

# Decreased Optical Nonlinearities upon CF<sub>3</sub> Substitution on Tricyanofuran Acceptors

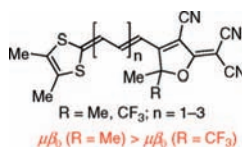
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## ABSTRACT



Replacement of the tricyanofuran (TCF) acceptor by its stronger analogue CF<sub>3</sub>-TCF results in decreased second-order optical nonlinearities in merocyanines bearing a proaromatic 1,3-dithiolenium donor. The TCF-containing derivatives display exceptionally high  $\mu\beta$  values up to 31000 × 10<sup>-48</sup> esu, unprecedented for 1,3-dithiolenium-based NLO-phores.

The growing field of organic photonic materials for use in data storage, telecommunications, and other technologies ultimately relies in the development of highly nonlinear optical chromophores (NLO-phores).<sup>1,2</sup> Most of these systems are of the donor- $\pi$ -acceptor (D- $\pi$ -A) type and show an intramolecular charge-transfer (ICT) transition, usually dominating the molecular hyperpolarizability  $\beta$ . A successful approach to optimizing  $\beta$  is based on tuning ground-state polarization and, hence, bond length alternation (BLA, the difference between average C–C and C=C bond lengths along the  $\pi$ -system) through modification of the end groups and the spacer, among other factors.<sup>3</sup> “Tricyanofuran” (TCF,

**1**),<sup>4</sup> its stronger analogue CF<sub>3</sub>-TCF (**2**),<sup>5</sup> and related derivatives are outstanding acceptors which, when linked to aromatic donors like anilines, give rise to NLO-phores with very high  $\beta$  values.<sup>6</sup>

As opposed to these compounds with predominantly covalent ground states, the linking of **1** to proaromatic donors results in zwitterionic merocyanines.<sup>7</sup>

Herein we describe new, very efficient NLO-phores end capped by a 1,3-dithiolenium proaromatic donor and either **1** or

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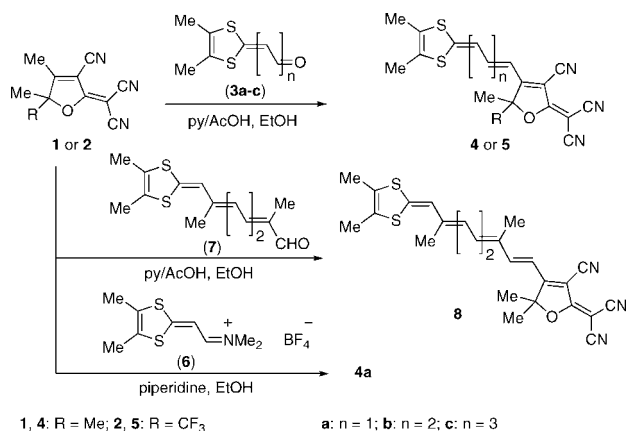
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2. They constitute the first examples of this kind of merocyanines displaying positive  $\beta$  values which, moreover, are diminished on introduction of the  $\text{CF}_3$  group.

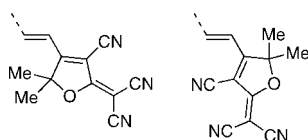
Target compounds **4** and **5** were synthesized by a Knoevenagel reaction of aldehydes **3**<sup>8</sup> with acceptors **1** and **2**, respectively (Scheme 1). Alternatively, compound **4a** was

**Scheme 1.** Synthesis of New Compounds **4**, **5**, and **8**



obtained in better yield from iminium salt **6**,<sup>9</sup> although this approach was not successful for the preparation of **4b,c** and **5**, since the reaction of the vinylogues of salt **6**<sup>8</sup> with either **1** or **2** only afforded a mixture of the expected and vinylene-shortened merocyanines<sup>8</sup> in low yield. Targets with still longer spacers are expected to show enhanced nonlinearities, but the limited stability of long acyclic polyenes has to be taken into account. Among the several strategies used to circumvent this drawback, we chose the introduction of methyl groups at the polymethine chain, despite the structural distortions they can cause,<sup>10</sup> because such substituents hinder trans  $\rightarrow$  cis isomerizations due to increased 1,3-allylic strain.<sup>11</sup> Thus, compound **8** was also prepared from **1** and the newly synthesized aldehyde **7** (see the Supporting Information).

