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# Enhanced electro-optic activity of two novel bichromophores which are synthesized by Cu(I) catalyzed click-reaction



PIĞMËNTS

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# ABSTRACT

Two novel bichromophores YL1 and YL2 based on traditional aniline chromophore YL were synthesized by Cu(I) catalyzed click-reaction and systematically investigated in this paper. The UV–Vis, electrochemical property, thermal stability and EO activity of these chromophores were systematically studied and discussed. These two bichromophores showed good thermal stability. Then nonlinear optical polymer films were fabricated by doping chromophores into polymethylmethacrylate (PMMA). The doped films containing bichromophores YL1 and YL2 showed r<sub>33</sub> values of 20 and 17 p.m./V at concentration of 25 wt% at 1310 nm. These values were respectively 2.85 times and 2.43 times of the EO activity of chromophore YL (7 p.m./V). High r<sub>33</sub> values indicated that the new structure of bichromophores YL1 and YL2 can reduce intermolecular electrostatic interactions, thus enhancing macroscopic EO activity. These properties suggested the potential use of the new bichromophores in nonlinear optical materials.

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# 1. Introduction

Organic electro-optic (EO) materials have attracted considerable attention over past three decades because of their potential applications in high-speed and broadband information technology [1–5]. The most highly studied material type in this field is called poled guest-host polymeric material in which EO chromophores are dispersed in a polymer matrix [6,7]. In recent years, many chromophores with large hyperpolarizability ( $\beta$ ) were synthesized successfully and studied [8–13]. However, the large microscopic hyperpolarizability  $(\beta)$  of chromophores usually could not be translated into high macroscopic nonlinear optical (NLO) activity (electro-optic coefficient r<sub>33</sub>) of polymer materials effectively due to very strong interchromphore dipole-dipole interactions. These interchromphore dipole-dipole interactions could lead to unfavourable anti-parallel packing of the chromophoric units [14–16]. Thus, how to suppress the dipole interactions among chromophores has become the focus of researchers.

Rational structure designs of bichromophores structure are considered as an effective solution along with much research [17]. The reason is that the core or other groups in bichromophores can act as isolation groups to weak interchromphore dipole-dipole interactions. And bichromophores also exhibit high physical stability, high chemical stability, and good optical transparency. Generally, bichromophores and trichromophores were mostly synthesized by incorporating chromophores with ester groups in past reports [18–21]. However, this single design method sometimes could not meet further processing requirements of all kinds of chromophores. We need some other high efficient methods to prepare bichromophores and trichromophores.

The Cu(I) catalyzed click-reaction mostly was used by synthesizing the azo-type chromophores in organic NLO materials field and this reaction usually has very high yield (about 90%) [22–24]. The triazole group in chromophores can act as isolation groups for enhancing macroscopic NLO effect. Moreover, the synthesis condition of click-reaction is moderate, which is an important advantage because most chromophores are unstable in acid or alkali. Moreover, the chromophores containing triazole groups also exhibit good chemical and thermal stability [25].

In this work, we utilized Cu(I) catalyzed click-reaction to



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produce EO bichromophores YL1 and YL2 with traditional aniline chromophore YL as branch and phenyl or pentafluorophenyl as core (Chart 1). The traditional aniline chromophore YL is easily synthesized and can represent aniline-type chromophores well. EO chromophores containing pentafluorophenyl groups have been reported in the literature and shown to exhibit enhancements in solubility and NLO coefficient ( $r_{33}$ ) [26,27]. At the same time, the bichromophore YL2 containing phenyl group was designed as comparative item. In this paper, the synthesis, UV–Vis, solvatochromic, electrochemical property, thermal stability and EO activity of these chromophores were systematically studied and compared to illustrate architectural influences on rational NLO bichromophore designs.

## 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), triethylamine ( $N(C_2H_5)_3$ ), tetrahydrofuran (THF) and acetone were distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). 2-Dicyanomethylene-3-cyano-4methyl-2,5-dihydrofuran(TCF) acceptor was prepared according to the literature [28]. Chromophore YL was synthesized according to the literature [18]. Compound 3, 4 and 5 were synthesized according to literature [29]. 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).

<sup>1</sup>HNMR spectra were determined using an Advance Bruker 400 (400 MHz) NMR spectrometer (tetramethylsilane as an internal reference). The MS spectra were obtained on MALDI-TOF-(Matrix Assisted Laser Desorption/Ionization of Flight) on a BIFLEXIII (Broker Inc.) spectrometer. The UV–Vis spectra were performed on a Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA Co) at a heating rate of 10 °C·min<sup>-1</sup> under the protection of nitrogen. Cyclic voltammetry (CV) experiments were performed on a CHI660D electrochemical workstation by a cyclic voltammetry (CV) technique in CH<sub>3</sub>CN solution, using a Pt disk electrode and a platinum 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. The melting points were obtained by TA DSC Q10 under N<sub>2</sub> at a heating rate of 10 °C·min<sup>-1</sup>.

