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Synthesis and optical nonlinear property of NLO chromophores with alkoxy chains of different lengths using 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine as donor

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ABSTRACT

Three chromophores **ZR1**, **ZR2** and **ZR3** based on the electron donor bearing different lengths of alkoxy chains, the same π-electron bridge and tricyanofuran acceptor, have been synthesized and systematically investigated. Density Functional Theory calculations and cyclic voltammetry measurements suggested that **ZR2** (with hexyloxy) and **ZR3** (with octoxy) had relatively small energy gaps between ground state and excited state than **ZR1** (with butoxy) due to the auxiliary electron-donating ability and steric hindrance of their longer alkoxy chains on the donor. The electro-optic coefficient of poled films containing 20% wt of the new dyes doped in amorphous polycarbonate afforded values of 48, 62 and 65 pm/V at 1310 nm for **ZR1**, **ZR2** and **ZR3** respectively. These results indicated that the introduction of the longer alkoxy chains on the donor could effectively reduce the intermolecular electrostatic interactions and aid the alignment of the chromophores. This conclusion is conducive to future molecular design.

1. Introduction

Organic and polymeric electro-optic (EO) materials have drawn much attention because of their attractive potential applications in optical data transmission and optical information processing [1]. Compared with traditional inorganic and semiconductor materials, the organic EO materials have many advantages such as larger nonlinear optical coefficients, simpler preparation and lower cost [2–6]. Generally, the nonlinear optical (NLO) chromophore molecules possessing a dipolar D-π-A type structure is the core component in such materials, which turned the design and preparation of NLO chromophores into a research hotspot in the area of organic EO materials [7,8]. Many great attentions have been paid to the rational design of chromophores with not only high first-order hyperpolarizability but also good thermal and photochemical stabilities, and in addition, have good solubility and compatibility with polymer matrix.

It is a well-established fact that the conjugation length and donor/acceptor strength of these D-π-A type push–pull chromophore molecules can cause dramatic influences to their second-order nonlinear responses [3,5–7]. In order to search for highly efficient NLO chromophores, finding an optimal combination of their donor/acceptor is still one of the critical challenges [9–11]. In the past decade, the researches on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors [12–18]. However, the electron donors, which are important components of NLO chromophores, have received much less attention as the general class of traditional alkyl and aryl anilines which were considered to be the ideal electron donors and were constantly-used [19,20].

Recently, by simple guest-host doping, single chromophore with ultrahigh EO coefficient value (r_{33} value) of over 300 pm/V has been designed by our group [5]. The EO coefficients of organic materials are large enough for practical application relative to inorganic materials (such as lithium niobate whose r_{33} value is only 32 pm/V) [10], while the intermolecular interaction is still a big problem due to the large dipole moment of the D-π-A type chromophores [21–23]. In this paper, we synthesized a series of chromophores

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that had the same type of isolated groups but different lengths of alkoxy chains (butoxy, hexyloxy and octoxy) on the donor. All of the chromophores have the same π-electron bridge and tricyanofuran (TCF) acceptor for easy comparison. The thermal, electrochemical, linear and nonlinear optical properties of all three chromophores were thoroughly investigated to understand the effects of the alkoxy chains on the chromophores. The alkoxy chains might play roles as auxiliary electron-donating and steric groups, and they could also increase the solubility of the chromophores in common solvents.

2. Experimental section

2.1. Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. Compound **1** was purchased from Chongqing Werlchem Fine Chemical Co. Ltd. Halohydrocarbons and 2-thienyl triphenylphosphonate bromide were purchased from Ouhechem Technology Ltd. The DMF and THF were freshly distilled prior to their use. TCF acceptor were prepared according to the literature [24]. ^{1}H NMR spectra were determined by an Advance Bruker 400 M (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 experiments 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. The glass transition temperatures were obtained by TA DSC Q10 under N_2 at a heating rate of 10 °C/min. 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 100 mV/s. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile is the electrolyte.

