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Effect of two methoxy groups bound to an amino-benzene donor unit for thienyl-di-vinylene bridged EO chromophores

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ABSTRACT

We report the molecular first hyperpolarizability (β) and absorption and ^{1}H NMR spectra of electro-optic (EO) chromophores comprised of amino-benzene with two methoxy groups at meta-positions as the donor units, thienyl-di-vinylene as the π-electron bridges, and 2-(dicyanomethylene)-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF), 2-(dicyanomethylene)-3-cyano-4,5-dimethyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-TCF) or 2-(dicyanomethylene)-3-cyano-4-methyl-5-phenyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-phenyl-TCF) as the acceptor units. Improvement in linear and nonlinear optical properties was found in EO chromophores with two methoxy groups compared with benchmark EO chromophores without these groups and EO chromophores with one methoxy group. The data obtained from measurements of hyperpolarizability (β) and absorption and ^{1}H NMR spectra indicate a possible mechanism that can contribute to improvement – double intra-molecular hydrogen bonding.

1. Introduction

The development of organic and polymeric electro-optic (EO) materials has been a subject of considerable interest during the past several decades due to their potential applications in ultra-high-speed and lower-power optical modulators and switches, and has opened doors to important application areas such as digital signal processing, and optical sensors [1–4]. One of the important themes in preparing highly effective EO materials is the development of EO chromophores with large molecular first hyperpolarizability (β) and excellent thermal and chemical stability. Large β can be obtained by adequate molecular design, that is, asymmetric substitution of a π-electron bridge with appropriate donor and acceptor moieties. The development of excellent electron acceptors such as 2-(dicyanomethylene)-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF), 2-(dicyanomethylene)-3-cyano-4,5-dimethyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-TCF), and 2-(dicyanomethylene)-3-cyano-4-methyl-5-phenyl-5-trifluoromethyl-2,5-dihydrofuran (CF_3-Ph-TCF) led to a breakthrough in the design of large β EO chromophores [5,6]. In combination with these excellent acceptors, good π-electron bridges, such as thienyl-di-vinylene and polyene bridges, were also developed, as well as good donor groups such as (dialkylamino)benzene and (diarylamino)benzene [7–10].

We previously reported the nonlinear optical properties of EO chromophores composed of a thienyl-di-vinylene bridge, TCF, CF_3-TCF, or CF_3-phenyl-TCF acceptor units, and amino-benzene donor units with one methoxy or benzyloxy group at its meta-position. EO side-chain polymers with these EO chromophores exhibited excellent EO properties [11]. In addition, we recently investigated the molecular first hyperpolarizability of a variety of EO chromophores that have amino-benzene with one methoxy or benzyloxy group as the donor units, polyene (monoene, diene, and triene), phenyl-di-vinylene, or thienyl-di-vinylene bridges as the π-electron bridges, and TCF, CF_3-TCF or CF_3-phenyl-TCF as the acceptor units, and found an improvement in nonlinear optical properties for the long π-conjugated EO chromophores having an amino-benzene donor with one methoxy or benzyloxy group, compared with the benchmark EO chromophores without methoxy or benzyloxy groups [12].

In this paper, we investigated the molecular first hyperpolarizability (β) with hyper-Rayleigh scattering (HRS) measurements [13] and absorption and ^{1}H NMR spectra of newly designed and synthesized electro-optic (EO) chromophores comprised of amino-benzene with two methoxy groups at meta-positions as the donor units, thienyl-di-vinylene as the π-electron bridge, and TCF, CF_3-TCF or CF_3-phenyl-TCF as the acceptor units. More improvement in linear and nonlinear optical properties was found in EO chromophores with two methoxy groups compared with EO chromophores with one methoxy group and benchmark EO chromophores without these groups. The data obtained from these

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measurements indicate a possible mechanism that contributes to improvement, that is, double intra-molecular hydrogen bonding, which may induce the improved structural stability in the planar trans-configuration, as well as reduce dynamical fluctuation of the conjugated system. In addition, a slightly improved high-temperature resistance of the chromophores with two methoxy groups as compared with benchmark chromophores and the chromophores with one methoxy group was also shown based on the thermogravimetric and differential thermal analysis. Addition of methoxy groups to meta-positions of the amino-benzene donor is an important area of progress in the design of EO chromophores and also induces several advantages.

2. Materials and methods

Fig. 1 shows the chemical structures of EO chromophores used in this study. The EO chromophores are composed of amino-benzene with two methoxy (–OCH_3) or one methoxy or without methoxy groups as the donor units, thienyl-di-vinylene bridge as the π-electron bridge, and TCF, CF_3-TCF, or CF_3-phenyl-TCF as the acceptor units. Among these chromophores, those with two methoxy groups are newly designed and investigated in this paper. Fig. 2 schematically shows the synthesis procedure including its reagents and conditions to obtain the new chromophores with two methoxy groups. Here, each process of the synthesis was described in detail.

