

# Nonlinear optical materials formed by push-pull (bi)thiophene derivatives functionalized with di(tri)cyanovinyl acceptor groups

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## ABSTRACT

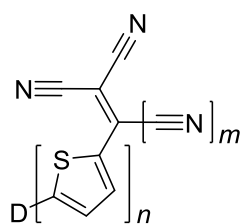
Studies of the second-order nonlinear optical susceptibilities of six NLOphores bearing di(tri)cyanovinyl acceptor groups linked to (bi)thiophene heterocyclic donor systems were performed for the first time in polymethyl methacrylate (PMMA) matrices with a 1064 nm laser working in the 20 ns time pulse regime. Absorption spectra and DFT calculations were also performed. This multidisciplinary study showed that modulation of the optical (linear and nonlinear) properties can be achieved by increasing the length of the  $\pi$ -conjugated heterocyclic system (thiophene *vs.* bithiophene), the strength of the electron donor groups (H $\rightarrow$ MeO/EtO $\rightarrow$ Et<sub>2</sub>N) as well as the strength of the electron acceptor moieties (DCV *vs.* TCV, two *vs.* three electron withdrawing cyano groups). Due to the relatively high second-order susceptibilities (0.08 to 6.45 pm/V), the studied push-pull chromophores can be denote as very potent NLOphores.

**Keywords:** (bi)thiophene; di(tri)cyanovinyl acceptor groups; push/pull systems; nonlinear optics; PMMA, structure-property relationships

## 1. Introduction

Polarized  $\pi$ -conjugated molecules end-capped with electron donors (D) and acceptors (A) groups with intramolecular charge-transfer (ICT) represent perspective organic materials for optoelectronics. Such D- $\pi$ -A molecules possess several remarkable properties such as well-defined structure with tunable properties, distinctive color, high dipolar character, and

intrinsic (hyper)polarizabilities. In this respect, thiophene proved to be one of the most polarizable  $\pi$ -conjugated heterocyclic unit used for the construction of D- $\pi$ -A molecules whilst it was also denoted as auxiliary electron-donor [1-4]. (Oligo)thiophene-derived molecules functionalized with strong electron-acceptors such as dicyanovinyl (DCV) and tricyanovinyl (TCV) moieties [5-11] proved to be very efficient nonlinear optical (NLO) chromophores (NLOphores) [12-21]. Beside their optical nonlinearities, thiophene push-pull chromophores found also widespread applications in organic electronics and photonics as it has recently been summarized in the book of Perepichka and Perepichka [22]. In principle, the NLO response of an organic material primarily depends on the number of polarizable  $\pi$ -electrons, extent of the intramolecular charge-transfer, prepolarization of the given  $\pi$ -system by suitable and strong electron donors and acceptors groups, the overall planarity of the  $\pi$ -linker and given environment [23-28]. Hence, in this work we have investigated nonlinear optical properties of organic charge-transfer chromophores **1-6** (Figure 1) that consist of (bi)thiophene central  $\pi$ -system end-capped with typical electron donating groups such as alkoxy and *N,N*-dialkylamino and strong electron acceptors such as DCV and TCV units. The tuning of the properties has been achieved by i) the extension of the  $\pi$ -system (thiophene *vs.* bithiophene central  $\pi$ -linkers,  $n = 1, 2$ ), ii) the number and strength of the appended electron donors D (H $\rightarrow$ MeO/OEt $\rightarrow$ Et<sub>2</sub>N) and iii) the structure and composition of the acceptor unit (DCV *vs.* TCV, two *vs.* three electron withdrawing cyano groups,  $m = 0, 1$ ). Such systematic structural changes would allow investigation of the structure-NLO property relationship.



