



Comparative studies on structure–nonlinearity relationships in a series of novel second-order nonlinear optical chromophores with different aromatic amine donors



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ABSTRACT

A series of second-order nonlinear optical chromophores containing an identical π -bridge and electron acceptor but different, aromatic amine electron-donating groups have been synthesized and systematically investigated. The donors studied here include traditional donors carbazole, triphenylamine and *N,N*-diethylaniline and novel donor phenothiazine, phenoxazine and *N*-(4-methoxyphenyl)phenoxazine. The ultraviolet absorption, solvatochromic, redox properties, density functional theory calculations, thermal stabilities and electro-optic activities of these chromophores were systematically studied to compare the strength of the donors and illustrate the structure–performance relationships within six chromophores. The results show that the new donors have stronger electron-donating ability than traditional donors. Moreover, they show reduced energy gap, much larger molecular quadratic hyperpolarizability ($\mu\beta$) and r_{33} value. Exemplified by the *N*-(4-methoxyphenyl)phenoxazine chromophore, it showed nearly three times higher $\mu\beta$ and more than four times higher r_{33} value than that of the *N*-hexylcarbazole containing chromophore.

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1. Introduction

Organic electro-optic (OEO) materials have attracted great attention in recent years due to their potential applications in optical switches, optical sensors, information processors, and telecommunications [1–3]. The OEO materials have many advantages over inorganic materials including lower cost, ease of processing, larger EO coefficients and so on [4–6]. The second-order nonlinear optical (NLO) chromophores are the key construction blocks for OEO materials [7]. One of the most critical challenges in developing these materials is to design and synthesize chromophores with a large molecular quadratic hyperpolarizability ($\mu\beta$), excellent thermal and chemical stabilities, good transparency as well as easy syntheses [8–10]. In addition, organic NLO chromophores, especially those demonstrating high $\mu\beta$ values, typically have large

ground state dipole moments. The strong inter chromophore dipole–dipole interactions may lead to unfavorable antiparallel packing of the chromophores, thus reducing the optical nonlinearities [11], so, weak molecular electrostatic interaction in the polymer matrix is needed to effectively translate these large $\mu\beta$ values into bulk EO activities [12,13].

In general, these chromophores have been constructed with a typical electron donor- π bridge-electron acceptor (D- π -A) configuration [14,15]. When considering the design of second-order nonlinear optical materials, optimization of π -conjugated bridge, electron-donor and electron-acceptor characteristics of the substituents are needed to obtain maximum nonlinearity at the molecular level [16]. Many studies on NLO chromophores have mainly focused on the design of electron bridges and electron acceptors [17–19]. The electron donors, who also play a crucial role in determining the performance of NLO chromophores, have received relatively little attention [16]. Donors derived from 4-(dialkylaminophenyl) examples) groups or triphenylamine were used in most cases [20–22].

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Many different amine-based donors have been used in organic materials chemistry such as second-order NLO [23], third-order NLO [24], two-photon absorption [25] and hole-transport materials [26]. Previously, Marder et al. have systematically compared the strength of electron donors in a series of aminoaryl systems (mainly the aminophenyl examples) using density functional theory (DFT) calculations which provides a valuable guideline for the design of NLO chromophores [27]. However, apart from a few studies very little experimental or theoretical research has been focused on the comparison of different aromatic amine electron-donating groups in the performance of NLO chromophores [16,28].

So, in this study we compare the structure–property relationship between the second-order chromophores with six different donors. The donors are traditional carbazole (CBZ) [29], triphenylamine (TPA) [20] and *N,N*-diethylaniline (FTC) [30] which is often used in second-order chromophore and phenothiazine (PTZ), phenoxazine (POZ) and *N*-(4-methoxyphenyl)phenoxazine (PPZ) which is often employed in dye-sensitized solar cells (DSSCs) [31,32]. The r_{33} values of traditional aryl amine chromophore are much lower than those obtained from their alkyl D- π -A analogs [33]. Recent studies showed that introducing additional heteroatoms into the benzene ring moiety of donor could provide abundant opportunities for further modifications of chromophores thus influence nonlinear optical properties of chromophores [34–36]. So, aryl donors PTZ, POZ and PPZ units were introduced to the second-order NLO chromophores due to its additional electron-rich sulfur or oxygen heteroatom.

