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Synthesis and features of nonlinear optical switches based on dithienylethene unit

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ABSTRACT

Two nonlinear optical (NLO) chromophores **C1** and **C2** based on dithienylethene were designed and synthesized as the ultraviolet NLO switches. The open/close behavior of **C1** and **C2** were investigated through the UV–vis spectra. Through quantum chemical calculations of the dipole moments, first and second hyperpolarizabilities, *etc.* we analyzed both opening and closure states of **C1** and **C2**. The NLO switch ability of the chromophores were studied through monitoring of the SHG at the opening/closure states, which were performed under illumination of fourth harmonic generation of the nanosecond Nd:YAG laser ($\lambda = 266$ nm). The obtained results indicated that the maximal SHG changes were observed at energy density equal to about 90 J/m^2, and the samples **C1**, **2′** closure states possess significantly higher value of the second order susceptibility compared to the opening states. After switching off of the external UV light, the induced second order susceptibilities remain up to 150 h without a decrease, which indicated that the obtained chromophores have the potential application as the NLO switches applied in photonics.

Introduction

Nonlinear optical (NLO) materials are recently intensively explored due to their important application in the field of photonics and electro-optics [1–3]. Among them, the materials with commutable NLO properties can offer some more potential novel application, for example, molecular-scale memory devices with multiple storage and non-destructive reading capacity [4]. Just because of this, these materials with switchable NLO behavior attract more attentions in recent years. Based on much experimental and theoretical works, many NLO switches exhibit larger changes in the first hyperpolarizability, β [5–10] described by third rank polar tensors.

Usually, the molecular chromophore with "D-π-A" structure, π-conjugated donor-acceptor system, have promising first order NLO property, and the NLO properties could be effectively tuned through changing the strength of donor or acceptor [3]. To realize the on/off switching, modulating the electronic and optical properties using an external trigger has been proved to be an effectively strategy. The donating capability of the donor can be reduced by oxidation and protonation. On the other hand, the electron-withdrawing ability of the acceptor can also be tuned by reduction. The reversible redox switching and acido-switching have been demonstrated to be useful for the NLO switching [4,11]. Photochromic effect is an important strategy for the smart materials' design and preparation. And such a process usually is accompanied by the change of inter-charge transferring (ICT) ability, which could directly influence the NLO properties [12].

Dithienylethene (DTE) is an extensively used photochromic unit. The conjugated ring could be changed between the opening state and closure state under the irradiation by ultraviolet (UV) and visible light [9,13]. Push-pull DTE system has first order NLO properties, and also the variation of conjugated length will cause the changes of NLO property due to enhanced charge transfer, which will provide potential NLO switches. Here, using the DTE unit as the conjugated electron bridge, two NLO chromophores (Scheme 1) were designed, synthesized and characterized, and

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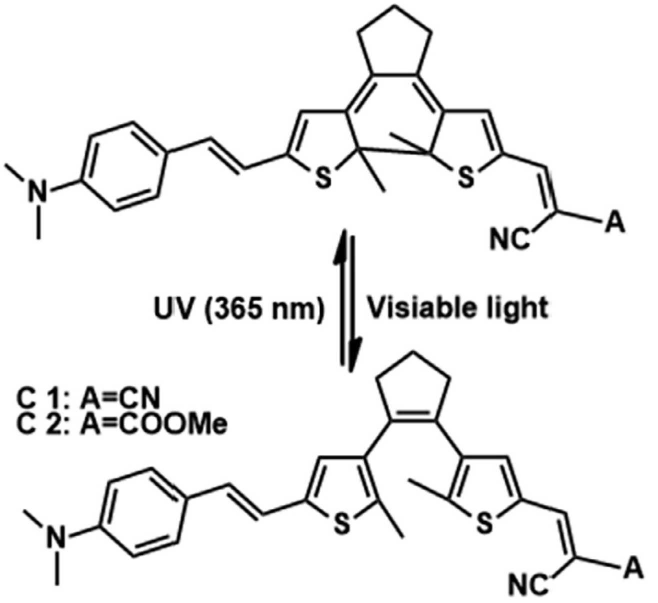