Small single crystals of **4a** were grown by slow evaporation from  $\text{CDCl}_3$  solution. The crystal structure analysis established that **4a** is fully planar, except for the *gem*-dimethyl groups, and that it adopts a *s-cis* conformation around the bond linking the TCF acceptor to the rest of the conjugated system (Figure 1, rotamer B).



**Figure 1.** Rotamers A (left) and B (right) of the NLO-phores.

Examples of both *s-cis* and *s-trans* geometries around that bond are known in the solid state<sup>12</sup> and, except for one

case,<sup>12a</sup> their calculated energies are very similar.<sup>13</sup> The same holds for compounds **4** and **5**, for which calculations indicate very small energy differences (ca. 1 kcal/mol) between both rotamers (see the Supporting Information). Concerning the solution structure of these compounds,  $^3J_{\text{HH}}$  values along the polyenic chain show that the  $\text{HC}=\text{CH}$  and  $\text{HC}-\text{CH}$  bonds have (*E*)- and *s-trans* geometries, respectively. Unlike related derivatives bearing a pyridylidene group,<sup>7</sup>  $^1\text{H}$  NMR spectra of **4** and **5** either in  $\text{CDCl}_3$  or in  $\text{CD}_2\text{Cl}_2$  do not show the presence of separate signals for rotamers A and B (Figure 1). Nevertheless, NOE experiments on **4b** in  $\text{CD}_2\text{Cl}_2$  show that on irradiating the geminal methyl groups, the signals of the vinylic protons  $\alpha$  and  $\beta$  to the furan ring are enhanced. Taken together, these observations point to a rapid equilibrium at room temperature between both rotamers in solution. Theoretical calculations also predict that rotamers B have lower BLA values and are more zwitterionic than rotamers A. Not surprisingly, the ground-state zwitterionic character (BLA parameter) increases (decreases) for the  $\text{CF}_3$ -substituted derivatives **5**.

The electrochemical properties of the new compounds were studied by CV. All of them show two irreversible waves, corresponding to the oxidation of the dithiafulvene fragment and the reduction of the acceptor moiety, respectively (Table 1). The stronger electron-withdrawing effect of acceptor **2** is demonstrated by the more anodic  $E_{\text{ox}}$  and the less cathodic  $E_{\text{red}}$  values of compounds **5** when compared to **4**. Similar behavior has recently been reported for quadrupolar TCF-containing chromophores.<sup>14</sup> The decrease in  $E_{\text{ox}}$  and  $|E_{\text{red}}|$  values on going from compounds **a** to **c** indicates a weaker interaction between the end groups for the longer derivatives, but the decrease in oxidation potentials on lengthening the spacer is more marked than that on reduction potentials. The same trend is confirmed by theoretical calculations, which show an increase in HOMO energies on passing from **a** to **c**, whereas the LUMO energies remain approximately constant for all compounds of each family (**4** or **5**). These factors give rise to a narrowing of the HOMO–LUMO gap, corroborated by UV–vis absorption data.

Compounds **4**, **5**, and **8** show broad, low energy ICT bands with their  $\lambda_{\text{max}}$  values shifting bathochromically on increasing the length of the spacer (Table 1). Replacement of methyl

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**Table 1.** Electrochemical and UV–vis Data and Experimental and Calculated Nonlinearities of Compounds **4**, **5**, and **8**