# 2.2. Syntheses

## 2.2.1. Synthesis of compound 1

A solution of 4-[(2-hydroxyethyl)(methyl)amino]-benzaldehyde (1 g, 5.6 mmol) and Et<sub>3</sub>N (1.15 mL, 7.3 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was stirred for 10 min at room temperature. para-Toluenesulfonyl chloride (1.6 g, 8.4 mmol) was added to the reaction mixture, which was stirred for 22 h. The reaction mixture was extracted with a saturated solution of NaHCO<sub>3</sub>. The organic phase was dried over anhydrous MgSO<sub>4</sub>. After filtration and removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1: 1) to give compound 1 as a white solid in 80% yield (1.49 g, 4.48 mmol).

<sup>1</sup>HNMR (400 MHz, Acetone)  $\delta$  9.74 (s, 1H), 7.68 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 4.29 (t, *J* = 5.2 Hz, 2H), 3.82 (t, *J* = 5.1 Hz, 2H), 3.01 (s, 3H), 2.38 (s, 3H).

MS (EI): *m*/*z* calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>4</sub>S: 333.10; found: 333.15.

## 2.2.2. Synthesis of compound 2

Sodium azide (12 g, 185 mmol) was added into a solution of compound 1 (15 g, 45 mmol) in 50 mL dry DMF. The reaction mixture was stirred at room temperature to subside heat by this exothermic reaction. After stirring for 24 h, the resulting mixture was poured into 200 mL of cold water with crushed ice and extracted with  $3 \times 50$  mL of ethyl acetate. The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated via rotary evaporation. The residual amount of DMF was removed in vacuo. After removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1: 6) to give compound 2 as a white solid in 90% yield (8.26 g, 40.5 mmol).

<sup>1</sup>HNMR (400 MHz, Acetone)  $\delta$  9.77 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 3.74 (t, J = 5.8 Hz, 2H), 3.62 (t, J = 5.7 Hz, 2H), 3.14 (s, 3H).

MS (EI): *m*/*z* calcd for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>O: 204.10; found: 204.13.

## 2.2.3. Synthesis of compound 3

To a stirred solution of propargyl bromide (3.26 g, 27.37 mmol) and methyl 3,5-dihydroxybenzoate (2 g, 11.9 mmol), in acetone



Chart 1. Chemical structure for chromophores YL, YL1 and YL2.

(40 mL) were added potassium carbonate (7 g, 50.72 mmol). The reaction mixture was heated at reflux under nitrogen for 24 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 200 mL). The combined extracts were washed with water and dried over MgSO<sub>4</sub>. After filtration and removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1: 8) to give compound 3 as a white solid in 90% yield (2.19 g, 10.71 mmol).

<sup>1</sup>HNMR (CDCl<sub>3</sub>)  $\delta$ : 7.31 (s, 2H), 6.83 (s, 1H), 4.73 (d, J = 2.4 Hz, 2H), 3.92 (s, 3H), 2.55 (t, J = 2.4 Hz, 2H).

MS (EI): *m*/*z* calcd for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>: 244.07; found: 244.09.

# 2.2.4. Synthesis of compound 4

To a stirred solution of the compound 3 (6.9 g, 28.3 mmol) in anhydrous THF (100 mL) was added lithium aluminum hydride (2 g, 52.6 mmol) in small portions, and the reaction mixture was stirred at room temperature for 2 h. Beckstrom's reagent (7 g) was then added to quench the remaining lithium aluminum hydride. The reaction mixture was filtered under vacuum, the solid was rinsed with dichloromethane, and the filtrate was dried with MgSO<sub>4</sub>. After evaporation of the solvents, the crude product was purified by recrystallization from methanol to give compound 4 as white crystals in 90% yield (5.5 g, 25.47 mmol).

<sup>1</sup>HNMR (CDCl<sub>3</sub>)  $\delta$ : 6.56 (s, 2H), 6.46 (s, 1H), 4.61 (d, J = 2.4 Hz, 4H), 4.45 (s, 2H), 2.46 (t, J = 2.4 Hz, 2H).

MS (EI): *m*/*z* calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>: 216.08; found: 216.04.

# 2.2.5. Synthesis of compound 5

To a stirred solution of the compound 4 (4 g, 18.5 mmol) in anhydrous THF (100 mL) was added carbon tetrabromide (9.2 g, 27.75 mmol) followed by the portionwise addition of triphenylphosphine (7.27 g, 27.75 mmol). The reaction was stirred at room temperature for 1 h and the quenched with 50 mL of water. Tetrahydrofuran was evaporated, and the crude product was extracted with dichloromethane (2 × 100 mL). The organic layer was dried with MgSO<sub>4</sub>. After filtration and removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (Dichloromethane: Hexane = 1: 1) to give compound 5 as a pale yellow solid in 85% yield (4.39 g, 15.72 mmol).

<sup>1</sup>HNMR (CDCl<sub>3</sub>) δ: 6.57 (s, 2H), 6.46 (s, 1H), 4.58 (d, J = 2.4 Hz, 4H), 4.33 (s, 2H), 2.46 (t, J = 2.4 Hz, 2H).

MS (EI): *m*/*z* calcd for C<sub>13</sub>H<sub>11</sub>BrO<sub>2</sub>: 277.99; found: 277.91.