Scheme 1. Structures of **C1**, **2** chromophore**.**

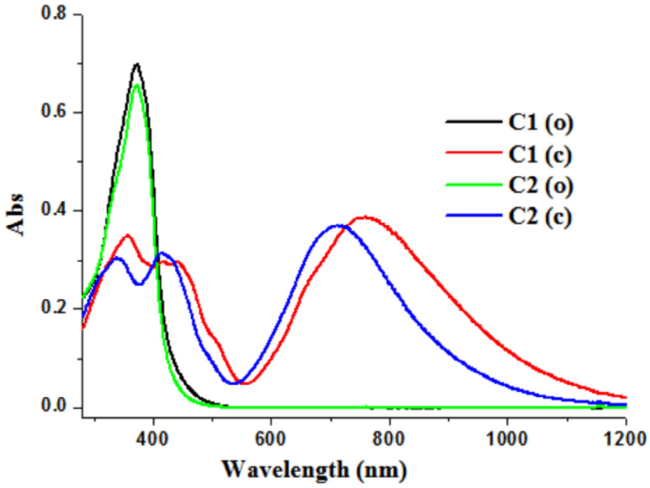


Fig. 1. . UV–vis spectra of **C1** and **C2** in their open (o) form and closed (c) form.

the NLO properties in their open and closed forms were also discussed.

Results and discussion

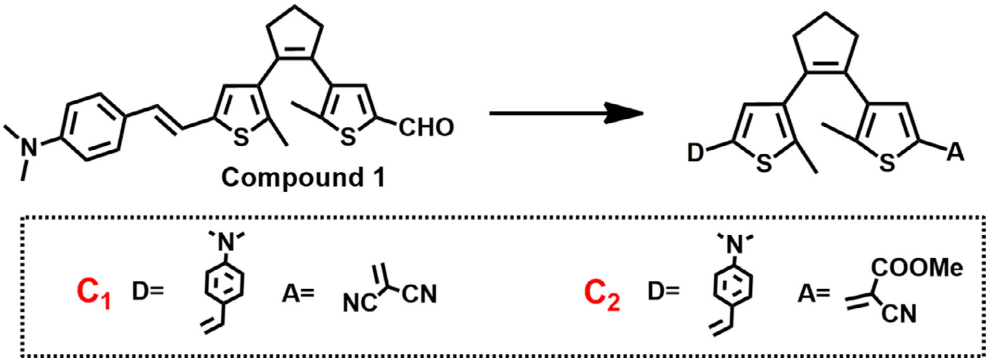
Following the Scheme 2, the target NLO chromophores **C1** and **C2** were prepared by the condensation between compound **1** and malononitrile and ethyl cyanoacetate, respectively. It is important to note that transesterification reaction between ethyl cyanoacetate and methanol solvent was occurred during the preparation of the **C2**. The target NLO chromophores were isolated as yellow powder in good yields. Further characterization by MS, ^{1}H NMR and ^{13}C NMR proved the successful preparation of the designed molecular, and the relative data were presented in Supplementary material.

Supplementary data (general experimental details, characterization data) associated with this article can be found, in the online version, at https://doi.org/10.1016/j.tetlet.2018.08.018.

UV–vis spectra of **C1**, **C2** were measured in CH_2Cl_2 solution to investigate the photophysical properties (Fig. 1), and the results are summarized in Table 1. **C1** and **C2** have some absorption near 371 nm in their opening form, however, generally it is not so huge to prevent the UV treatment. The photocyclization reaction of **C1** and **C2** were also monitored by UV–vis spectra. UV irradiation of the chromophores' CH_2Cl_2 solution at 365 nm, the closed isomers could obtained, and the relative data were also presented in Table 1. Owing to the changes of the conjugated system, the closure form of **C1** and **C2** all showed new absorption band near 730 nm, and the original peaks near 370 nm were decreased in intensity. Owing to the stronger electron-withdrawing ability of —CN compared ester group, the closure state of **C1** exhibited the longer wavelength absorption peak. Under irradiation at 650 nm, the closure states of **C1** and **C2** could return to the opening states, and such a cycle can be repeated more than 5 times without any obvious spectra changes.

Quantum chemical calculations of dipole moments, first order (β) hyperpolarizabilites (at a wavelength of 1064 nm) and second order (γ) hyperpolarizabilities as well as evaluations of HOMO, LUMO, UV–vis spectra were carried out using Gaussian W09 quantum chemical package. Molecular dynamics geometry optimization, calculation of first and second order hyperpolarizabilities, HOMO and LUMO shape were performed using DFT and B3LYP functional supplemented within a framework the standard 6-31G (d) basis set. UV–vis spectra were calculated using TD-DFT and B3LYP with 6-31G(d) basis set.

The calculated UV–vis spectra are presented in Fig. 2, and the related data are summarized in Table 1. The calculated results are in a good agreement with experiment both from the spectra and main peak position. Shapes of HOMO and LUMO plots for studied molecules are presented in Fig. 3. In the open form, both **C1** and **C2**'s HOMO orbitals are located at the donor part of the molecule, which include amino part and neighboring, interconnected



Scheme 2. The principles synthesis of **C1**, **2**.

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