Dyes and Pigments 157 (2018) 55–63

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Structure–function relationship exploration for enhanced electro-optic activity in isophorone-based organic NLO chromophores

Fenggang Liu[a,*], Hua Zhang[b], Hongyan Xiao[b], Huajun Xu[b], Shuhui Bo[b], Ling Qiu[b], Zhen Zhen[b], Lijie Lai[a], Shujie Chen[a], Jiahai Wang[a,**]

[a] *School of Chemistry and Chemical Engineering, Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, Guangzhou University, Guangzhou 510006, PR China*

[b] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*

ARTICLE INFO

Keywords:
Nonlinear optics
Chromophore
Isolation group
Electro-optic
Isophorone
Structure–function

ABSTRACT

Four isophorone-based chromophores FLD1-FLD4 has been synthesized and investigated based on julolidinyl donors, with modified isophorone-derived bridges and tricyanovinyldihydrofuran or phenyl-trifluoromethyl-tricyanofuran acceptors. The chromophore FLD3 was modified with a 2-((tert-butyldimethylsilyl)oxy)ethanethiol group covalently attached to the π-conjugate bridge to ensure its all-trans conformation and prevent close packing of molecules, which benefit the macroscopic electro-optic efficiency. The chromophore FLD3 possesses better thermal stability than chromophore FLD1 without the isolation group on the bridge. Moreover, density functional theory calculations suggested that the hyperpolarizability (β) value of chromophore FLD3 is larger than that of chromophore FLD1. Polymers doped with chromophore FLD3 have been poled to afford ultrahigh electro-optic coefficient (r_{33}) of 238 pm/V at 1.31 μm, which is nearly 60% higher than that obtained from chromophore FLD1 and three times higher than that of analogue chromophores FLD2 and FLD4.

1. Introduction

With the development of the information technology, conventional microelectronic materials, usually using electrons as the carriers, will have difficulty satisfying the needs for future communication technology [1]. Compared with electronic communication, transmission of information by photonics has many advantages such as high frequency, wide bandwidth, high speed, and good parallelism [2,3]. The ability to convert signals between electronic and photonic domains is central to photonic/electronic integration. Materials and devices that effect such transduction are referred to as “electro-optic” (EO) [4]. The organic electro-optic (OEO) materials have attracted great attention in last thirty years. Compared with inorganic materials, OEO materials have potential advantages such as lower cost, ease of processing, larger EO coefficients and so on [5,6].

The second-order nonlinear optical (NLO) chromophores are the key constructing blocks for OEO materials [7–11]. To meet the stringent requirements for the using of devices, OEO materials should be developed through rational design of nonlinear optical (NLO) chromophores to optimize their first hyperpolarizability (β), and effectively translate these large β values into bulk EO activities. Meanwhile, improvements of other auxiliary properties like high thermal and photochemical stability, good transparency, as well as easy syntheses are very important.

The second-order NLO chromophores are based on a push-pull system, which consists of an electron-donating group (Donor) and an electron-withdrawing group (Acceptor) coupled through a π-conjugated bridge which called (D–π–A) configuration [12]. The donor moiety has largely been of the amine structure [13]. Bridge moieties consisted of heteroaromatic (thiophene, pyrrole, furan) or polyene (phenyltetraene) structures have reported [14–17]. The acceptor moieties have developed from weaker nitro, cyano, alkoxy, isoxazolone, tricyanovinyl, diarlythiobarbituric acid groups to strong and effective tricyanovinyldihydrofuran (TCF) and phenyl-trifluoromethyl-tricyanofuran (CF_3-Ph-TCF) groups [1,13,18]. Among which, the CLD-type chromophores (containing the ring-locked tetraene bridges) with TCF or CF_3-Ph-TCF acceptor were widely investigated due to their large β and good utility for EO devices [19]. Relatively high electro-optic (EO) coefficients r_{33} around 40–70 pm/V measured at the wavelengths of 1.3 μm have been achieved from poled polymeric composites using these polyenic chromophores as dopants [20]. There remains strong

---

* Corresponding author.
** Corresponding author.
E-mail addresses: liufg6@gzhu.edu.cn (F. Liu), jiahaiwang@gzhu.edu.cn (J. Wang).

https://doi.org/10.1016/j.dyepig.2018.04.036
Received 28 February 2018; Received in revised form 1 April 2018; Accepted 20 April 2018

continued interest in improving the properties of these materials as well as the synthetic strategies for their preparation.

