



The design of nonlinear optical chromophores exhibiting large electro-optic activity and high thermal stability: The role of donor groups



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ABSTRACT

A novel chromophore based on *N*-(4-dibutylaminophenyl)tetrahydroquinolinyl donor group was synthesized to compare with traditional chromophores based on either diethylaminophenyl or triarylaminophenyl donor groups. Cyclic voltammetry measurements showed that the new chromophore had a much smaller energy gap than the structurally related chromophores. Density functional theory calculations suggested that the molecular quadratic hyperpolarizability ($\mu\beta$) value of tetrahydroquinolinyl chromophore is 65% and 110% larger than that of either the diethylaminophenyl or triarylaminophenyl chromophores, respectively. The doped film containing the tetrahydroquinolinyl chromophore showed an r_{33} value of 126 pm/V at the concentration of 25 wt% which is much higher than the electro-optic activity of the diethylaminophenyl derived chromophore (39 pm/V) and six times higher than that of the traditional triarylaminophenyl chromophore (19 pm/V). The tetrahydroquinolinyl chromophore possesses much higher thermal stability (with its onset decomposition temperature above 280 °C) than those of commonly used alkyl chromophores.

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1. Introduction

Functional materials displaying nonlinear optical (NLO) activity have been extensively studied in recent years because of their potential applications in the field of optical switches, high-speed and broadband information technology, and telecommunications [1–4]. Compared with inorganic materials, organic materials have the potential advantages in faster response time, ease of processing, higher nonlinear optical activity [5–7]. To meet the stringent requirements for device applications, one of the often critical challenges in making highly efficient electro-optic (EO) materials is to develop nonlinear optical (NLO) chromophores with large molecular quadratic hyperpolarizability ($\mu\beta$), good optical transparency, and excellent thermal and chemical stabilities [8,9]. Moreover, weak molecular electrostatic

interactions in the polymer matrix are needed to effectively translate these large $\mu\beta$ values into bulk EO activities [10].

Molecular NLO chromophores are traditionally constituted by electron donor and acceptor moieties covalently connected through a conjugated bridge, called the D– π –A system [11,12]. When considering the design of second-order nonlinear optical materials, optimization of the π -conjugated bridge, electron-donor and electron-acceptor characteristics of the substituents are needed to obtain maximum nonlinearity at the molecular level [13–17]. Alkyl and aryl amines type donors [18,19], the tricyanofuran-based (TCF) family of acceptors [20], and ring-locked tetraene [21] or 2,5-divinylthienyl [22] bridges have all proven to afford highly active and stable dipolar EO chromophores. Among all of the materials studied, the NLO chromophores bearing 4-(dialkylamino)phenyl groups or triarylamine groups as a donating group were the most promising due to their strong electron-donating ability and ease of synthesis [1,23].

The NLO chromophores with a triarylamine (TAA) donor and a thiophene-bridge exhibit the highest thermal stability of all reported chromophores, which seems to be the best candidate for the

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active EO materials in a practical device [24,25]. However, compared to their alkyl counterparts, TAA based chromophores usually exhibit reduced hyperpolarizabilities due to delocalization of the nitrogen lone pair into the two phenyl rings which do not connect with the bridge [26]. The E-O coefficients (r_{33}) values derived from aryl D- π -A chromophores remained between 10 and 20 pm V⁻¹ (at 1310 nm), which are much lower than those obtained from their alkyl D- π -A counterparts [27,28]. These may be due to π - π stacking interactions and charge transport between chromophores [13,29]. However, the dipolar chromophores with 4-(di-alkylamino)phenyl donor have demonstrated significantly weaker thermo- and photostabilities compared to their 4-(diarylamino) phenyl analogues although they show much higher r_{33} values [25,30].