#### 2.2.6. Synthesis of compound 6a

To a stirred solution of 5 (0.46 g, 1.65 mmol) and Pentafluorophenol (0.28 g, 1.5 mmol), in acetone (20 mL) were added potassium carbonate (0.23 g, 1.65 mmol) and 18-crown-6 (0.1 g, 0.4 mmol). The reaction mixture was heated at reflux under nitrogen for 24 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane ( $2 \times 100$  mL). The combined extracts were washed with water and dried over MgSO<sub>4</sub>. After filtration and removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1: 1) to give compound 6a as a pale yellow solid in 80% yield (0.46 g, 1.2 mmol).

<sup>1</sup>HNMR (400 MHz, Acetone)  $\delta$  6.77 (s, 2H), 6.67 (s, 1H), 5.24 (s, 2H), 4.80 (s, J = 1.6 Hz, 4H), 3.08 (s, 2H).

MS (EI): *m*/*z* calcd for C<sub>19</sub>H<sub>11</sub>F<sub>5</sub>O<sub>3</sub>: 382.06; found: 382.12.

#### 2.2.7. Synthesis of compound 6b

The procedure for compound 6a was followed to prepare 6b as white solid in 79% yield (0.34 g, 1.18 mmol).

<sup>1</sup>HNMR (400 MHz, Acetone)  $\delta$  7.27 (t, J = 7.4 Hz, 2H), 6.99 (d,

*J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.75 (s, 2H), 6.60 (s, 1H), 5.03

(s, 2H), 4.75 (d, *J* = 1.8 Hz, 4H), 3.03 (s, 2H).

MS (EI): *m*/*z* calcd for C<sub>19</sub>H<sub>11</sub>F<sub>5</sub>O<sub>3</sub>: 292.11; found: 292.16.

# 2.2.8. Synthesis of compound 7a

Compound 2 (1.18 g, 5.76 mmol), compound 6a (1 g, 2.62 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (10 mol%), NaHCO<sub>3</sub> (20 mol%), and ascorbic acid (20 mol%) were dissolved in tert-butanol/H<sub>2</sub>O (10 mL/10 mL) under nitrogen in a Schlenk flask. The mixture was stirred at 25 °C overnight, then extracted with chloroform, washed with 1N HCl, 1N NH<sub>4</sub>OH and water subsequently. The organic layer was dried over MgSO<sub>4</sub>. After filtration and removal of solvent under vacuum, the crude product was purified by silica chromatography, eluting with (Methanol: Dichloromethane = 1: 1) to give compound 7a as a yellow solid in 85% yield (1.76 g, 2.23 mmol).

<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.68 (s, 2H), 7.66 (s, 4H), 7.64 (s, 2H), 6.62 (t, *J* = 4.9 Hz, 4H), 6.60 (s, 2H), 6.54 (s, 1H), 5.11 (s, 4H), 5.07 (s, 2H), 4.61 (t, *J* = 5.7 Hz, 4H), 3.96 (t, *J* = 5.7 Hz, 4H), 2.83 (s, 6H).

MS(MALDI-TOF): *m*/*z* (M+, C<sub>39</sub>H<sub>35</sub>F<sub>5</sub>N<sub>8</sub>O<sub>5</sub>): calcd:791.27; found: 791.20.

#### 2.2.9. Synthesis of compound 7b

The procedure for compound 7a was followed to prepare 7b as white solid in 82% yield (1.51 g, 2.15 mmol).

<sup>1</sup>HNMR (400 MHz, Acetone) δ 9.72 (s, 2H), 8.04 (s, 2H), 7.67 (d, J = 8.2 Hz, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.76 (d, J = 8.4 Hz, 4H), 6.73 (s, 2H), 6.65 (s, 1H), 5.15 (s, 4H), 5.05 (s, 2H), 4.72 (t, J = 5.7 Hz, 4H), 4.05 (t, J = 5.7 Hz, 4H), 2.86 (s, 6H).

MS(MALDI-TOF): *m*/*z* (M+, C<sub>39</sub>H<sub>35</sub>F<sub>5</sub>N<sub>8</sub>O<sub>5</sub>): calcd:701.31; found: 791.35.

#### 2.2.10. Synthesis of chromophore YL1

A solution of 7a (1.57 g, 1.98 mmol) and TCF (0.87 g, 4.36 mmol) in 50 mL ethanol was refluxed for 2 h, then cooled to room temperature. After the removal of solvent, the residue was purified by column chromatography (Acetone: Hexane = 1: 2) to give a golden solid chromophore YL1 (1.37 g, 1.19 mmol) in 60% yield.

<sup>1</sup>HNMR (400 MHz, DMSO)  $\delta$  8.24 (s, 2H), 7.89 (d, *J* = 15.9 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 15.9 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 4H), 6.68 (s, 3H), 5.14 (s, 2H), 5.09 (s, 4H), 4.63 (t, *J* = 5.7 Hz, 4H), 3.99 (t, *J* = 5.7 Hz, 4H), 2.85 (s, 6H), 1.75 (s, 12H).

<sup>13</sup>CNMR (101 MHz, DMSO) δ 177.75, 176.06, 159.59, 153.04, 149.62, 143.15, 138.27, 133.11, 129.81 125.56, 122.95, 119.24, 115.68, 113.81, 112.97, 112.20, 109.45, 107.91, 102.24, 98.81, 93.41, 76.87, 68.97, 61.67, 56.31, 51.93, 47.45, 26.04.

