



Using phenoxazine and phenothiazine as electron donors for second-order nonlinear optical chromophore: Enhanced electro-optic activity



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ABSTRACT

Two novel chromophores based on the phenoxazine (chromophore L1) or phenothiazine (chromophore L2) donor, and tricyanofuran acceptors linked together via thiophene as the bridges have been synthesized and systematically investigated. Cyclic voltammetry measurements showed that chromophore L1 had smaller energy gap than chromophore L2 due to the stronger electron-donating ability. Moreover, Density functional theory calculations suggested that the β value of chromophore L1 is 17% larger than that of chromophore L2. The doped film containing the chromophore L1 showed an r_{33} value of 49 pm/V at the concentration of 25 wt% which is two times higher than the EO activity of the chromophore L2 (23 pm/V) and the traditional aryl chromophore (10–20 pm/V). High r_{33} value, high thermal stability (onset decomposition temperatures higher than 220 °C) suggests the potential use of the new chromophore in nonlinear optical materials.

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1. Introduction

Over the past decade, organic electro-optic (EO) materials have attracted great attention owing to their potential applications in optical communication and information technology [1–3]. Compared with inorganic materials, organic EO materials have many advantages over lower cost, ease of processing, larger EO coefficients and so on [4–8]. The second-order nonlinear optical (NLO) chromophores are the key constructing blocks for organic EO materials [9]. To meet the stringent requirements for the using of devices, one of the most critical challenges is to develop NLO chromophores with large hyperpolarizability (β), excellent thermal and chemical stabilities as well as good transparency [10–12]. Moreover, weak molecular electrostatic interaction in the polymer matrix is needed to effectively translate these large β values into bulk EO activities [13,14].

In general, the second-order NLO chromophore consist of an electron-donating group and an electron-withdrawing group

coupled through a π -conjugated bridge, called D- π -A system [15,16]. In order to search for highly efficient NLO chromophores, optimization of the π -conjugated bridge, electron-donor and electron-acceptor characteristics of the substituents are needed [17]. Many studies on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors [18–20]. The electron donors, which are important components of NLO chromophores, have received little attention [21]. Traditional alkyl and aryl amines were considered to be the ideal electron donors and were often used [22–24]. Besides, many kinds of organic chromophores based on carbazole [25], indoline [11] and other donating groups have been developed and have shown potential application for second-order NLO chromophores. The r_{33} values of traditional aryl chromophores (like triphenylamine or carbazole D- π -A chromophores) remained 10–20 pm/V, which are much lower than those obtained from their alkyl D- π -A counterparts (traditional chromophore FTC achieve r_{33} values of 39 pmV⁻¹ at 25 wt%) [2,21,26]. Recent studies showed that introducing additional heteroatoms into the benzene ring moiety of donor could provide abundant opportunities for further modifications of chromophores thus influence nonlinear optical properties of chromophores [27–29]. So, the phenothiazine (PTZ) unit was introduced to the

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second-order NLO chromophores due to its electron-rich sulfur and nitrogen heteroatoms. Besides, its ring is non-planar with a butterfly conformation at the ground state, which can impede the molecular aggregation [13]. The results show that donor group's efficacy in PTZ chromophore was higher than that of structurally similar triphenylamine and carbazole-based chromophore [13,26,30].

The phenoxazine (POZ) units were electron donating groups which were often employed to dye-sensitized solar cells (DSSCs) [31,32] due to unique electronic properties and strong electron-donating ability. The POZ unit with electron-rich nitrogen and oxygen heteroatoms may have stronger electron-donating ability than PTZ. However, strangely, the POZ units were seldom applied to construct second-order NLO chromophores as donating groups. In fact, to the best of the authors' knowledge, few studies have reported on the macroscopic EO response (r_{33} value) of poled films containing chromophores using POZ units as donors.

PTZ and POZ units were used as donor in this study due to its strong electron-donating ability. In this study, we had designed and synthesized two new chromophores L1 and L2 based on PTZ and POZ donors. We used a typical thiophene bridge and powerful tricyanovinylidihydrofuran (TCF) acceptor to construct our chromophores. (Chart 1) The UV–Vis, solvatochromic, redox properties, Density functional theory (DFT) quantum mechanical calculations, thermal stabilities and EO activities of these chromophores were systematically studied to prove the benefits of the POZ donors in applications of nonlinear optical chromophores design and synthesis.

2. Experimental

2.1. Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. N, N-dimethyl formamide (DMF), Phosphorus oxychloride (POCl_3), tetrahydrofuran (THF) and ether were distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). 10-hexyl-10H-phenoxazine (1a) and 10-hexyl-10H-phenoxazine-3-carbaldehyde (2a) were synthesized according to literature [33]. 10-hexyl-10H-phenoxazine (2b) and 10-hexyl-10H-phenoxazine-3-carbaldehyde (3b) were synthesized according to previous publication [13]. 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature [34]. TLC analyses were carried out on 0.25 mm thick precoated silica plates and spots were visualized under UV light. Chromatography on silica gel was carried out on Kieselgel (200–300 mesh).