These encouraged us to design and synthesis a novel chromophore combining the advantages of both alkyl and aryl amines type donors where both thermal stability and optical nonlinearity are very high. So, in this paper, we have designed and synthesized a series of chromophores containing an identical thiophene bridge and TCF acceptor, but with three different electron donors, including diethylaminophenyl (FTC), triarylamino phenyl (TPA), and *N*-(4-dibutylaminophenyl) tetrahydroquinolinyl groups (NT) (Chart 1). The diethylaminophenyl donor-based chromophore FTC and triarylamino phenyl donor-based chromophore TPA were chosen as a reference compound for comparison. We developed a novel donor modification approach by attaching an *N*-(4-dibutylaminophenyl) substituent on the donor part of the chromophore. By addition of another phenyl ring on the aromatic donor, the chromophore could exhibit a higher T_d [29]. In order to offset the reduced hyperpolarizability due to delocalization of the nitrogen lone pair into the phenyl rings which do not connect with the bridge, an additional electron-rich nitrogen atom was introduced onto the benzene ring of the donor. In the meantime, the ring-fused amino-phenyl structures in the tetrahydroquinolinyl donor facilitate the overlap of the p-orbital of the amino atom with the phenyl ring, thus providing a good mechanism to gradually increase the electron-donating strength [31,32]. In a properly designed system, significant enhancement in the $\mu\beta$ of the NLO chromophores can be achieved. All these modifications of

chromophore NT can increase the thermal stability and $\mu\beta$ as well as reduce dipole-dipole interactions so as to translate their $\mu\beta$ values into bulk EO performance more effectively. The synthesis, UV-Vis, solvatochromic behaviour, redox properties, DFT quantum mechanical calculations, thermal stabilities and EO activities of these chromophores were systematically studied and compared to illustrate the influence of electron-donating groups on rational NLO chromophore 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), Phosphorus oxychloride (POCl₃), tetrahydrofuran (THF) and ether 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 [33]. Compound **2a** was synthesized according to literature [34]. Compound **2c** was synthesized according to literature [35]. TLC analyses were carried out on 0.25 mm thick pre-coated 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 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 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. Cyclic voltammetric data were measured on a BAS CV-50W voltammetric analyser using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/AgNO₃ as the reference electrode at a scan rate of 100 mV s⁻¹. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile is the electrolyte. The melting points were obtained by TA DSC Q10 under N₂ at a heating rate of 10 °C min⁻¹.

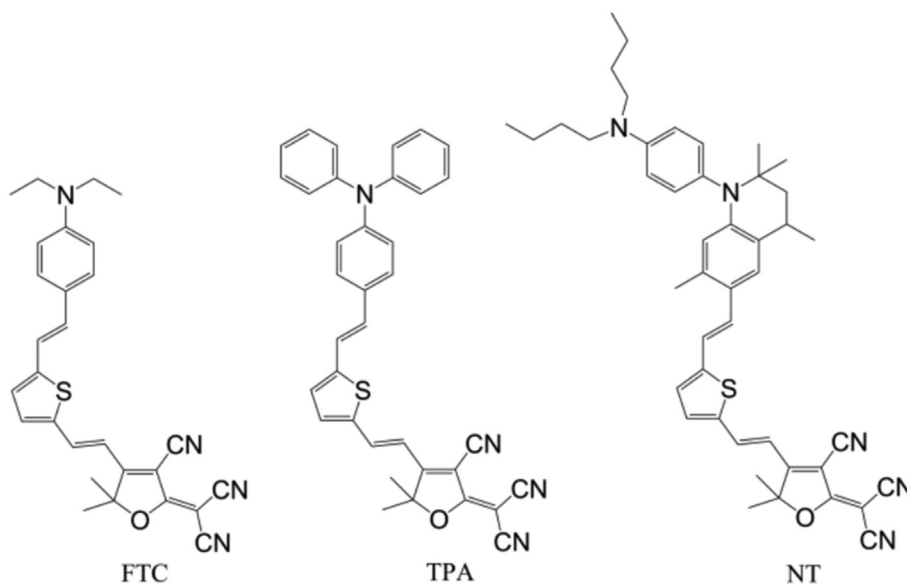


Chart 1. Chemical structure for chromophores FTC, TPA and NT.

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