MS(MALDI-TOF): m/z (M+, C<sub>61</sub>H<sub>49</sub>F<sub>5</sub>N<sub>14</sub>O<sub>5</sub>): calcd:1153.12; found: 1153.45.

HRMS (ESI) (M + H)<sup>+</sup>: calcd, 1153.4010; found, 1153.4003.

#### 2.2.11. Synthesis of chromophore YL2

The procedure for compound YL1 was followed to prepare YL2 as golden solid chromophore in 55% yield (1.16 g, 1.09 mmol).

<sup>1</sup>HNMR (400 MHz, DMSO)  $\delta$  8.23 (s, 2H), 7.89 (d, J = 15.9 Hz, 2H), 7.72 (d, J = 8.5 Hz, 4H), 7.29 (t, J = 7.5 Hz, 2H), 7.02–6.96 (m, 2H), 6.94 (t, J = 6.8 Hz, 1H), 6.89 (d, J = 15.9 Hz, 2H), 6.75 (d, J = 8.4 Hz, 4H), 6.67 (s, 2H), 6.63 (s, 1H), 5.10 (s, 4H), 5.00 (s, 2H), 4.62 (t, J = 5.7 Hz, 4H), 3.99 (t, J = 5.7 Hz, 4H), 2.84 (s, 6H), 1.74 (s, 12H).

<sup>13</sup>CNMR (101 MHz, DMSO) δ 177.75, 176.04, 159.60, 153.01, 149.62, 143.25, 140.00, 133.13, 129.89, 125.60, 122.96, 121.23, 115.21, 113.83, 112.67, 112.30, 109.47, 107.11, 101.27, 98.80, 93.46, 69.31, 68.97, 61.62, 56.31, 51.97, 47.45, 26.06.

MS(MALDI-TOF): *m*/*z* (M+, C<sub>61</sub>H<sub>54</sub>N<sub>14</sub>O<sub>5</sub>): calcd:1063.17; found: 1063.44.

HRMS (ESI) (M + H)<sup>+</sup>: calcd, 1063.4481; found, 1063.4473.

# 3. Results and discussion

# 3.1. Synthesis and characterization of chromophores

Chromophores YL, YL1 and YL2 were synthesized following the general route laid out in Scheme 1. Starting from 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde, the chromophore YL was synthesized through one step reaction.

The difference between bichromophores YL1 and YL2 is core group of the compound structures. At beginning, the synthesis was carried out in two aspects. On one hand, the derivative 2 was obtained by substituting of the hydroxyl group of 4-[(2hydroxyethyl)(methyl)amino]-benzaldehyde with azide group through two step reactions. The para-Toluenesulfonyl group is a good leaving group, which is beneficial for following SN<sub>2</sub> reaction. On the other hand, starting from 3,5-dihydroxybenzoate, dendritic compounds 6a-b were synthesized in good overall yields (40%– 50%) through four step reactions. The derivative 3 was obtained by substituting with propargyl bromide. Then the ester group of 3 was reduced to the hydroxyl group to give compound 4 with lithium aluminum hydride. After introduction of carbon tetrabromide, the compound 5 was prepared with a high yield (about 90%). Treatment of compound 5 with pentafluorophenol and phenol gave dendritic compounds 6a-b.



Scheme 1. Chemical structures and synthetic routes for chromophores YL1 and YL2.

Next, the compounds 7a-b were prepared by click reaction of the derivative 2 and dendritic compounds 6a-b. The target bichromophores YL1 and YL2 were successfully synthesized by condensing aldehydes 6a and 6b with acceptor TCF in ethanol.

All the chromophores were characterized by <sup>1</sup>HNMR, <sup>13</sup>CNMR, MS, UV–Vis spectroscopic analysis and the data obtained were in full agreement with the proposed formulations. These chromophores possess good solubility in common organic solvents, such as dichloromethane, trichloromethane and acetone.

## 3.2. Thermal stability

NLO chromophores must be thermally stable enough to withstand high temperatures (>200 °C) in electric field poling and subsequent processing of chromophore/polymer materials. Thermal properties of these two bichromophores were measured by Thermogravimetric Analysis (TGA) at a heating rate of 10  $^{\circ}$ C $\cdot$ min<sup>-1</sup> under nitrogen. Fig. 1 shows thermogravimetric analysis of bichromophores YL1 and YL2. The two bichromophores exhibited good thermal-stabilities and their decomposition temperatures (T<sub>d</sub>) were above 250 °C as summarized in Table 1. The triazole group formed by click reaction is thermally stable and the decomposition temperatures of compounds usually increase along with their molecular weight increase. We could conclude that the bichromophore YL2 had better thermal stability than the chromophore YL by comparing their decomposition temperatures. Furthermore, the decomposition temperature( $T_d$ ) of YL1 is lower by about 40 °C than that of YL2, possibly owing to the presence of the pentafluorophenyl group [30]. In a word, the excellent thermal stabilities of bichromophores YL1 and YL2 make them suitable for practical device fabrication and EO device preparation.