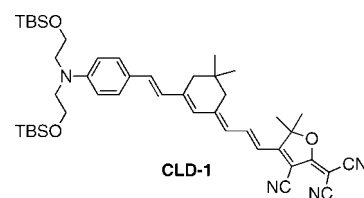
compd	$E_{ox}^a$ , V	$E_{red}^a$ , V	$\lambda_{max}$ , nm (log $\epsilon$ ) (CH <sub>2</sub> Cl <sub>2</sub> )	$\lambda_{max}$ , nm (DMSO)	$\mu\beta^{b,c}$	$\mu\beta_0^b$	$\mu\beta_0$ (rotamer A) <sup>d</sup>	$\mu\beta_0$ (rotamer B) <sup>d</sup>
<b>4a</b>	+0.94	−0.78	600 (sh), 653 (4.90)	605 (sh), 664	1300	609	623	495
<b>4b</b>	+0.75	−0.72	678 (4.79), 732 (4.77)	683 (sh), 751	5560	1938	2368	1767
<b>4c</b>	+0.61	−0.64	721 (4.74), 835 (sh)	710, 869 (sh)	16820	6173	5161	3929
<b>8</b>	+0.43	−0.65	742 (4.72), 968 (sh)	<i>e</i>	31000	10376	11525	7076
<b>5a</b>	+1.08	−0.66	630 (sh), 688 (5.14)	631 (sh), 688	910	379	903	688
<b>5b</b>	+0.81	−0.53	711 (sh), 791 (5.16)	707 (sh), 786	5270	1360	2959	2332
<b>5c</b>	+0.68	−0.46	789 (sh), 894 (4.71)	785 (sh), 893	25800	2434	6646	5182

<sup>a</sup> Potentials vs Ag/AgCl in 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>b</sup> In 10<sup>−48</sup> esu, in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> At 1907 nm. Experimental uncertainty <±15%, except for **5c** and **8** (±20%). <sup>d</sup> In 10<sup>−48</sup> esu. CPHF/6-31G\*/B3P86/6-31G\* level. The Me groups on the dithiole ring have been replaced by H atoms. <sup>e</sup> Decomposition.

by CF<sub>3</sub> gives rise to a marked bathochromic shift, well reproduced by TDDFT calculations, which has been tentatively ascribed to the inductive and/or hyperconjugative effects of the CF<sub>3</sub> group.<sup>5</sup> In fact, calculations on **4** and **5** show a shortening of the O–C<sub>5</sub> bond of the furan ring on introduction of the CF<sub>3</sub> substituent (e.g., from 1.455 Å to 1.438 Å on passing from **4a** to **5a**). This observation lends support to the above hypothesis, since similar shortening of the N–C(CX<sub>3</sub>)/O–C(CX<sub>3</sub>) bonds in ethylamine/ethanol derivatives on passing from X = H to X = F have been observed and shown to partly arise from the negative hyperconjugation and through-bond electrostatic effects of the CF<sub>3</sub> group.<sup>15</sup> Compounds **4** show a positive solvatochromism, whereas **5** show only a negligible or slightly negative solvatochromism. This behavior, together with the red-shifted absorptions of compounds **5** when compared to **4**, suggests that the former are more strongly polarized and closer to the cyanine limit than the latter. This is confirmed by inspection of the calculated charges, BLA and  $\Delta\mu_{01}$  (the difference between the excited- and ground-state dipole moments) values for **4a** and **5a** in CH<sub>2</sub>Cl<sub>2</sub> and in DMSO (Table 2). An increase in the zwitterionic character is

understand the second-order optical nonlinearities of the herein described compounds.

Their NLO responses were measured by electric field-induced second harmonic generation (EFISH) in CH<sub>2</sub>Cl<sub>2</sub> at 1907 nm to minimize resonance enhancements (although this wavelength is fairly close to harmonic resonance for **5c**) and the  $\mu\beta_0$  values were calculated from the corresponding  $\mu\beta$  values using the two-level model (see the Supporting Information). It can be seen (Table 1) that, for a given acceptor,  $\mu\beta$  values rapidly increase on lengthening the spacer. Thus,  $\mu\beta_0$  for the longest TCF-containing compound (**8**) is the highest ever reported for a 1,3-dithiole based NLO-phore<sup>8,16</sup> and compares favorably to that measured for benchmark chromophore CLD-1 ( $\mu\beta = 14065 \times 10^{-48}$  esu at 1907 nm).<sup>4</sup>



Rotamers A are predicted (Table 1) to contribute higher  $\mu\beta_0$  values than rotamers B,<sup>13b</sup> a fact which is partly due to the higher ground-state and transition dipole moments of the former (see the Supporting Information). Moreover, the strong electric field used in EFISH experiments is expected to increase the population of the more polar rotamers A.