**1-6**

D = H, OMe/OEt/NEt<sub>2</sub>

$n = 1, 2$

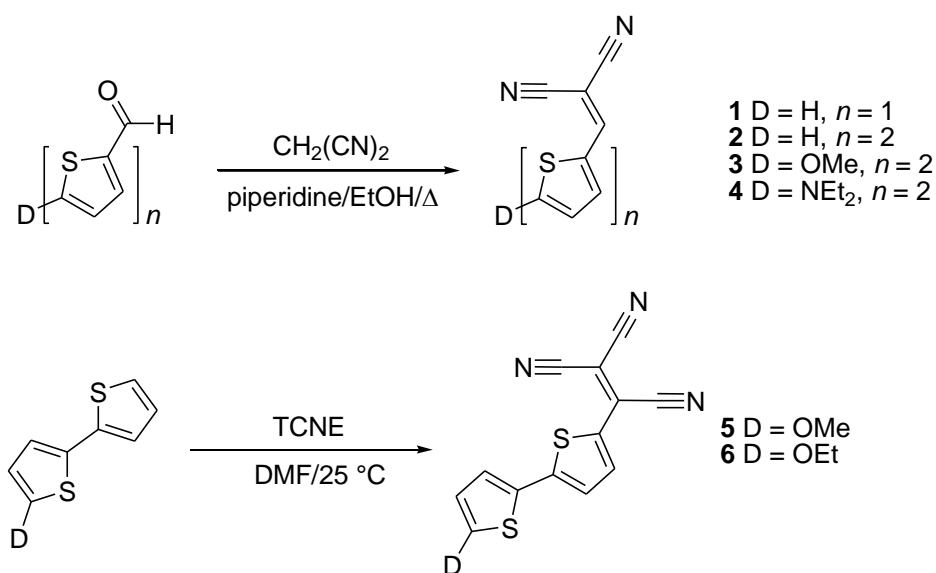
$m = 0, 1$

**Figure 1.** General structure of (bi)thiophene D- $\pi$ -A systems **1-6** with DCV and TCV acceptor units.

## 2. Results and discussion

### 2.1. Synthesis

The synthetic strategy leading to molecules **1-6** is outlined in Scheme 1. Heterocyclic NLOphores **1-6** were synthesized through Knoevenagel condensation or by tricyanovinyl reaction [29]. Therefore, compounds **1-4** with DCV acceptor units were prepared by Knoevenagel condensation between the appropriate bi(thiophene) aldehydes and malononitrile in the presence of piperidine. On the other hand, tricyanovinyl reaction of 5-alkoxy- or 5-*N,N*-dialkylamino-2,2'-bithiophene precursors [30] with tetracyanoethylene (TCNE) afforded compounds **5** and **6** in 53 and 70% yield, respectively. All target compounds **1-6** are highly colored and thermally stable solids. Target NLOphores **1** [31-32], **2** [11], **3-4** [29], **5-6** [29] and their full synthesis and spectral properties can be found in the given references.



**Scheme 1.** Reaction path leading to target NLO-phores **1-6**.

## 2.2. DFT simulations

All the calculations were performed in Gaussian 09 package at DFT level. Molecular geometries were optimized with B3LYP functional and 6-31G\* basis set. UV-VIS spectra were derived from TDDFT calculations carried out with the same functional and basis set. The hyperpolarizabilities were obtained from a polar=DCSHG run with CAM-B3LYP functional and 6-31++G\* basis set. The calculated data are presented in Table 1. As can be seen, the (TD)-DFT-derived energy gap steadily decrease when going from chromophore **1** (3.84 eV) to **6** (2.43 eV) as a consequence of the  $\pi$ -system elongation and increasing the number of electron donors and acceptors attached. A similar trend can be seen for the