2.2. Synthesis

*2.2.1. Synthesis of compound **2R***

To a solution of compound **1** (4.0 g, 14.6 mmol) and 1-Bromobutane (8 mL) in DMF (40 mL), anhydrous potassium carbonate (4.0 g, 28.9 mmol) was added. The mixture was allowed to stir at 100 °C for 24 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 (AcOEt: Petroleum ether = 1:10) to give **2R1** as a yellow powder in 71.8% yield (3.46 g, 10.5 mmol). MS, m/z: 329.471 (M^+), ^{1}H NMR (400 MHz, Acetone) δ 9.90 (s, 1H), 7.51 (s, 1H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.38–3.31 (m, 2H), 3.28 (dd, *J* = 6.7, 5.1 Hz, 2H), 1.87 (dt, *J* = 14.7, 6.9 Hz, 2H), 1.71 (ddd, *J* = 12.4, 7.1, 5.2 Hz, 4H), 1.52 (dt, *J* = 16.8, 7.5 Hz, 2H), 1.41 (s, 6H), 1.23 (s, 6H), 0.99 (t, *J* = 7.4 Hz, 3H).

The synthesis of compound **2R2** and **2R3** was similar to **2R1**. **2R2**: Yield: (1.71 g, 4.7 mmol, 32.7%). MS, m/z: 357.237 (M^+), ^{1}H NMR (400 MHz, Acetone) δ 9.91 (s, 1H), 7.51 (s, 1H), 3.95 (t, *J* = 6.8 Hz, 2H), 3.34 (dd, *J* = 14.3, 8.1 Hz, 2H), 3.28 (dd, *J* = 6.7, 5.1 Hz, 2H), 1.93–1.84 (m, 2H), 1.71 (ddd, *J* = 12.4, 7.2, 5.3 Hz, 4H), 1.51 (tt, *J* = 11.1, 5.6 Hz, 2H), 1.41 (d, *J* = 4.8 Hz, 6H), 1.40–1.33 (m, 4H), 1.23 (s, 6H), 0.90 (td, *J* = 6.8, 3.3 Hz, 3H). **2R3**: Yield: (2.0 g, 5.2 mmol, 71.0%). MS, m/z: 385.427 (M^+), ^{1}H NMR (400 MHz, Acetone) δ 9.91 (s, 1H), 7.48 (s, 1H), 3.96 (s, 2H), 3.35 (s, 2H), 3.28 (s, 2H), 1.93–1.83 (m, 2H), 1.75–1.65 (m, 4H), 1.56–1.45 (m, 2H), 1.42 (s, 6H), 1.31 (s, 8H), 1.23 (s, 6H), 0.88 (s, 3H).

*2.2.2. Synthesis of compound **3R***

To a solution of compound **2R1** (3.46 g, 10.5 mmol) and 2-thienyl triphenylphosphonate bromide (5.54 g, 12.6 mmol) in absolute ether (30 mL) was added NaH (2.5 g, 104 mmol). The solution was allowed to stir at room temperature for 24 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:Petroleum ether = 1:25) to give **3R1** (**3R1** was cis-trans-isomer mixture, Z/E = 1.26:1) as an orange oil in 86.1% yield (3.70 g, 9.0 mmol). MS, m/z: 408.815 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.27 (d, 1H), 7.14–6.47 (m, 5H), 3.90 (dt, *J* = 16.0, 6.7 Hz, 2H), 3.24–3.01 (m, 4H), 1.86 (tt, *J* = 13.6, 6.8 Hz, 2H), 1.81–1.71 (m, 4H), 1.63–1.54 (m, 2H), 1.47–1.42 (m, 6.H), 1.33 (s, 4H), 1.19 (s, 2H), 0.99 (dt, *J* = 25.3, 7.4 Hz, 3H).

