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Second-order nonlinear optical properties of tetrathiafulvalene-π-3-(dicyanomethylidene)indan-1-one chromophores

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Abstract

Novel conjugated donor-acceptor chromophores, based on the strong electron donating tetrathiafulvalene moiety and the strong electron-withdrawing 3-(dicyanomethylidene)indan-1-one acceptor, exhibit large second-order optical nonlinearities. The effect of increasing the length of the polyenic spacer on the NLO properties of the new molecules has been studied by using the electric field-induced second harmonic generation (EFISH) method.

Keywords: Tetrathiafulvalenes; electronic spectra; electrochemistry; non-linear optics

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] In order to optimize the nonlinear optical response of such molecules, it is important to know the influence of different donors and acceptors, the spatial molecular structure, and the degree of conjugation.[2]

In this context, we have recently reported the syntheses of the first NLO materials containing the tetrathiafulvalene (TTF) unit as the donor moiety in D-π-A systems containing dicyanomethylene (**1a**)[3,4,5] and (thio)barbituric acid (**1b**) chromophores[6] as acceptor units (Figure 1). Stimulated by the promising results obtained for some of these TTF systems ($\mu\beta$ = 960. 10^{-48} esu for the thiobarbituric acid derivative **1b** when n = 2 and R = Et), and as part of our ongoing effort to develop chromophores for NLO applications, in this paper we report the synthesis, nonlinear optical and redox properties of a series of new D-π-A systems (**6** Scheme 1) containing TTF units. We use the 3-dicyanovinylindan-1-one (**4**) and 1,3-bis(dicyanovinyl)indane (**5**) as the acceptors due to their good electron acceptor strength and their ability to produce chromophores with impressive optical nonlinearities in materials of type **2**.[7,8]

Compounds **6a-c** were prepared by condensation of formyltetrathiafulvalenes **3a-c**[4,9] with the moderate electron acceptor 3-dicyanovinylindan-1-one (**4**)[10,11] in 45-52 % yield by simply refluxing stoichiometric

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amounts of both reagents in acetic anhydride, while the mixture was protected from light and oxygen. Compounds **6a-c** were obtained as stable crystalline solids.

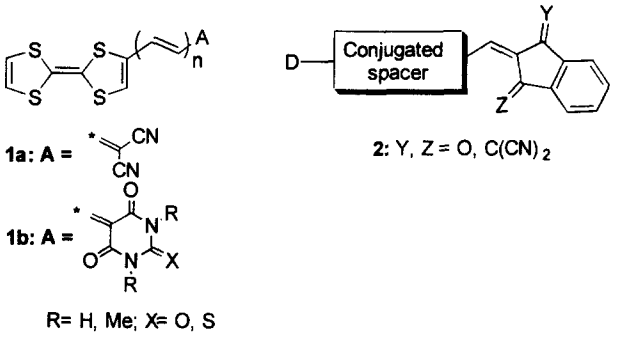
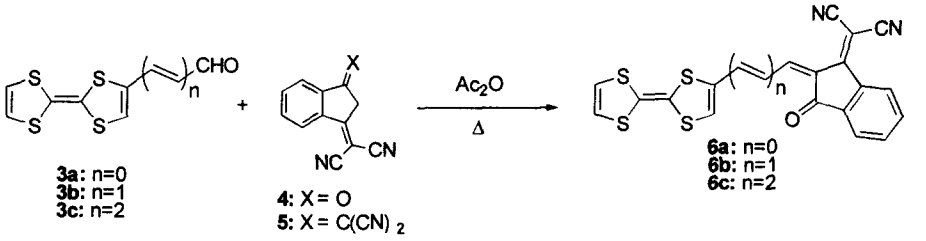


Figure 1

When an analogous reaction was carried out using 1,3-bis(dicyanovinyl)indane (**5**)[12] 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 **5**, formation of a charge transfer complex in solution between the two has to be taken into consideration. In fact, Batsanov *et al.* have reported that the parent TTF and **5** form a 1 :1 complex exhibiting semiconducting properties.[13]



Scheme 1

The electrochemical properties of the novel compounds were determined by cyclic voltammetry at room temperature and the data are collected in the Table. 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 around -0.9 V for **6a-c**. Both redox potentials in **6a-c** are not significantly influenced by the distance between the donor and acceptor moieties (Table). However, the observed redox potential values are slightly shifted in comparison with the independent molecules (**4** and TTF) which indicates some electronic interaction between both electroactive fragments.