## 3.3. Optical properties

The UV–Vis absorption spectra of three chromophores (c =  $1 \times 10^{-5}$  mol L<sup>-1</sup>) were measured in a series of solvents with different constants as shown in Fig. 2. In order to reveal the effect of bichromophores on the intramolecular charge-transfer (ICT) of dipolar chromophores, the chromophore YL was used as reference spectrum.

As shown in Fig. 2, the synthesized YL, YL1 and YL2 chromophores exhibited a similar  $\pi - \pi^*$  intramolecular chargetransfer absorption band in visible region. The maximum absorption



Fig. 1. TGA curves of chromophores YL1 and YL2 with a heating rate of 10  $^\circ C$  min $^{-1}$  in nitrogen atmosphere.

# Table 1

Thermal and Optical Properties data of the Chromophores.

Cmpd	$T_d (^{\circ}C)$	$\lambda_{\max}^{a}(nm)$	$\lambda_{\max}^{b}(nm)$	$\Delta\lambda^{c}(nm)$
YL	283	587	532	55
YL1	264	566	522	44
YL2	309	567	523	44

 $^{a}$   $\lambda_{max}$  was measured in DMF.

<sup>b</sup>  $\lambda_{max}$  was measured in dioxane.

<sup>c</sup>  $\Delta\lambda$  was the difference between  ${}^{a}\lambda_{max}$  and  ${}^{b}\lambda_{max}$ .

wavelengths ( $\lambda_{max}$ ) of YL, YL1 and YL2 in different solvents show a red shift with increase of solvent polarity. In the case of molecules held together via a terminal ring, the most significant UV–Vis absorption is attributed to monochromophore antenna, as literature reported [31]. Besides, the absorption spectra was slightly broadened from monomer to bichromophores, which could be resulted from larger conformational disorder in the bichromophore [32].

The maximum absorption wavelengths ( $\lambda_{max}$ ) of YL, YL1 and YL2 are 587 nm, 566 nm and 567 nm in DMF respectively, as Table 1 shows. Therefore, compared with chromophore YL, the  $\lambda_{max}$  of bichromophores YL1 and YL2 show blue shifts, which may be attributed to spatial interactions between the two subchromophores in YL1 and YL2 [33,34]. This blue shift behaviour can be good for enhancement of transparency of EO device because the light absorptions of the bichromophores YL1 and YL2 are less than that of chromophore YL. In addition, as the core group of the bichromophores don't change their conjugate structure, the  $\lambda_{max}$  of YL1 is similar with that of YL2.

## 3.4. Electrochemical properties

In order to determine the redox properties of chromophores YL, YL1 and YL2, cyclicvoltammetry (CV) measurements were conducted in degassed anhydrous acetonitrile solutions containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF) as supporting electrolyte. The relative data and voltammograms of  $1 \times 10^{-4}$  mol/L chromophores YL, YL1 and YL2 were recorded, as shown in Table 2 and Fig. 3.

The HOMO and LUMO levels of the chromophores can be calculated from their corresponding oxidation and reduction potentials [35]. The difference between these two values provides the HOMO-LUMO energy difference  $\triangle E$  (CV), which are 1.788, 1.810 and 1.809 eV for chromophores YL, YL1 and YL2 respectively. Comparing the  $\triangle E$  (CV) value of chromophore YL, the values of bichromophores YL1 and YL2 are a little bigger. This phenomenon may result from the electron withdrawing group-triazole in donor parts of YL1 and YL2. The narrower energy gap indicated easier charge transfer [36]. These results corresponded with the conclusion of UV–Vis spectra analysis.

# 3.5. Electro-optic performance

In order to study macroscopic EO response of these chromophores, the polymer films doped with 25 wt% chromophores into amorphous polymethylmethacrylate (PMMA) were prepared using cyclopentanone as solvent. The resulting solutions were filtered through a 0.2-µm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked at 70 °C in a vacuum oven overnight. The corona poling process was carried out at a temperature of 10 °C above the glass transition temperature ( $T_g$ ) of the polymer. The  $r_{33}$  values of poled films were measured by Teng–Man simple reflection method at a wavelength of 1310 nm using carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from



Fig. 2. UV-Vis absorption spectra of chromophores YL, YL1 and YL2 in six kinds of aprotic solvents with varying dielectric constants.

## multiple reflections [37,38].

The  $r_{33}$  values can be calculated by the following equation [39]:

Table 2

Summary of electro-chemical data and EO coefficients of chromophores.

Cmpd	$\Delta E(CV)^{a}(eV)$	$E_{ox}^{b}(V)$	$E_{red}^{c}(V)$	r <sub>33</sub> (pm/V)
YL	1.79	0.999	-0.789	7
YL1	1.81	1.036	-0.774	20
YL2	1.81	1.043	-0.766	17

 $^{a}$   $\Delta E(CV)$  was calculated from their corresponding oxidation and reduction potentials.

<sup>b</sup> Oxidation potentials referenced to ferrocene/ferrocenium standard.

<sup>c</sup> Reduction potentials referenced to ferrocene/ferrocenium standard.



**Fig. 3.** Cyclic voltammograms of chromophores YL, YL1 and YL2 recorded in CH3CN solutions containing 0.1 M  $Bu_4NPF_6$  supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>.