Julolidinyl-based group as the electron donor has been reported with better solubility, stronger electron-donating ability and larger steric hindrance than the classical dimethylanilino moiety [21]. The ring-fused aminophenyl structures in julolidinyl donors facilitate the overlap of the p-orbital of the amino atom with the phenyl ring thus providing a good mechanism to increase the electron-donating strength [22]. Meanwhile, the steric hindrance and tension of the rigid structure from the julolidinyl-based donor in chromophore can also suppress aggregations. So, the electro-optic coefficient of the chromophore can be further improved by using julolidinyl-based group as the donor. Previous study showed that the CLD-type chromophores are often a mixture of trans and cis isomers. The chromophore with cis and trans configuration showed reduced μβ value than that of chromophore with all-trans conformation. And attempts to purify these isomers through column chromatography for higher NLO activity are proven to be very difficult [20].

So, in this paper, we want to increase the electro-optic activity of isophorone-based chromophore furthermore. We use julolidinyl group as the donor of the chromophore. Meanwhile, we utilized epoxyisophorone ring-opening chemistry to efficiently incorporate the 2-((tert-butyldimethylsilyl)oxy)ethanethiol (STBDMS) group to the bridge of julolidinyl-based chromophores FLD3-FLD4 (Chart 1) to ensure its all-trans conformation. The modification of STBDMS group on the chromophore can prevent close packing of molecules, which in turn, may attenuate the strong dipole-dipole electrostatic interactions bewteen chromophores to improve poling efficiency of EO polymers. And compared with the nonsubstituted analogue chromophore FLD1, thiolated chromophore FLD3 achieves higher molecular hyperpolarizability because of unique and moderate π-accepting ability of the substituted group. In the meantime, we synthesized chromophore FLD4 with the same donor and bridge but with a different CF_3-Ph-TCF acceptor.

We compare the structure-property relationship between the 4 s-order chromophores with julolidinyl-based donors and tetraene-derived bridge, but with different position and quantity of the functionalized connecting spacer and different acceptor. As shown in Chart 1, the chromophores FLD1 and FLD2 have only one side-group covalently attached to the donor. The chromophores FLD3 and FLD4 have one side-groups covalently attached to the donor and other one side-groups covalently attached to the π-system bridge. The four chromophores have similar D-π-A structure, but differ in the position and quantity of the spacer, allowing us to investigate the influence of the spacer on the poling-induced alignment of the chromophores. The UV–Vis, solvatochromic behavior, DFT quantum mechanical calculations, thermal stabilities and EO activities of these chromophores were systematically studied and compared to understand their structure-property relationships. An electro-optic (EO) coefficient of 238 pm/V at 1.31 μm was obtained for film FLD3/APC, which is nearly 60% higher than that obtained from analogue chromophore FLD1 and much higher than chromophore FLD2 and FLD4 as well as similar reported monolithic materials like chromophore CLD-1 [23] and chromophore YLD-124 [24].

2. Experimental

2.1. Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. *N*, *N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). Compounds 2b-6b and chromophores FLD1 and FLD2 were synthesized according to literature [25]. 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 on an Advance Bruker 400 M (400 MHz) NMR spectrometer (tetramethylsilane as internalreference). 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^{-1} under the protection of nitrogen.