^1H NMR spectra were determined by an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization) 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 $10\text{ }^\circ\text{C min}^{-1}$ under the protection of nitrogen. Cyclic voltammetric data were measured on a BAS CV-50W voltammetric analyzer using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/AgNO_3 as the reference electrode at a scan rate of 50 mV s^{-1} . The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile is the electrolyte. The elemental analysis was measured on Flash EA 1112 Elemental Analyzer. The melt points were obtained by TA DSC Q10 under N_2 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

2.2. Syntheses

2.2.1. Synthesis of (E)-10-hexyl-3-(2-(thiophen-2-yl)vinyl)-10H-phenoxazine (Compound 4a)

Under a N_2 atmosphere, to a solution of compound 3a (0.31 g, 1.00 mmol) and 3 (0.53 g, 1.20 mmol) in ether (60 mL) was added NaH (1.45 g, 6.00 mmol). The solution was allowed to stir for 48 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:20) to give compound 4a as orange oil with 87.3% yield (0.33 g, 0.87 mmol). MS, m/z : 375.27 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, $J = 4.8\text{ Hz}$, 1H), 7.02 (m, ArH, 2H), 6.98 (d, $J = 3.8\text{ Hz}$, 1H), 6.85 (d, $J = 8.4\text{ Hz}$, 1H), 6.81 (m, 2H), 6.74 (d, $J = 16.0\text{ Hz}$, 1H), 6.65 (m, 2H), 6.48 (d, $J = 7.9\text{ Hz}$, 1H), 6.41 (d, $J = 8.2\text{ Hz}$, 1H), 3.51–3.45 (m, 2H), 1.67 (m, 2H), 1.43 (m, 6H), 0.94 (t, $J = 5.8\text{ Hz}$, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.1, 144.69, 143.28, 132.82, 132.54, 129.96, 127.48, 125.29, 123.54, 122.77, 120.78, 119.35, 115.40, 112.00, 111.36, 111.11, 44.06, 31.64, 26.59, 24.99, 22.67, 14.02. Anal. Calcd (%) for $\text{C}_{24}\text{H}_{25}\text{NOS}$: C, 76.76; H, 6.71; N, 3.73; found: C, 76.83; H, 6.82; N, 3.67.

2.2.2. Synthesis of (E)-10-hexyl-3-(2-(thiophen-2-yl)vinyl)-10H-phenothiazine (Compound 4b)

The procedure for compound 4a was followed to prepare 4b from 3b to 3 as orange oil with 85.7% yield (0.34 g, 0.86 mmol). MS, m/z : 391.14 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s, 1H), 7.17 (m, 2H), 7.13 (d, $J = 7.8\text{ Hz}$, 2H), 7.02 (d, $J = 3.4\text{ Hz}$, 1H), 6.92 (dd, $J = 8.2, 4.6\text{ Hz}$, 2H), 6.87 (d, $J = 8.1\text{ Hz}$, 1H), 6.81 (d, $J = 8.2\text{ Hz}$, 1H), 6.63 (d, $J = 11.9\text{ Hz}$, 1H), 6.44 (d, $J = 11.9\text{ Hz}$, 1H), 3.95–3.81 (m, 2H), 1.84 (m, 2H), 1.54–1.41 (m, 2H), 1.34 (m, 4H), 0.91 (t, $J = 6.7\text{ Hz}$, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.88, 143.51, 142.12, 138.79, 132.80, 132.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 12.98. Anal. Calcd (%) for $\text{C}_{24}\text{H}_{25}\text{NS}_2$: C, 73.61; H, 6.43; N, 3.58; found: C, 73.71; H, 6.48; N, 3.63;

2.2.3. Synthesis of (E)-5-(2-(10-hexyl-10H-phenoxazin-3-yl)vinyl)thiophene-2-carbaldehyde (Compound 5a)

Under a N_2 atmosphere, 4a (0.33 g, 0.87 mmol) was dissolved in 100 mL of freshly distilled THF and cooled to $-78\text{ }^\circ\text{C}$. Approximately 2 equivalents of BuLi in hexanes (0.73 mL, 1.74 mmol) was added drop wise over 20 min. Reaction continued at $-78\text{ }^\circ\text{C}$ for 1 h at which time DMF (0.13 g, 1.74 mmol) was added over 1 min. The reaction was allowed to reach RT while the solution stirred for 1 h. The organic phase was extracted by CH_2Cl_2 , washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:5) to give compound 5a as a red solid with 75.6% yield (0.27 g, 0.66 mmol). m.p.: $126.90\text{ }^\circ\text{C}$. MS, m/z : 403.56 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 9.81 (s, 1H), 7.61 (d, $J = 3.9\text{ Hz}$, 1H), 7.05 (d, $J = 3.9\text{ Hz}$, 1H), 6.93 (d, $J = 3.4\text{ Hz}$, 2H), 6.86 (dd, $J = 8.3, 1.5\text{ Hz}$, 1H), 6.82–6.76 (m, 2H), 6.69–6.59 (m, 2H), 6.47 (d, $J = 8.3\text{ Hz}$, 1H), 6.40 (d, $J = 8.3\text{ Hz}$, 1H), 3.49–3.43 (m, 2H), 1.65 (m, 2H), 1.38 (m, 6H), 0.92 (t, $J = 6.7\text{ Hz}$, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 182.23, 153.17, 145.22, 144.74, 140.95, 137.14, 134.22, 132.46, 132.15, 128.81, 125.66, 124.05, 123.69, 121.31, 118.09, 115.45, 112.31, 111.57, 111.11, 44.20, 31.53, 26.56, 25.10, 22.60, 13.94. Anal. Calcd (%) for $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{S}$: C, 74.41; H, 6.24; N, 3.47; found: C, 74.49; H, 6.19; N, 3.53;

2.2.4. Synthesis of (E)-5-(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)thiophene-2-carbaldehyde (Compound 5b)

The procedure for compound 6a was followed to prepare 6b from 5b as red solid in 73.2% yield (0.26 g, 0.63 mmol). m.p.:

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