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Novel chromophores with excellent electro-optic activity based on double-donor chromophores by optimizing thiophene bridges

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ABSTRACT

Three novel nonlinear optical chromophores based on the same bis(*N*,*N*-diethyl)aniline donor have been synthesized and systematically characterized. These chromophores showed good thermal stability and chromophore y1 showed the best thermal stability of 249 °C. Besides, compared with the chromophore (y1) without the substituted group, chromophores y2 and y3 show better intramolecular charge-transfer absorption. Most importantly, the high molecular hyperpolarizability of these chromophores can be effectively translated into large electro-optic coefficients. The electro-optic coefficient of poled films containing 25% wt of chromophores y1–y3 doped in amorphous polycarbonate afforded values of 149, 138 and 157 pm/V at 1310 nm for chromophores y1–y3 respectively. These results indicated that the double donors of bis(*N*,*N*-diethyl)aniline unit can efficiently improve the electron-donating ability and the special structure can reduce intermolecular electrostatic interactions, thus enhancing the macroscopic electro-optic activity. These properties, together with good solubility, suggest the potential use of these chromophores as advanced materials.

1. Introduction

Polymeric electro-optic (EO) materials with nonlinear optical (NLO) chromophores have shown commercial potential as active media in high-speed broadband waveguides for optical switches, optical sensors, and information processors [1–5]. In the past two decades, the NLO materials have continuously drawn great interest and have stimulated a research boom for materials with large EO activities, both at molecular level (β) and as processed materials (r_{33}). Considerable progress has been made on developing organic and polymeric electro-optic (EO) materials for applications in high-speed and broadband information technology [2,5–7]. However, one major obstacle that hinders the rapid development of this technology is the lack of an effective mechanism to translate high-molecular nonlinearities (β) into large macroscopic EO activities (r_{33}) [8,9]. Efficient translation of large β chromophores into thermally and chemically stable materials with macroscopic EO responses can be achieved by careful modification of the molecular structure of chromophores and host polymers under mild electric-field poling [10–12]. Thus, chromophores with large β and weak inter-molecular electrostatic interaction, as the decisive factor, must be designed and prepared.

In general, dipolar NLO chromophores used in polymeric EO materials consist of electron-donor and electron-acceptor groups interacting through a conjugated bridge. In such molecules, the donor and acceptor substituents provide the requisite ground-state charge asymmetry, whereas the π-conjugation bridge provides a pathway for the ultrafast redistribution of electric charges under an applied external electric field [4,13,14]. The traditional chromophore moieties have a rod-like structure, which leads to strong inter-molecular dipole–dipole interactions in the polymeric matrix and makes the poling-induced noncentrosymmetric alignment of the chromophores a daunting task. For this reason, many efforts have been carried out to design and synthesize novel NLO chromohores, seeking to engineer NLO molecules both microscopically (β) and macroscopically (r_{33}). On one hand, it has been well established that large β values of the chromophores can be

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achieved by careful modification of the strength of donor and acceptor moieties, as well as the nature of the π-conjugated spacer [15,16]. Until now, NLO chromophores containing thiophene based bridges have been widely used [17,18]. Further modification was also widely studied to achieve excellent and better performance [19–22]. On the other hand, controlling the shape of the chromophore was proven to be an efficient approach for minimizing intermolecular dipole–dipole interaction and enhancing the poling efficiency [23]. So modifying the thiophene bridge may be one of a reasonable way to achieve excellent and better performance.

Based on above point, as well as our previous work on the "double-donor chromophore" [5,9,24], we designed and synthesized three new double donor chromophores y1, y2, and y3. In our previous work, it has been shown from both theoretical and experimental analysis that the linear and nonlinear optical properties of double-donor chromophores are excellent. It also can translate the high β values of the chromophores to large macroscopic optical nonlinearities (r_{33}) values. The double donors with two *N, N*-diethylaniline can improve the electron-donating ability thus enhance the optical nonlinearity. The one of the *N, N*-diethylaniline unit can act as both the additional donor and the isolation group (IG). On the other hand, the double benzene rings with an appropriate angle make the special structure different from the general NLO chromophores and can decrease the intermolecular electrostatic interactions so enhance the macroscopic EO activity. However, to our regret, the solubility of double-donor chromophore is not so excellent and limited its application, which encourage us to optimize double-donor chromophore. In this paper, a new synthetic methodology of attaching two different substituents onto the π-conjugation bridge of NLO chromophore was developed to obtain two new NLO chromophores. The motivation is to improve the solubility as well as the EO activities of guest-host EO materials by a simple bridge-modifying method for NLO chromophores. These modified chromophores showed great solubility in common organic solvents, better thermal stability (with their onset decomposition temperatures all above 220 °C), good compatibility with polymers, and large EO activity in the poled films. ^1H NMR and ^{13}C NMR analysis were carried out to demonstrate the preparation of these chromophores. Thermal stability, photophysical properties and DFT calculations of these chromophores were systematically studied. Furthermore, the macroscopic EO activity (r_{33}) of these chromophores in amorphous polycarbonate were also analysed Chart 1.

