** (±20%). [g] In 10^{-30} esu.

vinylene shift is similar to that displayed by cyanine dyes,[25] thus confirming the strong conjugation between the donor and acceptor ends. TD-DFT calculations support the ICT character of the lowest energy absorption band and qualitatively reproduce the experimental trends, although λ_{max} values are strongly underestimated, due to the interplay of different factors: gas phase calculations, use of compounds **3'** (devoid of methyl substituents), and poor description of charge transfer transitions by TD-DFT.[26] Compounds **3** also show a positive solvato-chromism which increases with the length of the spacer; this fact will be discussed together with their NLO properties.

On the other hand, TTF derivatives **8** show a hypsochromic shift on increasing the length of the spacer. This quite unusual feature has already been reported in other TTF−π−A compounds,[20b,24c] and a possible explanation for this behavior will be reported in due course. Although the calculated vinylene shift on passing from **8a** to **8b** is much smaller than that calculated for the **3'** series, the experimental trend is not well reproduced by TD−DFT. The limited solubility of compounds **8** has precluded a full comparative study, but they show negative solvatochromism, in agreement with previous reports on related TTF−π−A compounds.[27] In fact, the excitation energy of **8a** calculated by TD−DFT using the PCM solvation model is blue-shifted by 0.01 eV on moving from CH_2Cl_2 to DMSO.

Nonlinear Optical Properties. The second-order NLO properties of compounds **3** and **8** were determined by EFISH measurements at 1907 nm in dichloromethane, and $\mu\beta_0$ values were calculated using the two-level model. Inspection of Table 5 reveals that $\mu\beta_0$ values increase with the conjugation path and that compound **3c** possesses the highest $\mu\beta_0$ value ever reported for a dithiafulvene-based NLO-phore,[28] a value which, moreover, is not resonance enhanced (for the sake of comparison, $\mu\beta_0 \approx 400 \times 10^{-48}$ esu for Disperse Red 1, a common benchmark in organic NLO-phores).[29]

Calculated $\mu\beta_0$ values for compounds **3'** and **8** (CPHF/6-31G*//B3P86/6-31G* model) are in very good agreement with the experimental values. Although CPHF-calculated $\mu\beta_0$ values are usually closer to the experimental ones than those calculated by TD-DFT, we have also used the latter method in order to

obtain a more intuitive description of the observed trends in the NLO behavior of the studied compounds. To that end, we have calculated the parameters involved in the two-level model ($\beta_0 \propto \Delta\mu_{ge}f/E^3$, where $\Delta\mu_{ge}$ is the difference between the excited and ground state dipole moments, μ_e and μ_g, respectively, f is the oscillator strength, and E is the excitation energy).[30] A summary of these parameters is gathered in Table 5. For compounds **3'**, both $\Delta\mu_{ge}$ and f increase in the series **3'a** < **3'b** < **3'c**, whereas the reverse holds for E. Therefore, calculated $\mu\beta_0$ values increase form **3'a** to **3'c**, in good agreement with experiments. Moreover, the strongly positive solvatochromism of **3c**, when compared to **3a** (vide supra), can be accounted for by the calculated $\Delta\mu_{ge}$ values since, on lengthening the chain, the rise in μ_e is steeper than that of μ_g. The smoother variation of the latter is the result of two counterbalanced effects: the increased separation of the D and A moieties and the decreased charge transfer (Table 2).[31]