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{3/2}}{(n^2 - 2\sin^2 \theta)} \frac{1}{\sin^2 \theta}$$

where  $r_{33}$  is the EO coefficient of the poled polymer,  $\lambda$  is the optical wavelength,  $I_c$  is the output beam intensity,  $I_m$  is the amplitude of the modulation,  $V_m$  is the modulating voltage, and n is the refractive indices of the polymer films.

If intermolecular electrostatic interactions are neglected, the electro-optic coefficient ( $r_{33}$ ) should increase linearly with chromophore density, dipole moment, first hyperpolarizability and the strength of electric poling field. But chromophores with a large dipole moment generate intermolecular static electric field dipole-dipole interaction, which leads to the unfavourable antiparallel packing of chromophores. So the number of truly oriented chromophore is small. To achieve high EO coefficient, the chromophores should have large  $\mu\beta$ , meanwhile the dipole-dipole interactions of chromophores has been considered as an excellent method which not only can take use of chromophores with high first hyperpolarizability ( $\beta$ ) but also restrain the dipole-dipole interactions of chromophores to some extent [17].

The EO coefficient r<sub>33</sub> values of the poled films of YL/PMMA, YL1/PMMA and YL2/PMMA are 7, 20 and 17 p.m./V, respectively. The r<sub>33</sub> values of YL1/PMMA and YL2/PMMA are 2.85 times and 2.43 times of YL/PMMA, which can be attributed to the effect of novel structures of these bichromophores. Comparing with regular chromophore YL, the unfavourable antiparallel packing of bichromophores YL1 and YL2 in EO polymeric material may become difficult. This should because the triazole groups formed by click reaction can act as the intramolecular isolation groups of



Fig. 4. UV–Vis absorption spectra of the poled and depoled YL/PMMA, YL1/PMMA and YL2/PMMA films.

bichromophores, which are utilized frequently in dendrimer EO

materials [25]. In addition, the  $r_{33}$  value of YL1/PMMA is a little bigger than that of YL2/PMMA. The reason may be that the pentafluorophenyl groups can obviously improve the compatibility of bichromophores in polymer. We have tried to prepare EO films doped different concentrations of bichromophores YL1 and YL2. When the doping concentration of YL2 reached 25 wt%, the YL2/ PMMA system was at the edge of the phase separation. However, the YL1 bichromophores with pentafluorophenyl in structure show better compatibility and the highest doping concentration can be 30 wt%. Besides, the pentafluorophenyl can act as a better isolation group in EO materials as the literature [23] reported.

The order parameters ( $\Phi$ ) of poled EO films were also studied by recording UV-Vis absorption spectra of poled films and depoled films. After corona poling, the chromophores in the polymer were aligned, and the absorption intensity decreased due to birefringence. The order parameters  $(\Phi)$  can be calculated according to the following equation:  $\Phi = 1 - A_1/A_0$ , where  $A_0$  and  $A_1$  are the absorbance of depoled and poled EO films at normal incidence. So the order parameters  $(\Phi)$  can indicate proportion of aligned chromophores in poled films, which represent poling efficiency of EO films to some extent. Depoled films can be obtained by heating poled films above Tg for 20 min to make chromophores become disorganized again. The  $\Phi$  values of YL/PMMA, YL1/PMMA and YL2/ PMMA films were about 11%, 20% and 16% respectively. These values reached the average values (10%-20%), which meant that the poling process was typically efficient [8]. The  $\Phi$  values of YL1/ PMMA and YL2/PMMA films both were bigger than that of YL/ PMMA films. The result was in accordance with the EO coefficient  $r_{33}$  values, which can illustrate the advantage of bichromophores in poling process. We verified the conclusion that triazole groups can act as excellent isolation groups to suppress possible aggregation. Besides, the  $\Phi$  values of the YL1/PMMA and YL2/PMMA also had small difference that might be ascribed to the effect of pentafluorophenyl group (see Fig.4).

# 4. Conclusions

Two novel bichromophores basing on simple aniline chromophore were designed by utilizing Cu(I) catalyzed click-reaction and synthesized successfully. The yields of bichromophores were relatively high (about 20%) through 8 steps. Moreover, the reaction condition of Cu(I) catalyzed click-reaction is moderate, which could be applied to many chromophores. The decomposition temperatures ( $T_d$ ) of bichromophores YL1 and YL2 were both above 250 °C. The ability of intramolecular charge-transfer (ICT) of bichromophores YL1 and YL2 become a little weaker comparing chromophore YL from the UV-Vis spectra and cyclic voltammogram. This effect can lead to the improvement of transparency of EO device made by bichromophores. The doped EO films containing bichromophores YL1 and YL2 showed higher r<sub>33</sub> values and poling efficiency comparing with chromophore YL. These results indicated that there were advantages of the novel bichromophores structures in promoting the translation from microscopic hyperpolarizability  $(\beta)$  of chromophores to macroscopic nonlinear optical (NLO) activity of corresponding polymer materials. We believe that the novel bichromophores can be used in exploring high-performance organic EO materials which have high optical nonlinearity, good thermal stability and low optical loss.

