



Nonlinear optical properties of the novel kind of organic donor-acceptor thiophene derivatives with click chemistry modification



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ABSTRACT

Two new classes of organic third-order optical chromophores, D- π -A-D and D- π -A-D-A- π -D, were designed and synthesized using a Sonogashira coupling reaction and the high-yielding [2 + 2] click reaction. The photophysical and click chemistry were characterized by means of UV/Vis absorption spectroscopy. The electrochemical properties were characterized by means of cyclic voltammetry. Moreover, the third-order nonlinear properties, including the nonlinear refraction and the nonlinear absorption, were investigated by using Z-scan techniques. The chromophores with a D- π -A-D-A- π -D motif, **Bt₁-X** and **Bt₂-X**, exhibited the larger third-order susceptibility $\chi^{(3)}$ value than the analogues (D- π -A-D), **St₁-X** and **St₂-X**, whereas the bithiophene chromophores, **St₂** and **Bt₂**, exhibited a larger $\chi^{(3)}$ value than their single thiophene counterparts, **St₁** and **Bt₁**. Upon the introduction of electron acceptors, third-order nonlinear absorption of the products **St_n-X** showed a typical SA-RSA transition. Interestingly, the chromophores with a D- π -A-D-A- π -D motif, **Bt_n-X**, exhibited more diversified NLO phenomenon. All of the click compounds showed the considerable third-order susceptibility $\chi^{(3)}$ values. The results of these studies could provide new molecular-design strategies for third-order nonlinear optical materials for optoelectronic device components.

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1. Introduction

The nonlinear optical materials have received wide attention in the last years due to a wide range of applications in electronic and optoelectronic devices.^{1–4} Among these, the organic materials were gaining great interest as a promising class of materials because of their large nonlinear optical (NLO) response, chemical stability and process ability.^{5–7} Donor-acceptor conjugated organic materials bearing electron Donor (D) and acceptor (A) groups linked by π -conjugated bridges were known to exhibit outstanding NLO properties.^{8,9} The presence of donor or acceptor units is important and permits the fine-tuning of the optical properties while also influencing the charge carrier mobility.^{10,11} However, it is costly and

time consuming to introduce NLO active donor-acceptor chromophores into compounds due to the required tedious chemosynthesis and purification processes.

For the purpose of solving these problems, the diversity of modern organic synthetic methods creates some fascinating properties of organic materials, which allows incorporation of functional groups. In addition, the synthetic method enables chemists to tune the photophysical properties of thiophene to enhance NLO effect. In recent years, formal [2 + 2] cycloaddition-cycloreversion (CA-CR) between electron-rich alkynes and electron-deficient alkenes, such as tetracyanoethene (TCNE) or 7, 7, 8, 8-tetracyano-*p*-quinodi-methane (TCNQ) or 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ), has been developed as a powerful and convenient way for preparing π -conjugated, nonplanar, donor-acceptor chromophores that exhibit intense, intramolecular charge-transfer (ICT), low-energy, and high third-order optical nonlinearities.^{12–15} Moreover, the transformations are generally fast, 100% atom-economic, catalyst-free, high-yielding, and the aimed products can be easily purified by

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washing or precipitation. These noticeable features of click chemistry^{12–15} served to establish a synthetic protocol for new and diversified multi-D- π -A-D thiophene derivatives.

With this in mind, we wondered the various quantities thiophene units, different click reagents and structure symmetry could have any positive effect on the NLO properties of the targeted compounds, especially NLO absorption. In order to investigate the effects of molecular structure symmetry and electron-donor groups on nonlinear optical properties. These two types of structures D- π -A and D- π -A- π -D were picked for the research. Generally, two classes of thiophenes have been found to be optical nonlinearity chromophores, a dipolar form with a donor- π -acceptor (D- π -A) functionality, and a quadrupolar mode with a D- π -A- π -D motif are highlighted by its excellent NLO response.^{16,17} Subsequently, we designed and synthesized two kinds of D- π -A-D or D- π -A-D-A- π -D type thiophene derivatives by using click chemistry. These two novel thiophene derivatives did exhibit a broader absorption and narrower bandgap in the visible and near infrared (NIR) region. Our approach opens a new platform of multi-D- π -A-D thiophene derivatives as wideband nonlinear optical materials synthesis using in appropriate photonic applications.

2. Results and discussion

2.1. Synthesis and characterization

To fully understand the relationships between the molecular structure and NLO properties of thiophene derivatives, we synthesized two known thiophene systems with excellent NLO properties, D- π -A and D- π -A- π -D, by a sonogashira coupling reaction.^{18,19} After that, we designed and synthesized two novel thiophene derivatives with more diverse structures, D- π -A-D and D- π -A-D-A- π -D, by the high-yielding [2 + 2] click reaction²⁰ using the first electron acceptors (TCNE, TCNQ, and F₄-TCNQ) as click reagents (see Fig. 1).^{21–23} Before occurrence of click reaction, these systems share a common structural motif which employs the phenylacetylene functionality as the π -conjugated link. The dihexadecylamino functionality was used as an electron-donor, while a thiophene group acted as the weak electron-acceptor. However, the thiophene functional group turned into a weak electron-donor, as a result of the introduction of strong electron-acceptor CN and F atoms. All the new compounds were adequately characterized by FT-IR, NMR, UV/Vis and other spectroscopic ways. The thiophene derivatives with different conjugation lengths and electron withdrawing groups were predicted to represent different photoelectric properties and then maybe enhance the NLO properties.

