



The influence of different donor/acceptor matches on chromophore's nonlinear optical activity



Huajun Xu ^{a, b}, Haoran Wang ^{a, b}, Chaolei Hu ^{a, b}, Mingkai Fu ^{a, b}, Yanling He ^{a, b},
Jialei Liu ^{a, **}, Xinhou Liu ^{a, *}

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

^b University of Chinese Academy of Sciences, Beijing 100043, PR China

ARTICLE INFO

Article history:

Received 4 March 2016

Received in revised form

7 April 2016

Accepted 9 April 2016

Available online 11 April 2016

Keywords:

NLO

Chromophore

Donor

Heteroatom

Electro-optical

ABSTRACTS

In this work, a series of novel second order nonlinear optical chromophores modified by heteroatom-groups in electron-donor has been synthesized and systematically investigated. The resulting nonlinear optical chromophores exhibited both good thermal stability and good solubility in common organic solvents. UV–Vis spectra and density functional theory calculations were carried out to investigate the influence of heteroatom-groups on the electro-optic activities. The results revealed that increasing the electron-donor strength will not always improve the nonlinear optical activity of chromophore. There is a best match for electron-donor and acceptor. As to electro-optic activities, the doped polymer film-**d3** displayed the highest electro-optic coefficient value of 37 pm/v at the doping concentration of 25 wt%. These results indicated that the nonlinear optical activities could be enhanced by finding the best match for electron-donor and acceptor in chromophore design.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

During last two decades, polymeric electro-optic (EO) materials have drawn much attention due to their attractive potential applications in high speed EO devices with broad bandwidth and low driving voltage [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 hot research spot in the area of organic EO materials [7–12]. Much great attentions have been paid to the rational design of chromophores with not only high first-order hyperpolarizability (β) 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 [3,5–7,13–15]. In order to search for highly efficient NLO chromophores, finding an optimal combination of their donor/acceptor still represents one of the critical challenges [16–18]. In the past decade, the researches on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors [19–22]. As the important components of NLO chromophores, however, the electron donors have received much less attention due to that the general class of traditional alkyl and aryl amines were considered to be the idea electron donors and were constantly-used. These amines have been proven to possess suitable energy levels of the nitrogen nonbonding lone pair, which is well matched to donate electrons into the π^* of the attached aromatic ring [7,23].

Several studies have demonstrated that incorporating heteroatom-groups into the donor moiety of chromophores could dramatically modulate the conjugation of the π -electron networks and the electronic character of the charge transfer kinetics, which could further influence the chromophores' β value [5,24–30]. Meanwhile, additional heteroatoms can also provide abundant opportunities for further modifications [5,31]. In order to investigate the influence of heteroatom-group in traditional donor moiety

* Corresponding author.

** Corresponding author.

E-mail addresses: liujialei@mail.ipc.ac.cn (J. Liu), xhliu@mail.ipc.ac.cn, xinhoulou@foxmail.com (X. Liu).

of the NLO chromophores and to achieve better β value and macroscopic EO activities, we designed a series of chromophores in this article with one or two heteroatom-groups incorporated into electron-donor part (Scheme 1). Oxygen atom and nitrogen atom were selected as candidates due to their potential suitable electron-donating abilities. For reasonable comparison, these NLO chromophores all choose 2-dicyanomethylene-3-cyano-4,5,5-dimethyl-2,5-dihydrofuran (TCF) as electron acceptors. ^1H NMR, MS and crystal structure analysis were carried out to demonstrated the preparation of these chromophores. Thermal stability, photo-physical properties, density functional theory (DFT) calculations and EO activities of these chromophores were systematically studied and compared to illustrate the influences of the suitable additional heteroatoms on rational NLO chromophore designs.

2. Experimental section

2.1. Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. N, N-dimethyl formamide (DMF) was distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). Acetone was dried with anhydrous MgSO_4 , then distilled and stored over molecular sieves (pore size 3 Å). The 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature [32–34]. 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).

2.2. Measurements and instrumentation

^1H -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 $10^\circ\text{C min}^{-1}$ under the protection of nitrogen. The single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo- $K\alpha'$ radiation ($\lambda = 0.71073 \text{ \AA}$) at -120°C on a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector.