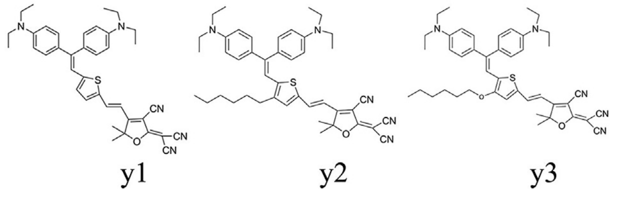

Chart 1. Structure of chromophore y1–y3.

2. Experiments

2.1. Materials and instrumentation

^1H NMR spectra were determined by an Advance Bruker 400 (400 MHZ) NMR spectrometer (tetramethylsilane as internal reference). The MS spectra were obtained on MALDI-TOF-(Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII(Broker Inc.) spectrometer. The UV–Vis spectra were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA Co) with a heating rate of 10 °C/min under the protection of nitrogen. Cyclic voltammetry (CV) experiments were performed on a CHI660D electrochemical workstation by a cyclic voltammetry (CV) technique in CH_3CN solution, using Pt disk electrode and a Pt wire as the working and counter electrodes, respectively, and a saturated Ag/AgCl electrode as the reference electrode in the presence of 0.1 M n-tetrabutylammoniumperchlorate as the supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc+) couple was used as an internal reference. All chemicals, commercially available, are used without further purification unless stated. The DMF, $POCl_3$ and THF were freshly distilled prior to its use. The 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature [25].

2.2. Synthesis

2.2.1. Synthesis of chromophore **y1**

Chromophore y1 was synthesized according to the literature [24].

2.2.2. Synthesis of compound 2b

Dry DMF (3 mL) was dropwise added to 3 mL of phosphorus oxychloride (0.0327 mol) maintained at 0 °C. After the solution was stirred for 30 min, compound 1b (4.60 g, 0.0274 mol) was added to the above Vilsmeier reagent, and the mixture was heated to 90 °C for an additional 2 h. After cooling, the clear red solution was added dropwise to $NaHCO_3$ (aq) with stirring, and the resulting mixture was allowed to stand for 2 h and extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were washed with water and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography to give a red liquid product (87%).

^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.58 (d, J = 5.0 Hz, 1H), 6.96 (d, J = 5.0 Hz, 1H), 2.98–2.62 (m, 2H), 1.73–1.53 (m, 2H), 1.37–1.12 (m, 6H), 0.83 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.18, 152.90, 137.71, 134.42, 130.80, 31.65, 31.61, 31.45, 30.42, 30.18, 29.00, 28.53, 22.63, 14.09.

MS (EI): m/z calcd for $C_{11}H_{16}OS$: 196.09; found: 196.31.

2.2.3. Synthesis of compound **3b**

To a suspension of diethyl bis(4-(diethylamino) phenyl) methylphosphonate (1.5 g, 3.36 mmol), and 2b (588 mg, 3 mmol) in 20 mL dry THF and NaH (0.36 g, 15 mmol) were added and the mixture turned yellow. The mixture was stirred at room temperature for 24 h. Saturated NH_4Cl was added and the resulting mixture was extracted with EtOAc (20 mL × 3). The combined extracts were washed with water and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography to give a yellow product (0.66 g, 45%).

^1H NMR (400 MHz, Acetone) δ 7.07–7.01 (m, 2H), 6.90 (s, 1H), 6.87–6.82 (m, 3H, overlap), 6.63 (d, J = 3.8 Hz, 1H), 6.62 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.8, 2H), 3.29 (m, 8H), 2.63–2.54 (m, 2H), 1.49 (m, 2H),1.31–1.20 (m, 6H), 1.04 (m, 12H), 0.75 (m, 3H).

MALDI-TOF: m/z calcd for $C_{32}H_{44}N_2S$: 488.32 $[M]^+$; found: 488.09.

2.2.4. Synthesis of compound **4b**

To a solution of 3b (0.98 g, 2.0 mmol) in dry THF (20 mL) was added a 2.4 M solution of n-BuLi in hexane (1.3 mL, 3.0 mmol) dropwise at −78 °C under N_2. After this mixture was stirred at this temperature for 1 h, and the dry DMF (0.20 mL, 2.4 mmol) was introduced. The resulting solution was stirred for another 1 h at −78 °C and then allowed to warm up to room temperature. The