2.2. Syntheses

2.2.1. Synthesis of 8-(2-((tert-butyldimethylsilyl)oxy)ethoxy)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde (Compound 2a)

Under a N_2 atmosphere, anhydrous potassium carbonate (2.4 g, 15 mmol) was added to a solution of compound 1 (2.73 g, 10 mmol) and compound tert-butyl(2-chloroethoxy)dimethylsilane (2.92 g, 15 mmol) in DMF (90 mL). The mixture was allowed to stir at 90 °C for 12 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 = 1:10) to give compound 2a as a yellow powder with 90.7% yield (3.91 g, 9.07 mmol). MS (MALDI-TOF), *m/z*: 431.59 (M^+). ^1H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.58 (s, 1H), 4.06–3.99 (m, 4H), 3.32–3.26 (m, 2H), 3.25–3.20 (m, 2H), 1.74–1.57 (m, 4H), 1.44 (s, 6H), 1.26 (s, 6H), 0.91 (s, 9H), 0.11 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.72, 161.44, 148.29, 126.10, 125.73, 120.91, 117.04, 79.10, 62.48, 47.49, 47.45, 46.86, 46.83, 39.38, 35.69, 32.56, 32.04, 29.87, 26.03, 25.90, 18.37, −5.12. Anal. Calcd (%) for $C_{25}H_{41}NO_3Si$: C, 69.56; H, 9.57; N, 3.24; found: C, 69.57; H, 9.55; N, 3.23;

2.2.2. Synthesis of (E)-3-(2-(8-(2-((tert-butyldimethylsilyl)oxy)ethoxy)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)vinyl)-2-((2-((tert-butyldimethylsilyl)oxy)ethyl)thio)-5,5-dimethylcyclohex-2-en-1-one (Compound 3a)

To a solution of ethanol (30 mL) was carefully added sodium metal (0.23 g, 10.00 mmol) under N_2 atmosphere. The solution was vigorously stirred at room temperature until the sodium was completely dissolved. 1-Butanethiol (0.78g, 10 mmol) was added to the above solution by syringe, and the mixture was stirred for 10 min followed by addition of isophoroneoxide (1.54 g, 10.00 mmol). The mixture became dark shortly and was stirred at room temperature for another 1h to form intermediate. Compound 2a (2.16 g, 5.00 mmol) was added to the mixture which was then heated to 65 °C for 18 h. After the removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to afford a red solid 3a in 76.3% yield (2.40 g, 3.82 mmol). MS (MALDI-TOF), *m/z*: 628.03 (M^+). ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, $J = 16.2$ Hz, 1H), 7.39 (s, 1H), 7.34 (d, $J = 16.2$ Hz, 1H), 4.04 (t, $J = 5.1$ Hz, 2H), 3.90 (t, $J = 5.1$ Hz, 2H), 3.56 (m, 3H), 3.27–3.21 (m, 2H), 3.20–3.12 (m, 2H), 2.82 (t, $J = 5.2$ Hz, 2H), 2.65 (s, 2H), 2.44 (s, 2H), 1.75–1.69 (m, 4H), 1.43 (s, 6H), 1.29 (s, 6H), 1.07 (s, 6H), 0.91 (s, 9H), 0.13(s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.20, 161.16, 157.25, 144.72, 135.40, 126.94, 126.16, 123.62, 122.53, 122.21, 116.68, 76.33, 62.55, 60.27, 51.64, 47.41, 46.83, 41.47, 39.89, 38.78, 36.18, 32.71, 32.36, 32.22, 30.81, 30.12, 30.09, 28.45, 28.42, 26.06, 26.02, 18.48, −5.11. Anal. Calcd (%) for $C_{36}H_{57}NO_4SSi$: C, 68.85; H, 9.15; N, 2.23; found: C, 68.83; H, 9.13; N, 2.24;

2.2.3. Synthesis of (E)-3-(2-(8-(2-((tert-butyldimethylsilyl)oxy)ethoxy)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)vinyl)-2-((2-((tert-butyldimethylsilyl)oxy)ethyl)thio)-5,5-dimethylcyclohex-2-en-1-one (Compound 4a)

To a solution of compound 3a (1.88 g, 3.00 mmol) and imidazole (0.25 g, 3.60 mmol) in DMF (10 ml), tert-Butyldimethylsilyl chloride (0.55 g, 3.60 mmol) was slowly under N_2 at room temperature. After