Although it is not possible to draw firm conclusions based solely on the number of compounds herein reported, experiments and calculations reveal that lengthening the π-spacer gives rise to a much steeper increase in the $\mu\beta_0$ values of compounds **3** than those of compounds **8**. Furthermore, a comparison of previously reported $\mu\beta_0$ values for dithiafulvene- and TTF-based merocyanines featuring a common acceptor group (dicyano-methylene,[9b,17,20b] dicyanomethyleneindanone,[9c,20b] or thiobar-biturate)[7b,20b] discloses the same trend, clearly suggesting that higher $\mu\beta_0$ values can be expected for dithiafulvene derivatives with long polyenic spacers. The lower efficiency of their TTF counterparts can be related to their much lower oscillator strengths, which can be traced back to the poor HOMO/LUMO overlap in TTF−π−A derivatives (see Supporting Information). In fact, the extent to which the HOMO couples to the orbitals of a conjugated π-system is an important factor for determining the π-donor strength of a group[32] and, according to the optical properties of the corresponding derivatives, the TTF moiety turns out to be a weaker π-donor than the dithiafulvene moiety. The reverse holds concerning the electron transfer donor strength of both groups, which is determined by their HOMO energies (see the Electrochemistry section).

The thermal stabilities of the studied chromophores were investigated using thermogravimetric analysis (TGA). The decomposition temperature (T_d) was estimated as the temperature that is the intercept of the leading edge of the weight loss by the baseline of the TGA scans. Dithiafulvene derivatives showed T_d values of 188 °C, 222 °C, and 165 °C for **3a**, **3b**, and **3c**, respectively, whereas T_d values for TTF derivatives were lower (108 °C for **8a**, and 148 °C for **8b**).

In order to explore the nonlinear optical properties of these chromophores incorporated in bulk materials, we planned as a first step to prepare polymethylmethacrylate (PMMA) films with the chromophores embedded in. Although **3c** is the molecule with the highest $\mu\beta$ value measured in this study, the significant

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TABLE 6. $\mu\beta$ Values of the Chromophores and d_{ij} Coefficients of the Doped PMMA Films

film	$\mu\beta^a$	$d_{13}{}^b$	$d_{33}{}^b$
DR1/PMMA	660	1.0	3.0
3b/PMMA	2250	2.7	8.0

a In 10^{-48} esu. EFISH measurements in CH_2Cl_2 at 1.9 μm. Experimental accuracy: $\pm 10\%$. *b* In pm/V. Chromophore concentration 3×10^{20} cm^{-3}. Experimental accuracy: $\pm 15\%$.

absorption of the **3c**/PMMA films made the determination of NLO coefficients from SHG measurements difficult. Moreover, its thermal stability is not very good, and **3c**-doped films showed progressive damage when electric field poling processes at $T > T_g$ were repeated. Therefore, **3b**, with moderately good nonlinear response and better thermal stability, was chosen for this study. It was mixed (5% molar) with PMMA as matrix polymer, and for the sake of comparison, films with Disperse Red 1 (DR1) in a similar concentration were prepared.

The second-order nonlinear optical properties of both films were evaluated by SHG measurements. The usual thermal corona poling process was performed as follows: the films were heated up to 125 °C with the electric field on and maintained at this temperature for 15 min. Then, they were cooled down to room temperature with the poling field still applied, and finally this field was removed. It is well known that molecular relaxation tends to reduce gradually the polarization in poled guest–host polymeric films. We have measured the harmonic intensity generated by these films at different times after the poling. As usual, the harmonic signals showed an initial fast relaxation, followed by a slower one. The "quasistable" d_{ij} values given in Table 6 were determined from Maker fringes measurements performed two weeks after the poling, when the decay of the signals was quite slow. The obtained values for DR1/PMMA are in the range of those reported in the literature, taking into account dye concentration and excitation wavelength corrections.[33] Indeed, an approximate ratio $d_{33}/d_{31} = 3$ is obtained for both, DR1/PMMA and **3b**/PMMA films. This result agrees with the predicted ratio under the assumption of low poling electric field ($\mu E/kT < 1$).[34] The comparison between the nonlinear coefficients of the two dye–doped PMMA films is consistent with the higher molecular nonlinear response of **3b**, the ratio of the nonlinear macroscopic coefficients being somewhat lower than the corresponding $\mu\beta$ values ratio. Keeping in mind the similar chromophore concentration (about 3×10^{20} cm^{-3}), this suggests that, under our experimental conditions, the achieved orientation degree is not much different in the two studied doped polymers.