The electronic and spatial structures of the donors are quite different. The CBZ and TPA are both typical aryl donors with one electron-rich nitrogen heteroatom, the geometry of CBZ is totally planar, while the three phenyl rings of TPA are symmetrically twisted from the central plane. The PTZ, POZ and PPZ units have strong electron-donating ability with its additional electron-rich nitrogen and sulfur or oxygen heteroatoms. The geometry of PTZ and POZ are not totally planar but are rather slightly bent in the middle to give a butterfly shape [37]. As for PPZ, the two benzene rings exhibited almost planar structures, the *N*-(4-methoxyphenyl) substituent located on the nitrogen atom almost perpendicular with average plane (Fig. 1).

In this study, we have designed and synthesized six chromophores containing an identical thiophene bridge and

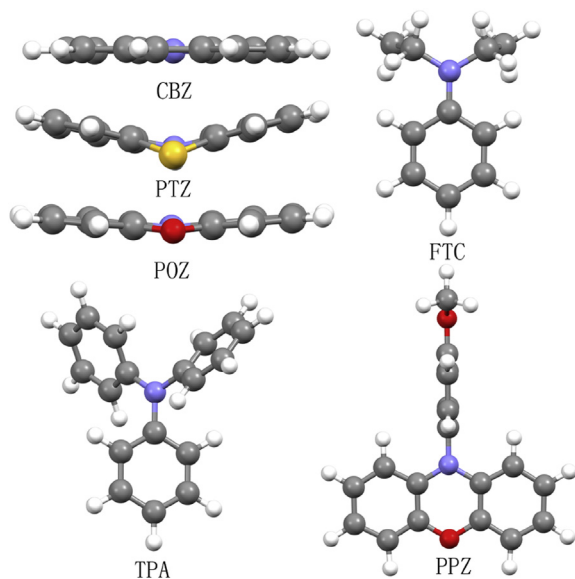


Fig. 1. Optimized structures of the six donors.

tricyanovinylidihydrofuran (TCF) acceptor but different aromatic amine electron-donating groups (Chart 1). The synthesis, UV–vis, solvatochromic behavior, 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 (POCl_3), tetrahydrofuran (THF) and ether were distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). 10-Hexyl-10*H*-phenoxazine (2b) and 10-hexyl-10*H*-phenoxazine-3-carbaldehyde (3b) were synthesized according to the literature [38]. 10-Hexyl-10*H*-phenothiazine (2c) and 10-hexyl-10*H*-phenothiazine-3-carbaldehyde (3c) were synthesized according to previous publication [12]. 10-(4-Methoxyphenyl)-10*H*-phenoxazine (2d) and 10-(4-methoxyphenyl)-10*H*-phenoxazine-3-carbaldehyde (3d) were synthesized according to literature [39]. 2-Dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature [40]. Triphenylamine based chromophore TPA was synthesized according to literature [20]. *N,N*-diethylaniline based chromophore FTC was synthesized according to the literature [30]. 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 400M (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-

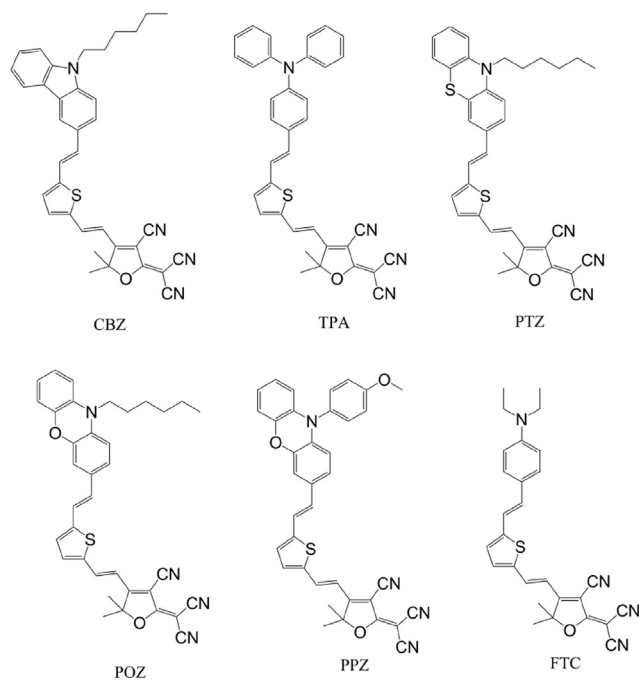


Chart 1. Chemical structure for chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC.

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