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Effect of modified donor units on molecular hyperpolarizability of thienyl-vinylene nonlinear optical chromophores

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ABSTRACT

Highly efficient and thermally stable nonlinear optical chromophores based on the phenyl vinylene thiophene vinylene (FTC) donor-π-acceptor structure have been synthesized and investigated. The donor part of the chromophores was modified with additional donor units, resulting in the enhanced nonlinear optical property with large molecular hyperpolarizability. Hyper-Rayleigh scattering measurement indicated nearly threefold increase of the molecular hyperpolarizability for novel chromophores compared with the benchmark FTC chromophore. Furthermore, measurement of the electro-optic coefficient confirmed that enhancement of microscopic molecular hyperpolarizability of the chromophores can be effectively translated into macroscopic electro-optic property. Measured electro-optic coefficients were nearly twofold larger than that for the benchmark FTC. Thermal analysis indicated that the synthesized chromophores showed the excellent temperature stability with decomposition temperatures up to 280 °C.

Over the past few decades, considerable progress has been made in the development of organic and polymeric electro-optic (EO) materials for applications in ultrafast optical modulators, optical sensors, and information processors.[1–3] One of the challenges encountered in preparing highly efficient EO materials is the development of nonlinear optical (NLO) chromophores with large molecular hyperpolarizability (β), high optical transparency, and excellent thermal and chemical stabilities.[4–9] Most of expected chromophores have a π-electron conjugated structure and are coupled to electron donor and electron acceptor units, which indicate large intramolecular charge-transfer transitions at high β values. A successful approach for preparing chromophores with large β values is to consider their ground-state polarization and bond-length alternation upon modification with electron donors, electron acceptors, and π-electron bridges.[10–14] In particular, high-β chromophores with excellent EO responses have been obtained when the strong electron acceptors such as 2-dicyanomethylene-3-cyano-4,5,5-dimethyl-2,5-dihydrofuran (TCF) and 2-dicyanomethylene-3-cyano-4,5-dimethyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-TCF) were used.[12] Although many studies have been performed on the investigation of electron acceptors and π-electron bridges in the synthesis of chromophores, few studies have examined the use of various types of electron donors to obtain chromophores with large molecular hyperpolarizability.[15–17]

This paper describes our experimental approach to the design and synthesis of NLO chromophores containing strong donor subunits and with large molecular hyperpolarizability. The use of new π-electron donors as the additional subunits to the donor part in the donor-π-acceptor molecules was examined (Fig. 1). The synthesized chromophores contained a phenyl vinylene thiophene vinylene bridge and a TCF acceptor part. The NLO property of the synthesized chromophores was characterized using the hyper-Rayleigh scattering (HRS) technique. The HRS method is a reliable technique for measuring the molecular hyperpolarizability. The chromophore denoted as FTC, having 4-(dibutylamino)aryl group as the donor, was chosen as a benchmark chromophore for comparison. In order to determine the electro-optic property of the chromophores, electric-poled polymer films containing synthesized chromophores were prepared and the EO coefficients (r_{33}) were measured at 1.31 μm using reflection technique. In addition to NLO measurements, relevant linear optical spectra and thermal properties are presented and discussed herein.

The synthesis of donor parts of the chromophores is depicted in Scheme 1. Modified 4-(dibutylamino)ary compounds **1b**–**1e** were synthesized from 4-(dibutylamino)salicylaldehyde **1a** by treatment with appropriate reagents and conditions. All the donor parts were obtained with high yield and were characterized by ^1H and