The thermal stability of the poling orientation was analyzed from the evolution of the remaining SH signal versus temperature. The samples were heated up from room temperature at a rate of 3 °C/min. The decrease of the **3b**/PMMA harmonic signal starts at about 75 °C, and at $T = 100$ °C the harmonic signal has almost disappeared (see Supporting Information). This decay did not show any significant difference when compared to that of DR1/PMMA films.

It should be mentioned that the d_{33} value obtained for **3b**/PMMA is far from the nonlinear coefficients one can find in

the literature over the past decade.[1b,12a,35] Nevertheless, this study provides a first insight into the NLO response of dithiafulvene-doped polymeric materials.

To sum up, the linking of a proaromatic 1,4-dithiafulvene donor moiety to the strong electron acceptor 1,1,3-tricyano-2-phenylpropene through a polyenic chain affords new push–pull compounds, one of them showing the highest $\mu\beta_0$ value ever reported for a 1,4-dithiafulvene-based NLO-phore. Full structural characterization of these compounds has been carried out by X-ray diffraction, ^{1}H NMR, and theoretical studies. They show close to optimal BLA values, and their ground state polarization decreases on lengthening the π-spacer. For the sake of comparison, closely related merocyanines featuring a TTF donor moiety have also been prepared. Due to its high-lying HOMO, TTF is a stronger electron transfer donor than dithiafulvene, but dithiafulvenes are stronger π-donors than TTFs in D–π–A compounds, thanks to the better overlap of their HOMO with the orbitals of the conjugated π-system.

Experimental Section

Compounds **1**,[13] **2a–c**,[15] **4**,[16] **7a,b**,[20] and **9**[21] were prepared as previously described.

Compounds 3: General Procedure. To a solution of the corresponding aldehyde **2a–c** (0.5 mmol) in 7 mL of Ac_2O was added 0.55 mmol of **1**. The mixture was heated under argon at 75 °C with exclusion of light for 1 h and then allowed to cool to room temperature. The resulting solid was isolated by filtration, washed with hexane, and dried. In the case of **3a**, CH_2Cl_2 (50 mL) was added to the filtrate, and then washed with NaOH 10% (3 × 50 mL) and water (2 × 50 mL). The organic layer was dried over $MgSO_4$ and evaporated, giving a second fraction.

(Z)-5-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-2-phenylpenta-1,3-diene-1,1,3-tricarbonitrile (3a). Yield: purple solid (156 mg; 90%). Mp: 218–219 °C. IR (Nujol, cm^{-1}): 2203 (C≡N). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.56 (d, $J = 12.9$ Hz, 1H), 7.56–7.48 (m, 3H), 7.40–7.37 (m, 2H), 6.79 (d, $J = 12.9$ Hz, 1H), 2.18 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 181.1, 173.1, 172.3, 166.9, 166.5, 148.2, 134.9, 131.8, 130.1, 129.5, 129.1, 115.7, 115.2, 114.5, 108.8, 13.7, 13.4. MS (EI$^+$) m/z (%): 347 (M$^{+\bullet}$, 100). CH$_2$-Cl$_2$, λ_{max} (nm): 590, lg $\epsilon = 4.87$. Anal. Calcd for C$_{19}$H$_{13}$N$_3$S$_2$: C, 65.68; H, 3.77; N, 12.09. Found: C, 65.39; H, 3.91; N, 12.22.