2.1. 4-Dibutylamino-3,5-dimethoxybenzene (s1)

3,5-Dimethoxybromobenzene (21.7 g, 100 mmol) and dibutylamine (13.0 g , 100 mmol) were added to dioxane (300 ml) together with potassium bis-trimethylsilylamide (22.0 g, 110 mmol) in Ar atmosphere. After stirring and refluxing for 12 h, the solution was added to iced water (2.0 l) and extracted with chloroform (200 ml) three times. The extracted solution was washed with brine and dehydrated with magnesium sulfate (unhydrous), and then evaporated. The residue was purified with the column chromatography using silica gel to afford s1 (23.4 g, 88%).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.95(6H, t, J = 8 Hz), 1.40(4H, m). 1.56(4H, m), 3.22(4H, t, J = 7 Hz), 3.75(6H, s), 5.83(3H, s), ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 20.2, 29.4, 50.7, 54.8, 87.0, 91.0, 149.8, 161.6.

2.2. 4-Dibutylamino-2,6-dimethoxybenzaldehyde (s2)

$POCl_3$ (16.0 g, 104 mmol) was added and stirred in n,n-dimethylformamide (DMF) (30 ml) at 5–10 °C in Ar atmosphere, and then

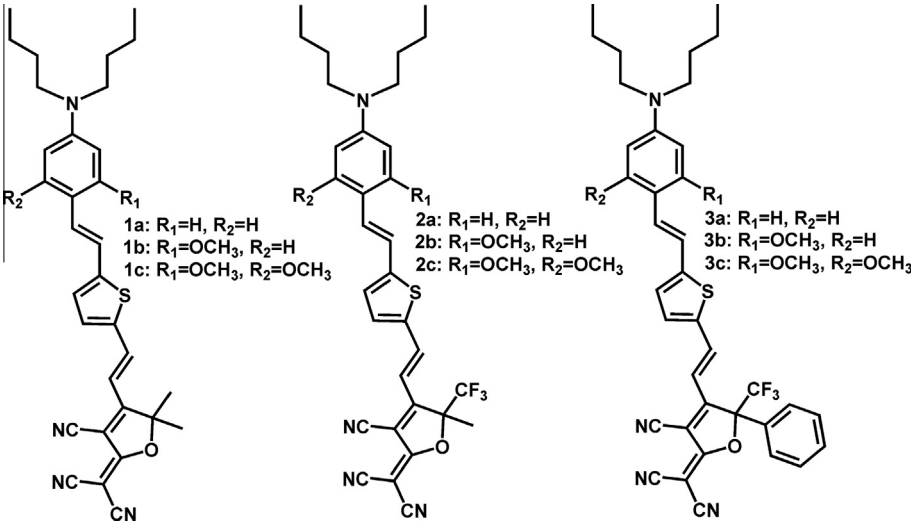

Fig. 1. Chemical structures of EO choromphores used in this study.

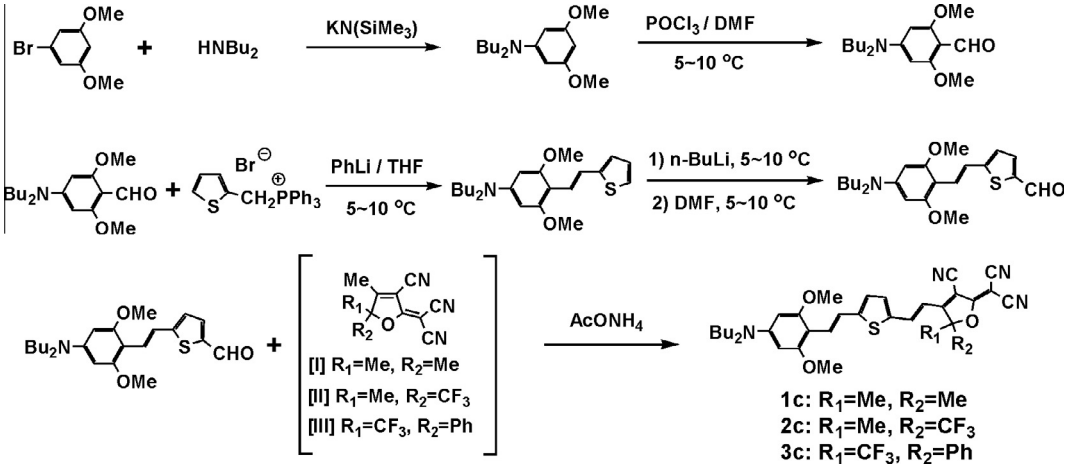

Fig. 2. Synthesis procedure of EO chromophores (1c–3c) with two methoxy (–OCH_3) groups.