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## References

- Sullivan PA, Dalton LR. Theory-inspired development of organic electro-optic materials. Accounts Chem Res 2010;43(1):10–8.
   Dalton LR, Sullivan PA, Bale DH. Electric field poled organic electro-optic
- [2] Dalton LR, Sullivan PA, Bale DH. Electric field poled organic electro-optic materials: state of the art and future prospects. Chem Rev 2010;110(1): 25–55.
- [3] Wu J, Bo S, Liu J, Zhou T, Xiao H, Qiu L, et al. Synthesis of novel nonlinear optical chromophore to achieve ultrahigh electro-optic activity. Chem Commun (Camb) 2012;48(77):9637–9.
- [4] Liu FG, Wang HR, Yang YH, Xu HJ, Yang D, Bo SH, et al. Using phenoxazine and phenothiazine as electron donors for second-order nonlinear optical chromophore: enhanced electro-optic activity. Dyes Pigments 2015;114:196–203.
- [5] Yang YH, Liu FG, Wang HR, Bo SH, Liu JL, Qiu L, et al. Enhanced electro-optic activity from the triarylaminophenyl-based chromophores by introducing heteroatoms to the donor. J Mater Chem C 2015;3(20):5297–306.
- [6] Hammond SR, Clot O, Firestone KA, Bale DH, Lao D, Haller M, et al. Site-isolated electro-optic chromophores based on substituted 2,2'-bis(3,4propylenedioxythiophene) pi-conjugated bridges. Chem Mater 2008;20(10): 3425–34.
- [7] He MQ, Leslie TM, Sinicropi JA, Garner SM, Reed LD. Synthesis of chromophores with extremely high electro-optic activities. 2. Isophorone- and combined isophorone-thiophene-based chromophores. Chem Mater 2002;14(11): 4669–75.
- [8] Hu CL, Liu FG, Zhang H, Huo FY, Yang YH, Wang HR, et al. Synthesis of novel nonlinear optical chromophores: achieving excellent electro-optic activity by introducing benzene derivative isolation groups into the bridge. J Mater Chem C 2015;3(44):11595–604.
- [9] Andreu R, Cerdan MA, Franco S, Garin J, Marco AB, Orduna J, et al. Decreased optical nonlinearities upon CF3 substitution on tricyanofuran acceptors. Org Lett 2008;10(21):4963–6.
- [10] Liao Y, Eichinger BE, Firestone KA, Haller M, Luo JD, Kaminsky W, et al. Systematic study of the structure-property relationship of a series of ferrocenyl nonlinear optical chromophores. J Am Chem Soc 2005;127(8):2758–66.
- [11] Luo JD, Haller M, Ma H, Liu S, Kim TD, Tian YQ, et al. Nanoscale architectural control and macromolecular engineering of nonlinear optical dendrimers and polymers for electro-optics. J Phys Chem B 2004;108(25):8523–30.
- [12] Si P, Liu JL, Zhen Z, Liu XH, Lakshminarayana G, Kityk IV. Synthesis and characterization of NLO chromophore with benzo [1,2-b:4,5-b ']dithiophene unit as pi-electron bridge. Tetrahedron Lett 2012;53(26):3393–6.
- [13] Sen Liu MAH, Ma Hong, Dalton Larry R, Jang Sei-Hum, Jen Alex K-Y. Focused microwave-assisted synthesisof 2,5-dihydrofuran derivatives as ElectronAcceptors for highly efficient nonlinear opticalchromophore. Adv Mater 2003;2003(15):603–7.
- [14] Liakatas I, Cai C, Bosch M, Jager M, Bosshard C, Gunter P, et al. Importance of intermolecular interactions in the nonlinear optical properties of poled polymers. Appl Phys Lett 2000;76(11):1368–70.
- [15] Wang HR, Yang YH, Liu JL, Liu FG, Qiu L, Liu XH, et al. Great improvement of performance for NLO chromophore with cyclopentadithiophenone unit as pielectron bridge. Mater Lett 2015;161:674–7.
- [16] Wu J, Xiao H, Qiu L, Zhen Z, Liu X, Bo S. Comparison of nonlinear optical chromophores containing different conjugated electron-bridges: the relationship between molecular structure-properties and macroscopic electrooptic activities of materials. RSC Adv 2014;4(91):49737-44.
- [17] Gao JK, Cui YJ, Yu JC, Lin WX, Wang ZY, Qian GD. Design and synthesis of bichromophores for nonlinear optical applications in polymer films. React Funct Polym 2011;71(4):496–501.
- [18] Gao JK, Cui YJ, Yu JC, Lin WX, Wang ZY, Qian GD. A 3-phenoxypropane-1, 2diol based bichromophore for enhanced nonlinear optical properties. Dyes Pigments 2010;87(3):204–8.
- [19] Sullivan PA, Akelaitis AJP, Lee SK, McGrew G, Lee SK, Choi DH, et al. Novel dendritic chromophores for electro-optics: influence of binding mode and attachment flexibility on electro-optic behavior. Chem Mater 2006;18(2): 344–51.
- [20] Sullivan PA, Rommel H, Liao Y, Olbricht BC, Akelaitis AJP, Firestone KA, et al.

Theory-guided design and synthesis of multichromophore dendrimers: an analysis of the electro-optic effect. J Am Chem Soc 2007;129(24):7523–30.