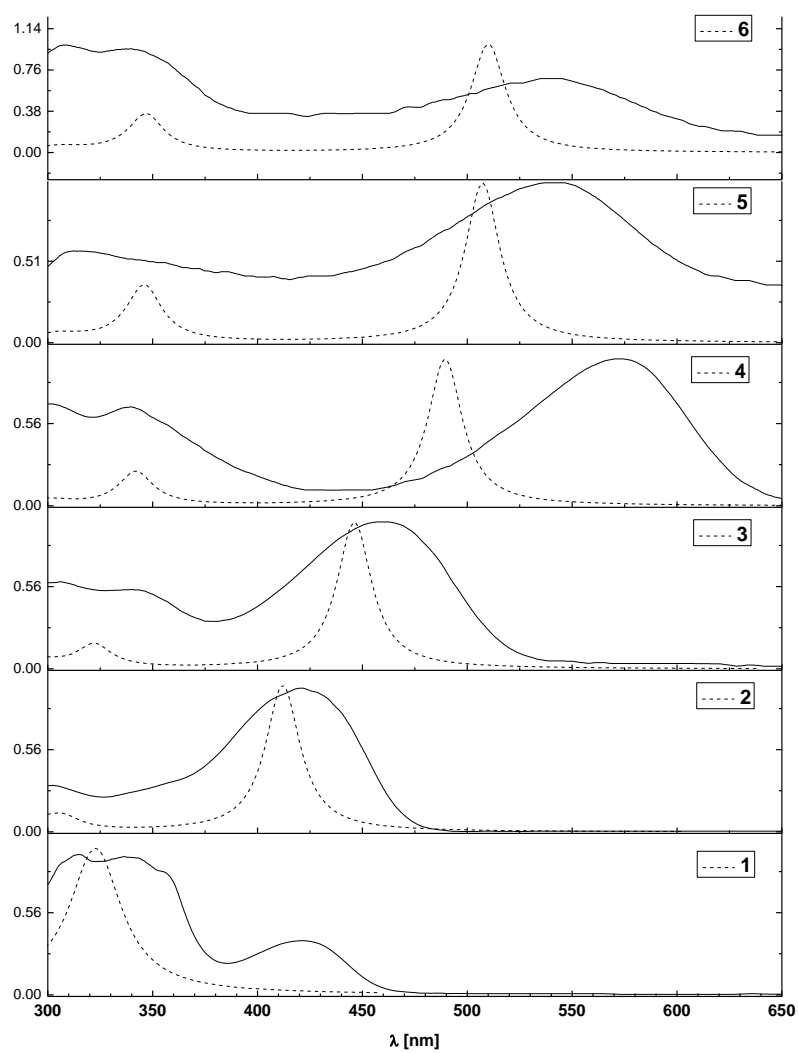
positions of the longest-wavelength absorption maxima  $\lambda_{\max}$  of the calculated as well as experimentally obtained UV-Vis absorption spectra (Table 1, Figure 2). Experimental absorption spectra were measured in THF at weight concentration ca. 0.004 %. In general, the theoretical spectra correspond well with the experimental data apart from compound **1**. In all TDDFT-derived UV-VIS spectra the main absorption peak corresponds to the HOMO→LUMO transition. Extension of the  $\pi$ -system and increasing the number and strength of the appended electron donors and acceptors led to a strong bathochromic shift with  $\Delta\lambda_{\max} = 119/187$  nm (**1**→**6**). As can be seen, the TDDFT calculation slightly underestimates the positions of the CT bands, however is capable to describe the trends within the whole series of compounds **1-6**.

**Table 1** Theoretically/experimentally obtained electronic parameters for **1-6**.

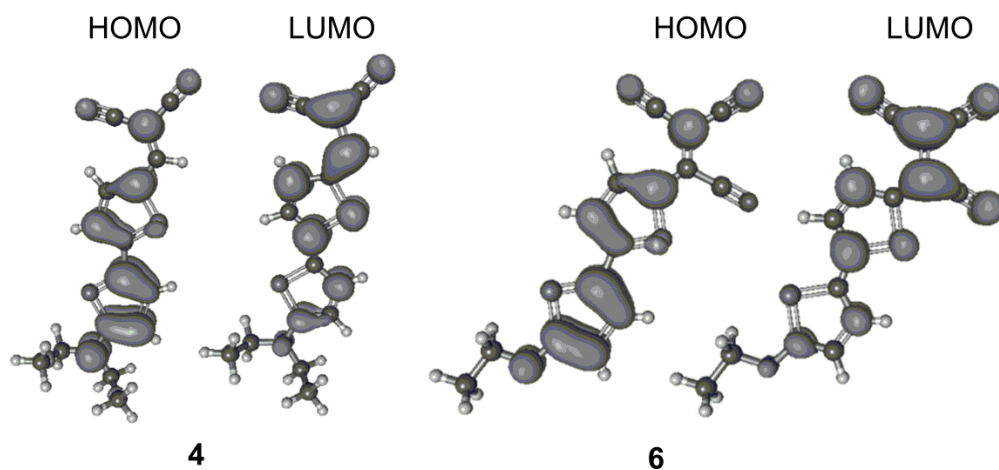
Comp.	Energy gap [eV] <sup>a</sup>	$\lambda_{\max}$ [nm] <sup>b</sup>	$\mu$ [D] <sup>c</sup>	$\mu^{ES}$ [D] <sup>d</sup>	$\beta(-2\omega, \omega, \omega)$ $\omega = 1064.0\text{nm}$ [ $\times 10^{30}$ esu] <sup>e</sup>	Effective second-order susceptibility [pm/V] <sup>f</sup>
<b>1</b>	3.84	421/323	6.7	7.5	8.2	0.08
<b>2</b>	3.01	421/412	8.7	12.6	82.3	1.35
<b>3</b>	2.78	459/446	10.6	15.6	205	3.09
<b>4</b>	2.78	572/489	14.5	19.9	570	5.98
<b>5</b>	2.78	540/507	12.2	17.2	540	5.93
<b>6</b>	2.78	540/510	12.8	17.8	606	6.45