(3Z,5E)-7-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-2-phenylhepta-1,3,5-triene-1,1,3-tricarbonitrile (3b). Yield: dark blue solid (34 mg; 18%). Mp: 232–233 °C. IR (Nujol, cm^{-1}): 2205 (C≡N). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.58–7.49 (m, 3H), 7.39–7.37 (m, 2H), 7.22 (d, $J = 12.3$ Hz, 1H), 6.90 (dd, $J = 12.8$ Hz, $J' = 12.2$ Hz, 1H), 6.56 (dd, $J = 12.8$ Hz, $J' = 12.3$ Hz, 1H), 6.42 (d, $J = 12.2$ Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 181.1, 166.3, 164.5, 162.8, 156.4, 146.8, 134.6, 131.7, 129.6, 129.1, 127.9, 121.0, 115.4, 114.9, 113.6, 111.9, 100.9, 13.7, 13.3. MS (EI$^+$) m/z (%): 373 (M$^{+\bullet}$, 100). CH$_2$Cl$_2$, λ_{max} (nm): 688, lg $\epsilon = 4.94$. Anal. Calcd for C$_{21}$H$_{15}$N$_3$S$_2$: C, 67.53; H, 4.05; N, 11.25. Found: C, 67.28; H, 4.28; N, 11.41.

(3Z,5E,7E)-9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-2-phenylnona-1,3,5,7-tetraene-1,1,3-tricarbonitrile (3c). Yield: dark blue solid (104 mg; 52%). Mp: 174–175 °C. IR (Nujol, cm^{-1}): 2206 (C≡N). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.59–7.49 (m, 3H), 7.40–7.37 (m, 2H), 7.20 (d, $J = 12.2$ Hz, 1H), 6.96 (dd, $J = 13.8$ Hz, $J' = 11.9$ Hz, 1H), 6.78 (dd, $J = 13.8$ Hz, $J' = 12.2$ Hz, 1H), 6.70 (dd, $J = 13.5$ Hz, $J' = 12.0$ Hz, 1H), 6.30 (d, $J = 12.0$ Hz, 1H), 6.23 (dd, $J = 13.8$ Hz, $J' = 11.9$ Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H). ^{13}C NMR spectrum was not registered due to its low solubility. MS (EI$^+$) m/z (%): 399 (M$^{+\bullet}$, 65). HRMS (EI$^+$) Calcd for

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$C_{23}H_{17}N_3S_2$: 399.0864. Found: 399.0867. CH_2Cl_2, λ_{max} (nm): 715, lg ϵ = 4.78. Anal. Calcd for $C_{23}H_{17}N_3S_2$: C, 69.14; H, 4.29; N, 10.52. Found: C, 68.86; H, 4.51; N, 10.72.

2-Benzoyl-4-(4,5-dimethyl-1,3-dithiol-2-ylidene)but-2-enenitrile (5). To a solution of salt **4** (29 mg, 0.1 mmol) in anhydrous DMF (2 mL) were added benzoylacetonitrile (14.5 mg, 0.1 mmol) and piperidinium acetate (14.5 mg, 0.1 mmol). The mixture was stirred under argon at room temperature for 1 h. Saturated aqueous NaCl (20 mL) was added, and the mixture was extracted with ethyl acetate (3 × 15 mL). The organic layer was dried ($MgSO_4$), evaporated, and purified by column chromatography (silica gel, CH_2Cl_2). Yield: red solid (22 mg; 73%). Mp: 183−185 °C. IR (Nujol, cm^{-1}): 2203 (C≡N), 1648 (C=O). ^1H NMR (CDCl$_3$, 400 MHz): δ 8.02 (d, 1H, J = 12.9 Hz), 7.86−7.82 (m, 2H), 7.56−7.50 (m, 1H), 7.49−7.43 (m, 2H), 6.73 (d, 1H, J = 12.9 Hz), 2.13 (br s, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 188.3, 167.9, 149.4, 137.9, 132.1, 128.5, 128.2, 127.7, 127.1, 118.5, 107.7, 98.8, 13.7, 13.3. MS (MALDI$^+$): m/z 300 (M + H). Anal. Calcd for $C_{16}H_{13}NOS_2$: C, 64.18; H, 4.38; N, 4.68. Found: C, 64.00; H, 4.52; N, 4.49.