- [21] Gao JK, Cui YJ, Yu JC, Lin WX, Wang ZY, Qian GD. Enhancement of nonlinear optical activity in new six-branched dendritic dipolar chromophore. J Mater Chem 2011;21(9):3197–203.
- [22] Wu W, Li C, Yu G, Liu Y, Ye C, Qin J, et al. High-generation second-order nonlinear optical (NLO) Dendrimers that contain isolation chromophores: convenient synthesis by using click chemistry and their increased NLO effects. Chemistry 2012;18(35):11019–28.
- [23] Wu W, Wang C, Li Q, Ye C, Qin J, Li Z. The influence of pentafluorophenyl groups on the nonlinear optical (NLO) performance of high generation dendrons and dendrimers. Sci Rep 2014;4:6101.
- [24] Tang RL, Zhou SM, Xiang WD, Xie YJ, Chen H, Peng Q, et al. New 'X-type' second-order nonlinear optical (NLO) dendrimers: fewer chromophore moieties and high NLO effects. J Mater Chem C 2015;3(17):4545–52.
  [25] Wu WB, Huang LJ, Song CF, Yu G, Ye C, Liu YQ, et al. Novel global-like second-
- [25] Wu WB, Huang LJ, Song CF, Yu G, Ye C, Liu YQ, et al. Novel global-like secondorder nonlinear optical dendrimers: convenient synthesis through powerful click chemistry and large NLO effects achieved by using simple azo chromophore. Chem Sci 2012;3(4):1256–61.
- [26] Knorr DB, Zhou XH, Shi ZW, Luo JD, Jang SH, Jen AKY, et al. Molecular mobility in self-assembled dendritic chromophore glasses. J Phys Chem B 2009;113(43):14180-8.
- [27] Kim TD, Kang JW, Luo J, Jang SH, Ka JW, Tucker N, et al. Ultralarge and thermally stable electro-optic activities from supramolecular self-assembled molecular glasses. J Am Chem Soc 2007;129(3):488–9.
- [28] He MQ, LaJAS TM. r-Hydroxy ketone precursors leading to a novel class of electro-optic acceptors. Chem Mater 2002;2002(14):2393-400.
- [29] Malkoch M, Schleicher K, Drockenmuller E, Hawker CJ, Russell TP, Wu P, et al. Structurally diverse dendritic libraries: a highly efficient functionalization approach using Click chemistry. Macromolecules 2005;38(9):3663–78.
- [30] Wu W, Ye C, Qin J, Li Z. Dendrimers with large nonlinear optical performance by introducing isolation chromophore, utilizing the Ar/ArF self-assembly effect, and modifying the topological structure. ACS Appl Mater interfaces 2013;5(15):7033-41.
- [31] Bazan GC. Novel organic materials through control of multichromophore interactions. J Org Chem 2007;72(23):8615–35.
- [32] Gao JK, Cui YJ, Yu JC, Wang ZY, Wang MQ, Qiu JR, et al. Molecular design and synthesis of hetero-trichromophore for enhanced nonlinear optical activity. Macromolecules 2009;42(6):2198–203.
- [33] Wu W, Ye C, Yu G, Liu Y, Qin J, Li Z. New hyperbranched polytriazoles containing isolation chromophore moieties derived from AB4 monomers through click chemistry under copper(l) catalysis: improved optical transparency and enhanced NLO effects. Chemistry 2012;18(14):4426–34.
- [34] Liao Y, Firestone KA, Bhattacharjee S, Luo JD, Haller M, Hau S, et al. Linear and nonlinear optical properties of a macrocyclic trichromophore bundle with parallel-aligned dipole moments. J Phys Chem B 2006;110(11):5434–8.
- [35] Mukundan Thelakkat H-WS. Synthesis and properties of novel derivatives of 1,3,5-Tris(diarylamino)benzenes for electroluminescent devices. Adv Mater 1998;10(3):219–23.
- [36] Xu HJ, Zhang ML, Zhang AR, Deng GW, Si P, Huang HY, et al. Novel secondorder nonlinear optical chromophores containing multi-heteroatoms in donor moiety: design, synthesis, DFT studies and electro-optic activities. Dyes Pigments 2014;102:142–9.
- [37] Teng CC, Man HT. Simple reflection technique for measuring the electrooptic coefficient of poled polymers. Appl Phys Lett 1990;56(18):1734–6.
- [38] Park DH, Lee CH, Herman WN. Analysis of multiple reflection effects in reflective measurements of electro-optic coefficients of poled polymers in multilayer structures. Opt Express 2006;14(19):8866–84.
- [39] Kajzar F, Lee KS, Jen AKY. Polymeric materials and their orientation techniques for second-order nonlinear optics. In: Lee KS, editor. Polymers for photonics applications ii: nonlinear optical, photorefractive and two-photon absorption polymers. Berlin: Springer-Verlag Berlin; 2003. p. 1–85.
- [40] Wu J, Luo J, Cernetic N, Chen K, Chiang K-S, Jen AKY. PCBM-doped electrooptic materials: investigation of dielectric, optical and electro-optic properties for highly efficient poling. J Mater Chem C 2016;4(43):10286–92.