<sup>a</sup>TDDFT-derived energy gaps; <sup>b</sup>Experimental (THF)/calculated positions of the longest-wavelength absorption maxima; <sup>c</sup>Calculated (B3LYP) ground state dipole moments; <sup>d</sup>Calculated (B3LYP) excited state dipole moments; <sup>e</sup>Calculated (CAM-B3LYP) first-order hyperpolarizability; <sup>f</sup>Experimentally measured nonlinearities.

Representative HOMO and LUMO localizations for compounds **4** and **6** bearing DCV and TCV acceptor unit are shown in Figure 3 (B3LYP/6-31G\*). Whereas the HOMO is spread over the donor-substituted bithiophene moiety, the LUMO is dominantly localized on the DCV and TCV units. When going from **1** to **6**, the HOMO and LUMO became clearly separated which indicates enhanced ICT and considerable molecule polarization accompanying extension of the  $\pi$ -system.



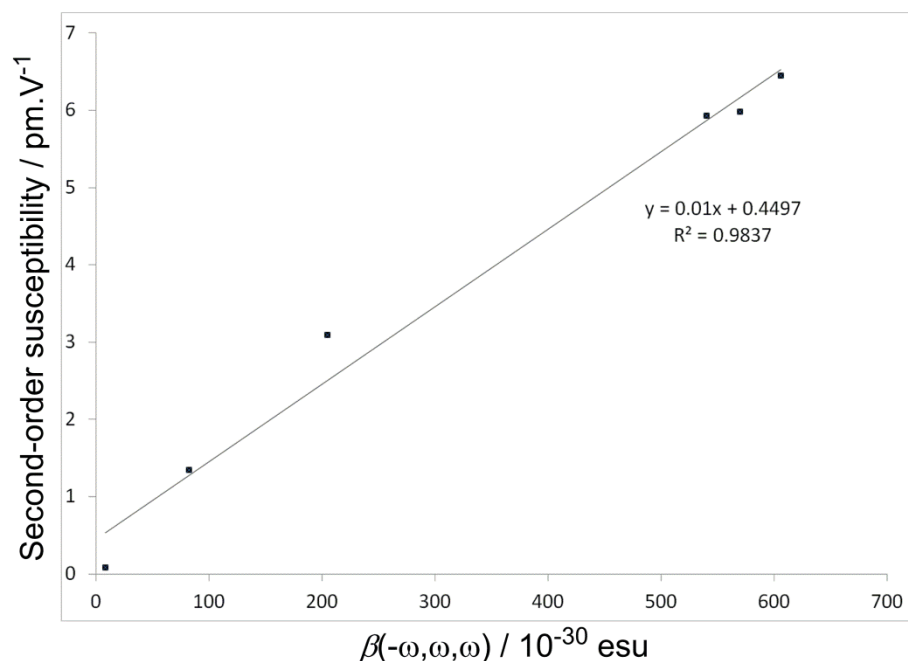
**Figure 2.** Theoretical (dashed lines, TDDFT) and experimental (solid lines, THF) UV-Vis absorption spectra of chromophores **1-6**.