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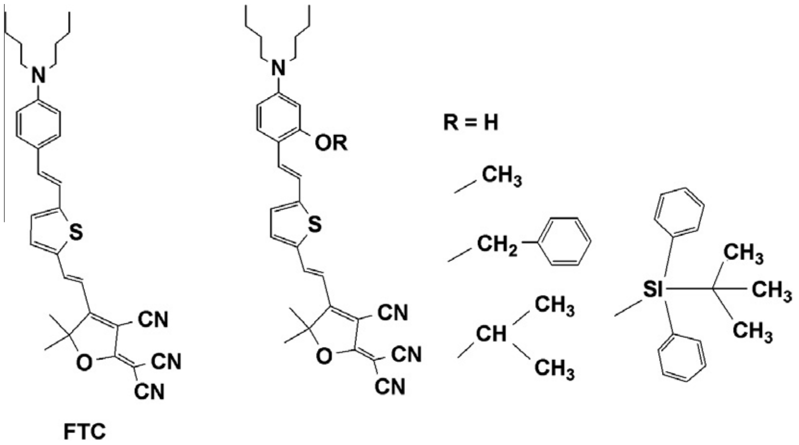
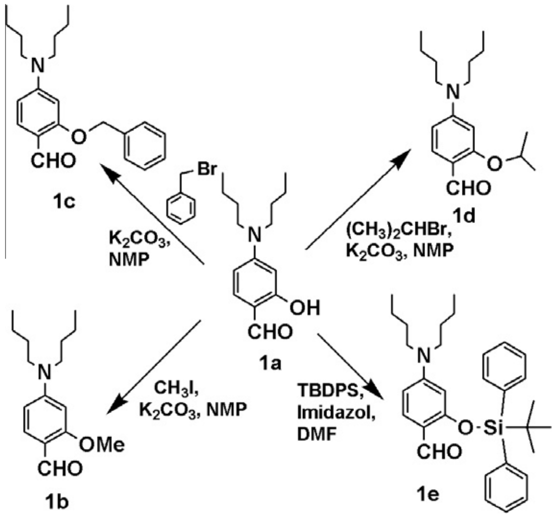


Figure 1. The molecular structure of synthesized chromophores and FTC benchmark.



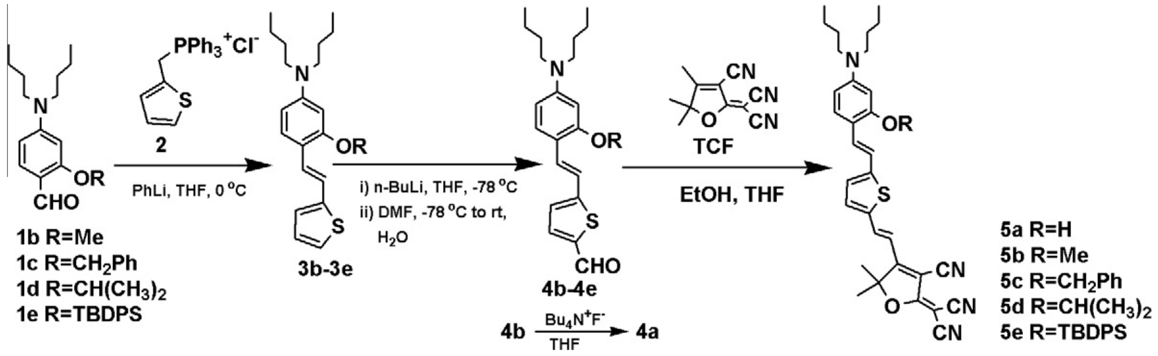
Scheme 1. Synthesis of the donors **1b**–**1e**.

^{13}C NMR spectroscopy. To clarify additional unit's π-donating interaction with the donor part, ^{13}C NMR spectra were used to systematically compare their electronic effect. From ^{13}C NMR, the chemical shifts of C1 position in the phenyl (**1a**–1**e**) are located at around 114–116 ppm. While, the chemical shift of C1 in 4-(dibutylamino)benzaldehyde is at 124.5 ppm and serves as a reference value. ^{13}C NMR analysis confirmed that any electron-donating groups (*RO*-) introduced at C2 position would increase the electron density at C1, resulting in a upfiled shift of C1 relative to 124.5 ppm.

For this study, five new NLO chromophores **5a**–**5e** consisting of modified donors, a conjugated thiophene bridge, and the TCF acceptor were synthesized following the general route shown in Scheme 2. The thiophene bridge was prepared in two steps for obtaining Wittig salt **2**. After Wittig condensation of the salt with the aldehydes **1b**–**1e**, the desired thiophene bridges were produced. The compounds **3b**–**3e** were then formylated effectively with *n*-butyl lithium and DMF to form **4b**–**4e**. The TCF acceptor was synthesized according to the literature method[12] and was coupled to the thiophene bridges by Knoevenagel condensation to afford chromophores **5b**–**5e**. Chromophore **5a** was synthesized from thiophene bridge **4a**, which was obtained after the deprotection reaction of **4e**.