The UV- Vis absorptions of the novel compounds were measured in the same solvent used for the EFISH measurements. The lowest energy absorption bands are shown in the Table. Interestingly, the wavelength of compounds **6a-c** decreases with increasing the length of conjugation of the spacer. This finding, which has been previously observed in related TTF derivatives, is under study in our laboratory.

$\mu\beta$ values of TTF derivatives (**6b,c**) were measured using the electric-field-induced second harmonic generation (EFISH) technique at 1907 nm in dichloromethane as solvent. As shown in the Table, an enhancement of the nonlinear response is observed with an increase in the spacer length of conjugation. In fact, compound **6c** exhibits the highest $\mu\beta$ value observed for a TTF derivative.

Table

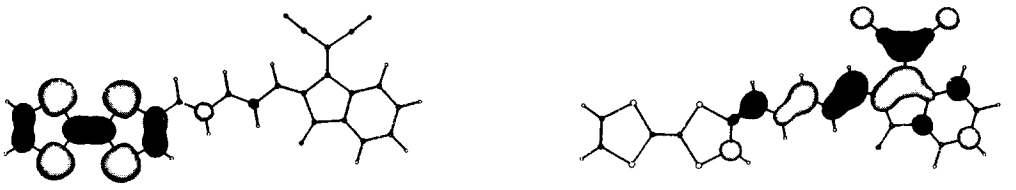
Compd.	λ_{max} /nm[a]	E^1_{ox} (a. p.)[b]	E^2_{ox} (a. p.)[b]	E^1_{red} (c. p.)[b]	$\mu\beta$[c]	$\mu\beta_0$[c]
4	–	–	–	-0.87	–	–
5	–	–	–	-0.64	–	–
6a	798	0.46	0.75	-0.92	–	–
6b	726	0.47	0.75	-0.96	700	259
6c	690	0.45	0.75	-0.97	1350	570
TTF	–	0.37	0.73	–	–	–

[a] Dichloromethane as solvent. [b] In Volts *vs* SCE, 0.1M tetrabutylammonium perchlorate in dichloromethane, glassy carbon electrode, scan rate 200 $mV.s^{-1}$. [c] All $\mu\beta$ values in (10^{-48} esu) units. Measured in CH_2Cl_2.

Molecular orbital calculations[14] on molecules **6b** and **6c** have been performed using the semiempirical PM3 hamiltonian. The HOMO and LUMO topologies depicted in **Figure 2** are similar to those calculated for other TTF-derived chromophores.[3,6] The HOMO is mainly located on the TTF moiety while the LUMO extends along the ethylenic spacer from the dicyano group to the first carbon atoms in the TTF ring. Thus, while the HOMO-LUMO transition has a charge transfer character, there is a HOMO-LUMO overlap that allows large nonlinear optical responses.[15]

The $\mu\beta_0$ values calculated using the Finite Field approach are largely underestimated (80 10^{-48} esu for **6b** and 97 10^{-48} esu for **6c**). Contrary to other reported TTF derivatives,[3,6] the FF-PM3 method exhibits in this case a poor agreement with the experimental values. A closer look at the theoretical results reveals that PM3 does predict a large value of total hyperpolarizability (β_{tot}) for these compounds but the vector component along the dipole moment direction (β_{vec}) is small. In other words, the angle formed by the dipole moment and the hyperpolarizablity vector is calculated to be 66.5° for **6b** and 67.7° for **6c** and hence the calculated $\mu\beta_0$ values

are small. This effect may be due to an erroneous calculation of the hyperpolarizability as well as to a poor molecular geometry and it is expected that the use of *ab initio* methods will result in improved β_{vec} values.



HOMO –8.04 eV LUMO -2.09 eV

Figure 2. Molecular Orbitals (PM3) of compound **6c.**

In summary, we report the synthesis of a new series of NLOphores showing the highest second-order nonlinear optical response observed for TTF derivatives. The trends observed for the λ_{max} in the UV-vis spectra and $\mu\beta$ values measured by the EFISH technique in compounds **6** are of interest in the search of better transparency-nonlinear efficiency trade-off.

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