**Figure 3.** Representative HOMO and LUMO localizations in chromophores **4** and **6**.

### 2.3. Nonlinear optical measurements

Nonlinear optical properties of compounds **1-6** in PMMA matrices were studied by a method similar to that described in ref. 33. Microcrystallites of  $\text{BiB}_3\text{O}_6$  have been used as a reference samples. Following the reflection light we have separated the doubled frequency signal versus the fundamental. Second-order susceptibilities were determined with precision about 0.2 pm/V. Light scattering and light absorption were simultaneously taken into account during measurements. Alignment of NLOphores **1-6** embedded into polymer matrices was carried out by external dc-electric field similarly to that described in ref. 34. A comparison of the SHG efficiency in the randomly oriented powder and aligned PMMA polymer has been followed [35]. The ground state dipole moments and spectral properties (position of the  $\lambda_{\text{max}}$ ) play the principal role for such kind of composites (see Fig. 2 and Table 1). It is crucial that differences between the values obtained from the powder and the optically aligned chromophore did not exceed 12 %. So the principal role here belongs to the intra-molecular charge transfer and related ground state dipole moments. The experimentally obtained second-order susceptibilities were further completed with calculated (CAM-B3LYP) hyperpolarizabilities  $\beta(-2\omega, \omega, \omega)$ . As can be seen from Figure 4, both experimental and calculated quantities showed very tight correlation ( $R^2 = 0.98$ ) and, therefore, we can consider the calculated  $\beta$  values capable to describe the trends within the series of particular NLOphores **1-6**.



**Figure 4.** Correlation between experimental and calculated second-order nonlinearities.

The experimental second-order susceptibilities range from 0.08 to 6.45 pm/V and rise with the extension of the  $\pi$ -system (e.g. thiophene vs. bithiophene  $\pi$ -linkers in **1** and **2**, 0.08 vs. 1.35 pm/V), increasing the electron-donating ability of substituent D (e.g. methoxy vs. *N,N*-diethylamino groups in **3** and **4**, 3.09 vs. 5.98 pm/V) and the number of electron-withdrawing cyano groups (e.g. DCV vs. TCV units in **3** and **5**, 3.09 vs. 5.93 pm/V). NLOphore **6** showed the maximal output second-order susceptibility of 6.45 pm/V. However, this compound also showed relatively high absorption at 532 nm (see Fig. 2). This fact may confirm a necessity to take into account the light absorption and therefore these samples were additionally controlled for the reflected light geometry. Considering the fact that chromophores **1-6** possess relatively small  $\pi$ -systems (the number of polarizable  $\pi$ -electrons) their high experimental (0.08-6.45 pm/V) as well as calculated ( $8.2\text{-}606 \times 10^{-30}$  esu) second-order nonlinearities indicates that they are very potent NLOphores among other known organic push-pull molecules [25-27, 36-39].

### 3. Conclusion

The second-order susceptibilities of six organic charge-transfer chromophores bearing di(tri)cyanovinyl acceptor groups linked to (bi)thiophene donor were evaluated in PMMA matrices using 1064 nm laser working in the 20 ns time pulse regime. In addition, absorption spectra and DFT calculations were performed. From the measured and calculated data we can conclude that increasing of the central heterocyclic  $\pi$ -system, increasing the number and donating/accepting ability of appended donors/acceptors in chromophores **1-6** resulted in lowered energy gap, extended HOMO/LUMO separation, bathochromic shift of the longest-wavelength absorption band and increased ground state dipole moment. Considering small molecules such as **1-6**, the observed changes in aforementioned quantities are remarkable. Hence, intramolecular charge-transfer can easily be affected by alternation of the chromophore arrangement and the donor/acceptor used. The measured second-order susceptibilities range from 0.08 to 6.45 pm/V and mimic the trends seen for the energy gaps and absorption spectra. In comparison with known organic push-pull chromophores, investigated molecules **1-6** can be denoted as very potent NLOphores with tunable properties.

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