Thermal properties of chromophores were measured by differential scanning calorimetry and are summarized in Table 1. Chromophore **5e** containing TBDPS unit shows a clear glass transition at 81 °C followed by the crystallization at 171 °C and a melting point at 205 °C. Chromophores **5b** and **5c** only exhibit glass transition temperatures (T_g), suggesting that these chromophores tend to form amorphous glasses. However, chromophores **5a** and **5d** did not exhibit any glass transitions. Thermo gravimetry and differential thermal analysis indicated that synthesized chromophores had high temperature resistance: their decomposition temperatures (T_d) were above 220 °C as summarized in Table 1. In particular, the highest T_d was observed for the chromophore **5e** (283 °C). The excellent thermal stability of these chromophores makes them suitable for practical device fabrication and EO applications.

The absorption spectra of the synthesized chromophores were measured in chloroform as shown in Figure 2a. The spectrum data



Scheme 2. Synthesis of chromophores **5a**–**5e**.

Table 1
Glass transition temperature, decomposition temperatures, absorption maximum, and solvatochromism data of the chromophores

Compounds	T_g (°C)	T_d[a] (°C)	λ_{max}[b] (nm)	λ_{max}[c] (nm)	$\Delta\lambda$[d] (nm)
FTC	–	220	685	624	61
5a	–	220	709	643	66
5b	76	274	717	643	74
5c	61	253	717	644	73
5d	–	262	720	643	77
5e	81	283	721	648	73

[a] T_d was the onset decomposition temperature measured by TG-DTA under nitrogen at a heating rate of 5 °C/min.

[b] λ_{max} were measured in chloroform.

[c] λ_{max} were measured in 1,4-dioxane.

[d] $\Delta\lambda$ was the difference between λ^a_{max} and λ^b_{max}.

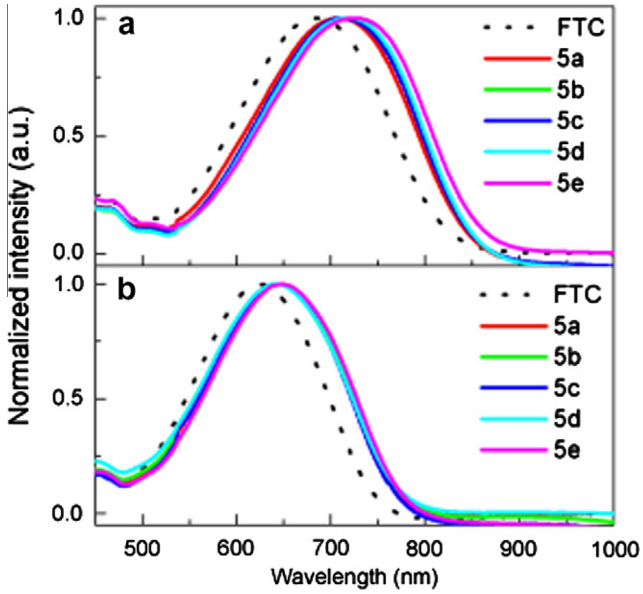


Figure 2. UV–vis absorption spectra in chloroform (a) and 1,4-dioxane (b).

is summarized in Table 1. The effect of the electric donor on the π-conjugated bridges was characterized by shifting the absorption maximum (λ_{max}) compared with λ_{max} of the benchmark FTC. When an additional hydroxyl group was added to the donor part of **5a**, λ_{max} was shifted 24 nm to the longer wavelength of 709 nm. A similar shift in the case of **5b** and **5c** indicates that the addition of methoxy and benzyloxy groups to the donor parts provides equivalent electron-donating effect on the π-conjugated bridge. Larger shifts of λ_{max} were measured for **5d** and **5e**, indicating the strong electron-donating effect of the isopropoxy and TBDPS units. The absorption spectra of the chromophores were also measured in 1,4-dioxane as shown in Figure 2b, so that solvatochromic behavior of the chromophores could be explored; their spectroscopic properties are summarized in Table 1. On the basis of simple solvent studies using polar chloroform and less polar 1,4-dioxane, it was found that chromophores **5b**–**5e** showed a larger energy shift of the charge-transfer band ($\Delta\lambda$ = 73–77 nm) than FTC ($\Delta\lambda$ = 61 nm). The resulting spectrum data confirm the concept that donor-enhanced FTC chromophores are more strongly polarizable than the benchmark.[11,12,14]