2.3. Synthesis

2.3.1. General procedure for Vilsmeier Reaction

A solution of 20 mL DMF was cooled to 0°C and was maintained

at this temperature during the dropwise addition of phosphorus oxychloride (0.64 g, 4.2 mmol). The solution was kept stirring at 0°C for 2 h and the temperature was kept constant during the dropwise addition of aromatic amine (2 mmol) in 10 mL DMF. The solution was stirred for 2 h at 0°C , then gradually warmed to room temperature and stirred for 3 h before being poured into 300 mL solution of potassium carbonate (10%) for quenching. The reaction mixture was extracted by ethyl acetate ($100\text{ mL} \times 3$), washed with brine, dried over MgSO_4 . The solvent was removed in vacuo. The resulting crude product was purified by column chromatography with hexane/ethyl acetate as solvent.

2.3.2. General procedure for the synthesis of chromophores

To a solution of aromatic aldehyde (3.0 mmol) and the TCF acceptor (0.64 g, 3.2 mmol) in EtOH (30 mL), several drops of triethylamine were added. The reaction was allowed to stir at 70°C for 2 h and then cooled to room temperature. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with hexane/ethyl acetate.

2.3.3. Synthesis of compound 3

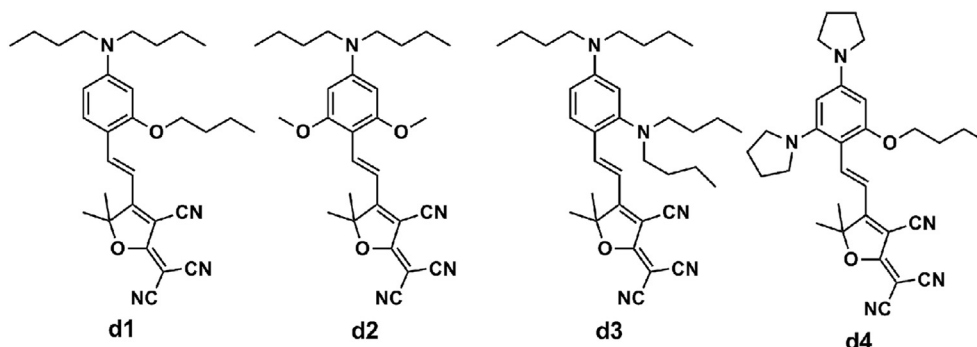
To a stirred solution of compound 2 (1.53 g, 10 mmol) and bromobutane (2.72 g, 20 mmol) in acetonitrile (50 mL) potassium carbonate (4.14 g, 30 mmol) and 18-crown-6 (0.1 g, 0.4 mmol) were added. The reaction mixture was heated at reflux under nitrogen for 24 h, filtered and evaporated to dryness. The crude product was purified by silica chromatography, eluting with ($V_{\text{AcOEt}}:V_{\text{Hexane}} = 1:8$) to give 3 as an orange powder with 82% yield (2.17 g, 8.20 mmol). ^1H NMR (400 MHz, CDCl_3) δ 5.86–5.80 (m, 3H), 3.77 (s, 6H), 3.27–3.17 (m, 4H), 1.62–1.51 (m, 4H), 1.39–1.28 (m, 4H), 0.99–0.90 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.63, 150.03, 91.38, 87.42, 54.84, 50.75, 29.49, 20.17, 13.72. MS, m/z: 265.31 (M^+).

2.3.4. Synthesis of compound 4

This compound was prepared from compound 3 (1.33 g, 5.0 mmol) according to the general procedure for the Vilsmeier Reaction. After column chromatography ($V_{\text{ethyl acetate}}/V_{\text{hexane}} = 1:4$), compound 4 was isolated with 58% yield (0.85 g, 2.9 mmol). ^1H NMR (400 MHz, CDCl_3) δ 10.16 (s, 1H), 5.66 (s, 2H), 3.80 (s, 6H), 3.28 (t, 4H), 1.62–1.49 (m, 4H), 1.38–1.27 (m, 4H), 0.93 (t, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.27, 164.36, 154.14, 87.36, 55.65, 50.90, 29.63, 20.21, 13.80. MS, m/z: 293.22 (M^+).

2.3.5. Synthesis of compound 7

To a stirred solution of compound 9 [35] (2.32 g, 10 mmol) and bromobutane (1.63 g, 12 mmol) in acetone (100 mL), anhydrous potassium carbonate (1.66 g, 12 mmol) and 18-crown-6 (0.025 g, 0.1 mmol) were added. The reaction mixture was heated at reflux under nitrogen for 5 h and then filtered, evaporated to dryness. The



Scheme 1. Synthetic scheme for chromophores d1–d4.

Download English Version:

<https://daneshyari.com/en/article/175293>

Download Persian Version:

<https://daneshyari.com/article/175293>

[Daneshyari.com](https://daneshyari.com)