



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



Yanling He <sup>a, b</sup>, Lu Chen <sup>a, b</sup>, Fenggang Liu <sup>a, b</sup>, Hua Zhang <sup>a, b</sup>, Fuyang Huo <sup>a, b</sup>, Zhuo Chen <sup>a</sup>, Jialei Liu <sup>a</sup>, Zhen Zhen <sup>a</sup>, Xinhou Liu <sup>a</sup>, Shuhui Bo <sup>a, \*</sup>

<sup>a</sup> Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100043, PR China

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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  $r_{33}$  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  $r_{33}$  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  $r_{33}$ ) of polymer materials effectively due to very strong interchromophore dipole-dipole interactions. These interchromophore 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 interchromophore 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

\* Corresponding author.

E-mail address: [boshuhui@mail.ipc.ac.cn](mailto:boshuhui@mail.ipc.ac.cn) (S. Bo).

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-4-methyl-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).

$^1H$ NMR 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  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  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 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<sup>+</sup>) couple was used as an internal reference. The melting points were obtained by TA DSC Q10 under  $N_2$  at a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

### 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  $Et_3N$  (1.15 mL, 7.3 mmol) in anhydrous  $CH_2Cl_2$  (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  $NaHCO_3$ . The organic phase was dried over anhydrous  $MgSO_4$ . 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).

$^1H$ NMR (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  $C_{17}H_{19}NO_4S$ : 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  $MgSO_4$  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).

$^1H$ NMR (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  $C_{10}H_{12}N_4O$ : 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

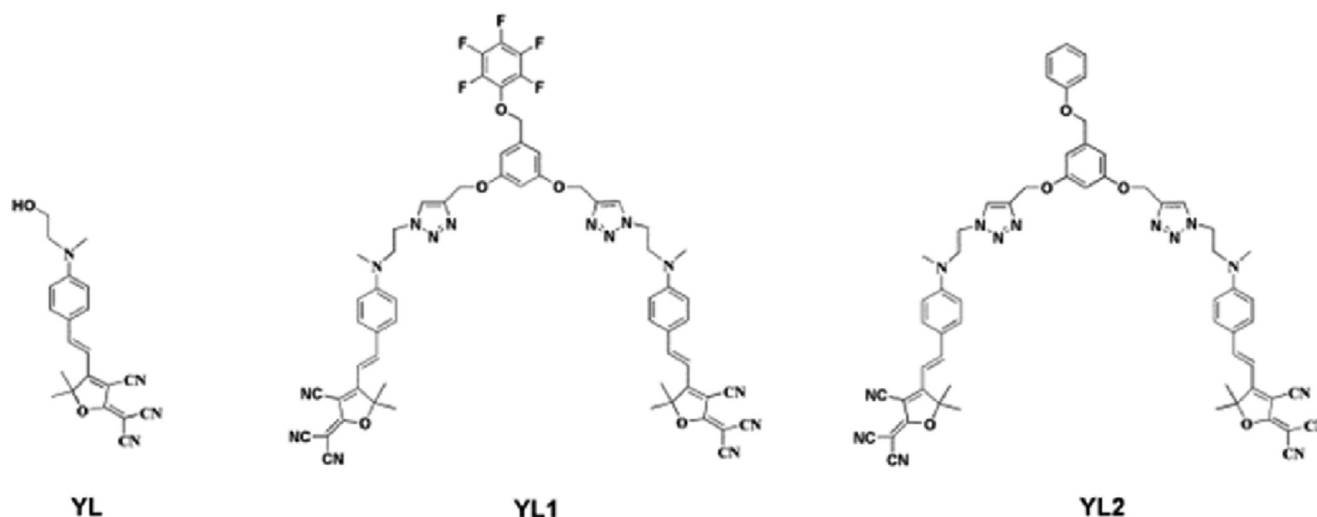


Chart 1. Chemical structure for chromophores YL, YL1 and YL2.

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