

Nonlinear Optical Chromophores for Electro-optical Applications

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(Received November 24, 2009; accepted February 3, 2010)

The large increase in molecular first hyperpolarizabilities (β) for the thienyl-vinylene bridge based nonlinear optical chromophores by modified acceptor and donor is reported. More than 3.5 times enhancement of β value is measured compared to the chromophore without the modification of acceptor and donor. This improvement is further proved by the intrinsic polarizations at zero frequency (β_0) converted from β with a two-level model. Furthermore, molecular first hyperpolarizabilities in the molecular can be effectively translated into electro-optic coefficient. The chromophores show the onset decomposition temperatures is above 200 °C, indicating that they possessing excellent thermal stability for the electro-optical applications.

Development of organic nonlinear optical chromophores for application in opto-electronic fields has attracted extensively interest, which is superior (easily processing and low power consumption in device, etc) to conventional inorganic materials¹⁻³. Most of these chromophores are of the donor- π -acceptor type and show an intramolecular charge-transfer transition, usually dominating the molecular first hyperpolarizability (β). A successful approach to optimizing molecular first hyperpolarizability is based on tuning ground-state polarization and bond length alternation through modification of the electron donor and acceptor groups as well as the π electron bridge⁴.

In this paper, we report a series of highly efficient nonlinear optical chromophores containing thiophene bridge based on the enhancement of electron strength of acceptor and/or donor, as shown in Fig. 1. Molecular linear and nonlinear optical properties of the chromophores are measured to understand structure-property relationships (Table 1). Molecular hyperpolarizability was measured by using Hyper-Rayleigh Scattering (HRS) technique at 1.56 μm ⁵. Quadratic dependence of HRS signal (chromophore F as an example) on laser intensity is confirmed in Fig. 2. The inset of Fig 2 indicates the expected linear dependence of the quadratic coefficient on molecular concentration. β can be obtained by comparing the linear slope with that of traditional FTC-chromophore. The measured results are listed in Table 1. New chromophores B-F show remarkable improvement in β than that of chromophore A without the modification of acceptor and donor. More than 3.5 times increase is measured in chromophore F, indicating β value as high as 7757×10^{-30} esu.

Some resonant enhancement should be expected in β value determined directly by HRS⁶⁻⁸. A popular two-level model could be used to estimate their static first molecular hyperpolarizabilities (β_0)⁹⁻¹¹, which reflects the intrinsic polarizations of the molecular at zero frequency. β_0 of the chromophores are also shown in Table 1. One can find the β_0 for chromophores B-F are higher than that of chromophore A. The increase of β_0 , around 2 times enhancement are realized in chromophore F compared to chromophore A. These results confirmed the enhancement of molecular hyperpolarizabilities by the modulation of electron donors and acceptors in nonlinear

Table 1 Electronic absorption, β and thermal stability

Sample	λ_{max} (nm)	T_d (°C)	β ($\times 10^{-30}$ esu.)	β_0 ($\times 10^{-30}$ esu.)
A	609	220	2201	731
B	669	217	5731	1235
C	677	219	6384	1279
D	682	214	5622	1065
E	688	194	6357	1169
F	691	252	7757	1342

λ_{max} are measured in 1,4-dioxane. β are measured using the Hyper-Rayleigh scattering technique at the laser wavelength of 1.56 μm in 1,4-dioxane solution. The precision in the β evaluation is estimated as 15%.

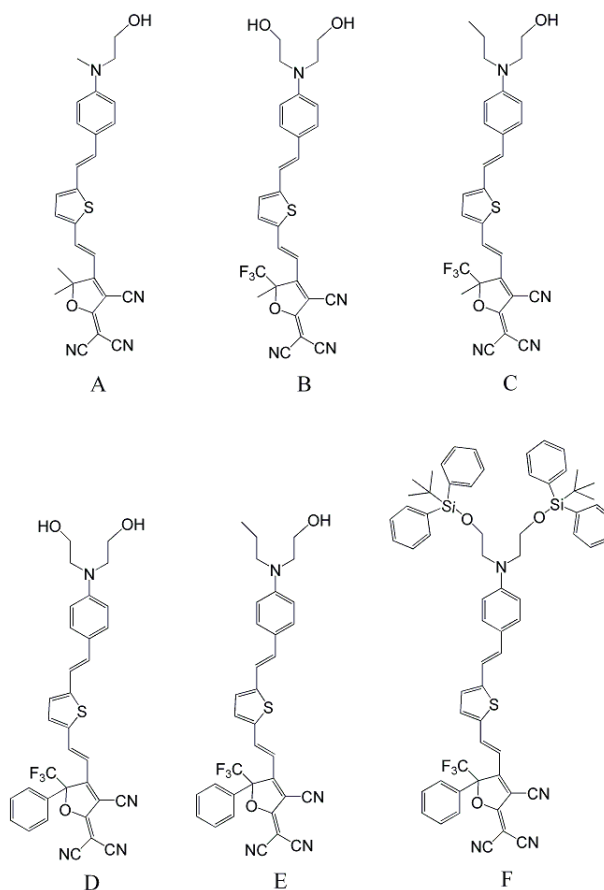


Fig. 1 Molecular structure of chromophores A-F.

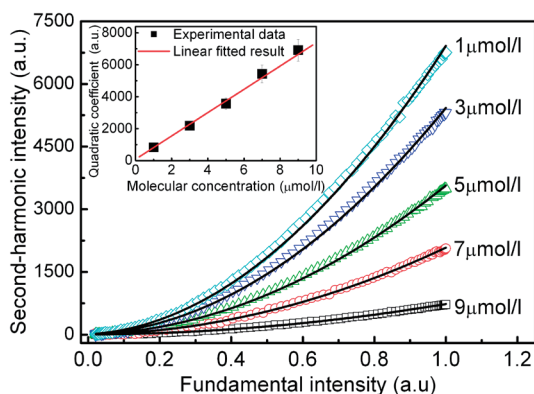


Fig. 2 Quadratic dependence of HRS signal (sample F) at different concentrations on laser intensity. Inset: Dependence of quadratic coefficient on molecular concentration.

optical chromophores.

Furthermore, β in these molecules can be effectively translated into electro-optic coefficient (r_{33}). The r_{33} of chromophore F (in PMMA host) can be reached to 72 pm/v measured by Teng-Man technique at the wavelength of 1.31 μm , which is over twice the value for lithium niobate (31 pm/v). All chromophores showed high temperature resistance beyond 200 $^{\circ}\text{C}$. In particular, the T_d of chromophore F is as high as 252 $^{\circ}\text{C}$. The high thermal stability of these chromophores makes them very suitable for practical electro-optic application.

In summary, we have synthesized five new chromophores with enhanced β by modified the electron acceptor and donor groups. These chromophores possessing high

electro-optic coefficient and excellent thermal stability have significantly potential applications in optical communication technology

We acknowledge the financial support from the global COE (Centers of Excellence) Program under Kyushu University, Japan.

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