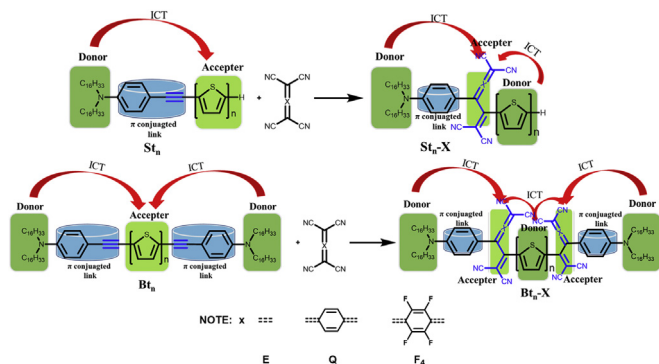


Fig. 1. General molecular framework showing “NLO” effect due to ICT from donor to acceptor.

2.2. UV/vis spectroscopy

The UV/Vis absorption spectra of the **St**₁, **St**₂, **Bt**₁ and **Bt**₂ were shown in Fig. 2a. The thiophenes with donor and acceptor functionalities displayed intriguing photophysical properties in solutions. Upon the covalent linking of one donor, dihexadecylamino, via the conjugated phenylacetylene linkage, functionalities displayed intriguing photophysical properties in solutions. Upon the covalent linking of one donor, dihexadecylamino, via the conjugated phenylacetylene linkage, to the thiophene backbone, a D- π -A system was achieved. The absorption maximum, λ_{\max} , of **St**₁ was 345 nm, whereas that of **St**₂ was 384 nm. Introduction of additional thiophene in compound **St**_n allowed the effect of increased conjugation and molecular dimensionality. Further incorporation of the two donors to the thiophene backbone resulted in **Bt**₁ and **Bt**₂ becoming a more pronounced ICT system D- π -A- π -D,²⁴ which led to a further red-shift of their absorption bands. In the case of **Bt**₁, the λ_{\max} was 397 nm, whereas that of **Bt**₂ shifted to 420 nm. The absorption bands of **St**₁, **St**₂, **Bt**₁ and **Bt**₂ were tentatively assigned as ICT transitions.²¹

Fig. 2b showed the UV/Vis absorption spectra measured for **St**₁ and **St**₁-X in CH₂Cl₂ solution. Fig. 2c showed the UV/Vis absorption spectra measured for **Bt**₁ and **Bt**₁-X in CH₂Cl₂ solution. The absorption maximum, λ_{\max} , of **St**₁ was 345 nm, whereas that of **Bt**₁ shifted to 397 nm. Interestingly, for click product **St**₁-X, the absorption peaks λ_{\max} were red-shifted by around 133 nm for **St**₁-E, 347 nm for **St**₁-Q and 591 nm for **St**₁-F₄ compared to **St**₁. Similarly, the absorption peaks λ_{\max} were red-shifted by around 89 nm for **Bt**₁-E, 289 nm for **Bt**₁-Q and 423 nm for **Bt**₁-F₄ compared to **Bt**₁. It is generally believed that by the elongation of conjugation lengths of the molecular backbones and enhancement of electron affinities via introduction of strong electron-withdrawing substituents CN and F to the **St**₁ could result in the compounds becoming two more complex and powerful ICT systems, D- π -A-D and D- π -A-D-A- π -D, which lead to a similar redshift of their absorption bands.^{25–27} All new thiophene derivatives exhibited an intense ICT band and the smaller optical gap in the UV/Vis spectra, with the λ_{\max} of click products of **St**₁ appearing between 478 and 836 nm, whereas that of **Bt**₁ appearing between 486 and 820 nm. The normalized UV/Vis absorption spectra of **St**₂ and **Bt**₂ were shown in Fig. S1. The spectral shapes and positions were very similar to the click products of **St**₁

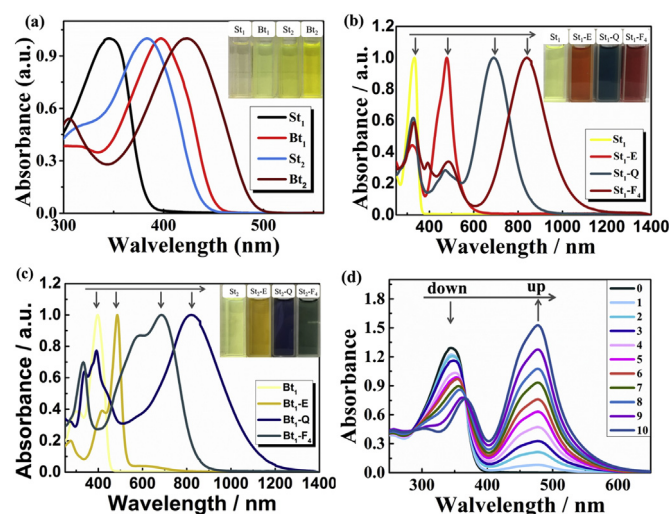


Fig. 2. Absorption spectra of (a) **St**₁, **St**₂, **Bt**₁ and **Bt**₂; (b) **St**₁, **St**₁-E, **St**₁-Q and **St**₁-F₄; (c) **Bt**₁, **Bt**₁-E, **Bt**₁-Q and **Bt**₁-F₄; (d) **St**₁ upon titration with TCNE(0–1.0 equiv.) in CH₂Cl₂ solution.

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