The synthesis of compound **3R2** and **3R3** was similar to **3R1**. **3R2**: Yield: (2.73 g, 6.2 mmol, E/Z = 1.34:1, 79.7%). MS, m/z: 437.223 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 39.6 Hz, 1H), 7.14–6.46 (m, 5H), 3.89 (dt, *J* = 15.6, 6.7 Hz, 2H), 3.24–3.03 (m, 4H), 1.97–1.82 (m, 2H), 1.76 (dd, *J* = 13.1, 6.4 Hz, 4H), 1.62–1.51 (m, 2H), 1.44 (t, *J* = 5.7 Hz, 6H), 1.42–1.33 (m, 4H), 1.31 (d, *J* = 8.6 Hz, 3H), 1.19 (s, 3H), 0.96–0.86 (m, 3H). **3R3**: Yield: (3.51 g, 7.5 mmol, E/Z = 1.6:1, 81.2%). MS, m/z: 465.044 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 40.2 Hz, 1H), 7.13–6.42 (m, 5H), 3.87 (dt, *J* = 15.5, 6.7 Hz, 2H), 3.22–2.99 (m, 4H), 1.95–1.65 (m, 6H), 1.52 (dt, *J* = 9.3, 7.5 Hz, 2H), 1.41 (dd, *J* = 11.1, 3.8 Hz, 6H), 1.39–1.21 (m, 11H), 1.18 (d, *J* = 12.1 Hz, 3H), 1.00–0.81 (m, 3H).

*2.2.3. Synthesis of compound **4R***

A solution of compound **3R1** (3.26 g, 7.9 mmol) in anhydrous THF (10 mL) was prepared in a three neck flask which was purged with nitrogen, then the solution was cooled to −78 °C and dropwise added n-BuLi (4.8 mL, 2.5 M in hexane), after this, the resulting mixture was stirred for 1 h. Anhydrous N,N-dimethylformamide (DMF) (0.93 mL) was added, and the mixture was stirred for one more hour, then the temperature rose to 0 °C and reacted for half an hour. 10 mL water was added to the solution to quench the reaction, the mixture was then warmed to room temperature and poured into water and the organic layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone:Petroleum ether = 1:8) to give **4R1** as a red powder in 86.8% yield (3.0 g, 6.8 mmol). MS, m/z: 437.181 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.64 (d, *J* = 3.9 Hz, 1H), 7.33 (d, *J* = 16.1 Hz, 1H), 7.27 (d, *J* = 5.9 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 3.84 (t, *J* = 6.7 Hz, 2H), 3.27–3.07 (m, 4H), 1.92–1.81 (m, 2H), 1.80–1.70 (m, 4H), 1.60–1.52 (m, 2H), 1.43 (s, 6H), 1.31 (s, 6H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.64, 155.65, 153.99, 142.32, 138.63, 136.30, 128.99, 123.33, 121.66, 121.45, 115.78, 114.32, 74.43, 46.41, 45.74, 39.11, 35.43, 31.70, 31.27, 30.14, 29.88, 29.02, 28.68, 24.50, 21.53, 18.54, 13.10.

The synthesis of compound **4R2** and **4R3** was similar to **4R1**. **4R2**: Yield: (2.15 g, 4.6 mmol, 83.6%). MS, m/z: 465.259 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.55 (d, *J* = 3.9 Hz, 1H), 7.24 (t, *J* = 11.7 Hz, 1H), 7.19 (d, *J* = 4.3 Hz, 1H), 6.96 (d, *J* = 3.9 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 3.81–3.69 (m, 2H), 3.11 (dd, *J* = 14.3, 8.2 Hz, 2H), 3.08–3.02 (m, 2H), 1.85–1.74 (m, 2H), 1.70–1.63 (m, 4H), 1.51–1.39 (m, 2H), 1.35 (s, 6H), 1.29 (td, *J* = 6.9, 3.3 Hz, 4H), 1.21 (d, *J* = 10.7 Hz, 6H), 0.83 (dd, *J* = 9.6, 4.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.29, 156.98, 155.27, 143.88, 139.99, 137.79, 130.52, 124.68, 122.91, 122.52, 116.85, 115.73, 75.81, 47.54, 47.03, 40.25, 36.68, 32.84, 32.40, 31.96, 31.27, 30.31, 30.23, 26.11, 22.70, 14.11. **4R3**: Yield: (3.30 g, 6.7 mmol, 89.3%). MS, m/z: 493.439 (M^+), ^{1}H NMR