The molecular hyperpolarizabilities of chromophores were measured in chloroform using the hyper-Rayleigh scattering (HRS) technique at a laser wavelength of 1.9 μm.[18,19] The technique allows the direct evaluation of β values, employing the reference chromophore with known β value. In our HRS setup, wavelength of excitation laser could be selected between 1.3 and 1.9 μm using an optical parametric oscillator with the Q-switched Nd:YAG laser. The experimental technique provides β values relative to the β of chloroform (0.49×10^{-30} esu), where the chloroform solvent acts as the internal standard. We confirmed that the β of benchmark FTC was comparable to the literature value at the laser wavelength of 1.3 μm.[20] However, in order to compare molecular hyperpolarizability among chromophores with different absorption characteristics, it must be taken to account for resonance effects.[21–25] Thus, we performed HRS measurement on the chromophores **5a**–**5e** at the longer laser wavelength of 1.9 μm. Since the HRS signal from pure chloroform is negligible at 1.9 μm, HRS intensity from the chromophore solution was converted to the β value using the external reference method using the benchmark FTC, which has a known β value as the reference at 1.9 μm.[20] The results of HRS measurement are presented in Table 2. HRS analysis indicates that the addition of donor groups is effective in increasing the β values. The result of the β enhancement for **5a**–**5e** was consistent with the result of absorption spectral analysis. The factors of increase in the β value of **5a** and **5b** were 1.51 and 1.78, respectively, by comparison with FTC. The enhancement of β value in **5c** and **5d** was more than twofold. In particular, the substantial increase in β value of **5e**, an almost threefold enhancement, was measured with the experimentally obtained β value of 4430×10^{-30} esu.

Polymer films for EO coefficient (r_{33}) measurements were prepared by mixing the chromophore in poly(methyl methacrylate) (PMMA) at a number density of 2.1×10^{20} molecules/cm^3 by using cyclopentanone as a solvent. The solution was filtrated through a 0.2 μm syringe filter and spin cast onto an indium-tin-oxide (ITO) glass substrate to produce a film with the thickness of 2 μm. The films were then baked at 80 °C in a vacuum to remove the residual solvent. The result of absorption spectra of the chromophores in PMMA films is summarized in Table 2. The λ_{max} of **5a**–**5e** shows at around 670 nm, which are 20 nm red-shifted compared to that of FTC/PMMA film. The trend of this shift is similar to the results measured in the chloroform and dioxane solutions. After sputtering a gold electrode on to the polymer film, the electric poling was carried out by applying an electrical field of about 100 V/μm at elevated temperatures up to near the glass transition temperature of PMMA. The r_{33} values of poled films were measured by the Teng–Man reflection method[26] with a 1.31 μm laser and are summarized in Table 2. As expected, all the films containing chromophores **5a**–**5e** achieved higher r_{33} values than the r_{33} of FTC benchmark. The results confirm that the enhancement of the microscopic β values in chromophores can be translated into the performance of macroscopic EO coefficient. Especially, **5c** and **5e** showed nearly twofold increase in the r_{33} values compared with that of FTC.

In summary, five new chromophores based on strong aryl-amino electron donors with FTC structure were synthesized. Efficient

Table 2
Optical properties and electro-optic coefficients of chromophores

Compounds	β/β_{FTC}	β[a] ($\times 10^{-30}$ esu)	λ_{max}[b] (nm)	r_{33}[c] (pm/V)
FTC	1	1500 ± 170	648	29 ± 5
5a	1.51	2260 ± 250	676	38 ± 3
5b	1.78	2670 ± 310	672	45 ± 5
5c	2.11	3160 ± 390	669	57 ± 4
5d	2.33	3490 ± 490	674	49 ± 5
5e	2.95	4430 ± 660	670	55 ± 5

[a] β values were measured in chloroform using the hyper-Rayleigh scattering at 1.9 μm. FTC was used as an external standard.

[b] λ_{max} was measured in PMMA film.

[c] r_{33} values were measured by Teng–Man reflection method at the wavelength of 1.31 μm.

synthetic approaches were developed to prepare these chromophores through simple chemical reactions. In addition to high T_d data, the linear and nonlinear optical properties of all chromophores were thoroughly investigated. Synthesized chromophores showed a nearly threefold enhancement in molecular hyperpolarizability. The EO coefficient of novel chromophores in PMMA host were nearly two times higher as compared to previously reported benchmark FTC chromophore.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.060.

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