To the best of our knowledge, replacement of TCF by the stronger CF<sub>3</sub>-TCF acceptor has always resulted in enhanced nonlinearities<sup>5,17</sup> but fluorinated compounds **5** show lower  $\mu\beta_0$  values than **4** for a given conjugation length, despite their red-shifted ICT absorptions. Although gas phase calculations do not reproduce this trend, PCM calculations

**Table 2.** Calculated<sup>a</sup> Solvent Effects on **4a** and **5a** (Rotamers A)

compd	solvent	BLA <sup>b</sup>	D		A	
			charge <sup>c</sup>	charge <sup>d</sup>	<i>E</i> (eV) <sup>e,f</sup>	$\Delta\mu_{01}$ (D) <sup>e</sup>
<b>4a</b>	CH <sub>2</sub> Cl <sub>2</sub>	0.018	+0.29	−0.37	2.39	2.06
<b>4a</b>	DMSO	0.011	+0.33	−0.41	2.36	1.43
<b>5a</b>	CH <sub>2</sub> Cl <sub>2</sub>	0.008	+0.33	−0.42	2.33	1.16
<b>5a</b>	DMSO	0.000	+0.38	−0.47	2.31	−1.06

<sup>a</sup> PCM-B3P86/6-31G\*. The Me groups on the dithiole ring have been replaced by H atoms. <sup>b</sup> In angstroms. <sup>c</sup> Charge in the dithiole ring (e). <sup>d</sup> Charge in the TCF ring (e). <sup>e</sup> PCM-TD-B3P86/6-31G\*. <sup>f</sup> Excitation energy.

observed on increasing solvent polarity, and BLA of **5a** in DMSO is predicted to vanish. Moreover,  $\Delta\mu_{01}$  values decrease for both compounds in DMSO and become negative for **5a** in that solvent. These results are important to

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(Table 2) and solvatochromism point to the fact that compounds **5** are close to the cyanine limit in strongly polar solvents and, therefore, lie in region C of Marder's plot.<sup>18</sup> This hypothesis, providing a rationale for the lower  $\mu\beta_0$  values of **5**, when compared to **4**, was confirmed by EFISH measurements of **5b** in DMF, a much more polar solvent. The negative  $\mu\beta$  value thus obtained (ca.  $-800 \times 10^{-48}$  esu at 1907 nm,  $\lambda_{\max} = 784$  nm) clearly shows that replacement of  $\text{CH}_2\text{Cl}_2$  by DMF makes **5b** pass across the cyanine limit, with a concomitant sign change of  $\Delta\mu_{01}$ , in good agreement with PCM calculations. (The quite limited stability of **5b** in DMSO prevented a similar study in that solvent). The NLO response of its nonfluorinated analogue (**4b**) also shows a strong decrease in DMF ( $\mu\beta_{1907} = 1500 \times 10^{-48}$  esu,  $\lambda_{\max} = 672, 740$  nm) and in DMSO ( $\mu\beta_{1907} = 2900 \times 10^{-48}$  esu) but remains positive, thus suggesting that compounds **4** are "left-hand side" chromophores, falling in the so-called region B.<sup>18</sup> This situation contrasts to that found with the only reported proaromatic donor- $\pi$ -TCF compounds, which are zwitterionic, "right-hand side" merocyanines.<sup>7</sup>

Thermogravimetric analysis shows high decomposition temperatures ( $T_d$ ) for the shortest (**a**) derivatives, which decrease on lengthening the  $\pi$ -spacer (compound,  $T_d$  (°C): **4a**, 270; **4b**, 266; **4c**, 181; **5a**, 257; **5b**, 233; **5c**, 162), this decrease being especially noticeable on passing from compounds **b** to **c**. Moreover, fluorinated compounds **5** show

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lower thermal stabilities than their nonfluorinated analogues, in agreement with previous reports on related derivatives.<sup>17a,19</sup>

To sum up, TCF-based merocyanines bearing a proaromatic donor and displaying very high, positive  $\mu\beta$  values have been prepared for the first time. Moreover, replacement of TCF by the stronger acceptor  $\text{CF}_3$ -TCF results in decreased NLO responses. Experiments and calculations suggest that this unprecedented behavior is due to the more polar, less alternated ground-state of the fluorinated NLO-phores.

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**Supporting Information Available:** General experimental methods, syntheses, and NMR spectra of new compounds, computed energies, Cartesian coordinates of optimized geometries, HOMO/LUMO plots of **4** and **5**, and gas phase-calculated structural and optical data of **4**, **5**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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