3-(4,5-Dimethyl-1,3-dithiol-2-ylidene)propene-1,1-dicarbonitrile (6). To a solution of **5** (45 mg, 0.15 mmol) in pyridine (3 mL) was added malononitrile (20 mg, 0.28 mmol). The mixture was heated under argon at 100 °C for 3 h and then allowed to cool to room temperature. Water (50 mL) was added, and the mixture was extracted with ethyl acetate (3 × 30 mL). The organic layer was washed succesively with 1 N aqueous HCl (30 mL) and saturated aqueous NaCl (30 mL), dried ($MgSO_4$), evaporated, and purified by column chromatography on silica gel using hexane/CH_2Cl_2 (1:1). Yield: red solid (20 mg, 60%). Mp: 222−223 °C, sublimation from ca. 148 °C (lit.[17] mp: 222−223 °C, sublimation from ca. 185 °C).

Compounds 8: General Procedure. To a solution of the corresponding aldehyde **7a,b** (0.5 mmol) in 7 mL of Ac_2O was added 0.55 mmol of **1**. The mixture was heated under argon at 75 °C with exclusion of light for 2−3 h (TLC monitoring) and then allowed to cool to room temperature. CH_2Cl_2 (50 mL) was added to the reaction mixture, and then the mixture was washed with NaOH 10% (3 × 50 mL) and water (2 × 50 mL). The organic layer was dried over $MgSO_4$, evaporated, and purified by column chromatography on silica gel.

(Z)-2-Phenyl-4-tetrathiafulvalenylbuta-1,3-diene-1,1,3-tricarbonitrile (8a). Chromatography eluent: hexane/CH_2Cl_2 (1:3). Yield: dark green solid (20 mg, 10%). Mp: 149−150 °C. IR (Nujol, cm^{-1}): 2224 (C≡N). ^1H NMR (CDCl$_3$, 300 MHz): δ 7.60−7.43 (m, 5H), 7.28 (s, 1H), 7.08 (s, 1H), 6.38 (d, J = 6.6 Hz, 1H), 6.34 (d, J = 6.6 Hz, 1H). ^{13}C NMR spectrum was not registered due to its low solubility. MS (EI$^+$) m/z (%): 407 (M$^{+\bullet}$, 100). Anal. Calcd for $C_{19}H_9N_3S_4$: C, 55.99; H, 2.23; N, 10.31. Found: C, 55.76; H, 2.38; N, 10.12.

(3Z,5E)-2-Phenyl-6-tetrathiafulvalenylhexa-1,3,5-triene-1,1,3-tricarbonitrile (8b). Chromatography eluent: hexane/CH_2Cl_2 (1:4). Yield: dark green solid (46 mg, 21%). Mp: 142−143 °C. IR (Nujol, cm^{-1}): 2217 (C≡N). ^1H NMR (CDCl$_3$, 300 MHz): δ 7.68−7.42 (m, 5H), 7.22 (d, J = 11.1 Hz, 1H), 6.89 (s, 1H), 6.88 (d, J = 14.6 Hz, 1H), 6.52 (dd, J = 14.6 Hz, J' = 11.1 Hz, 1H), 6.37 (d, J = 7.0), 6.32 (d, J = 7.0). ^{13}C NMR spectrum was not registered due to its low solubility. MS (EI$^+$) m/z (%) 433 (M$^{+\bullet}$, 82). Anal. Calcd for $C_{21}H_{11}N_3S_4$: C, 58.17; H, 2.56; N, 9.69. Found: C, 57.86; H, 2.73; N, 9.42.

Supporting Information Available: General experimental methods, NMR spectra of new compounds, X-ray crystallographic data in CIF format and diagram of the crystal structure of **9**, computed energies, Cartesian coordinates of optimized geometries, and HOMO/LUMO plots of compounds **3′** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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