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### 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  $\pi$ -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.

Keywords: Nonlinear optical materials; Chromophore; Second-order; Electro-optic; Donor; Heteroatom;

#### 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– $\pi$  bridge–electron acceptor (D– $\pi$ –A) configuration [14, 15]. When considering the design of second-order nonlinear optical materials, optimization of  $\pi$ -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-(dialkylamino)phenyl groups or triphenylamine were used in most cases [20-22].

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 ones) using density functional theory (DFT) calculations which provides a valuable guideline for the design of NLO chromophores [27]. However, apart from a few works, 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].

#### Chart 1

#### Fig. 1

So, in this study we would like to 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 and *N*-(4-methoxcyphenyl)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- $\pi$ -A analogues [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 is both typical aryl donor 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 (Figure 1).

In this study, we have designed and synthesized six chromophores containing an identical thiophene bridge and tricyanovinyldihydrofuran (TCF) acceptor but different aromatic amine electron-donating groups (Chart 1). 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), Phosphorusoxychloride (POCl<sub>3</sub>), tetrahydrofuran (THF) and ether were distilled over calcium hydride and stored over molecular sieves (pore size 3Å).10-Hexyl-*10H*-phenoxazine (2b) and 10-Hexyl-*10H*-phenoxazine-3-carbaldehyde (3b) were synthesized according to literature [38].

10-Hexyl-*10H*-phenothiazine (2c) and 10-Hexyl-*10H*-phenothiazine-3-carbaldehyde (3c) were synthesized according to previous publication [12]. 10-(4-Methoxyphenyl)-*10H*-phenoxazine (2d) and 10-(4-methoxyphenyl)-*10H*-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 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).

<sup>1</sup>HNMR spectra were determined on an Advance Bruker 400M (400 MHz) NMR spectrometer (tetramethylsilane as internalreference). 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<sup>-1</sup> under the protection of nitrogen. Cyclic voltammetric data were measured on a BAS CV-50W voltammetric analyzer using a conventional three-electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/AgNO<sub>3</sub> as the reference electrode at a scan rate of 100 mV s<sup>-1</sup>. The 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAPF) in acetonitrile is the electrolyte. The elemental analyses were measured on Flash EA 1112 Elemental Analyzer. The melt 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 9-hexyl-9H-carbazole (Compound 2a)

Under a N<sub>2</sub> atmosphere, potassium tert-butylate (5.07 g, 45 mmol) was added to a solution of compound 1a

(5.02 g, 30.0mmol) and n-hexylbromide (9.06g, 60.0mmol) in THF (60ml). The mixture was stirred at 48 °C for 12 h and then poured into water. The organic phase was extracted by  $CH_2Cl_2$ , washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane=1:10) to give compound 2a as a yellow oil in 93.4% yield (7.04 g, 28.02 mmol). MS, m/z: 251.17. (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, *J* = 7.6 Hz,2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 5.7 Hz, 2H), 4.26 (t, *J* = 7.1 Hz, 2H), 1.88 – 1.75 (m, 2H), 1.33 (m, 6H), 0.85 (t, J=8.6Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.41, 125.58, 122.85, 120.23, 118.58, 108.62, 43.05, 31.57, 28.79, 26.96, 22.45, 13.99. Anal. Calcd (%) for C<sub>18</sub>H<sub>21</sub>N: C, 86.01; H, 8.42; N, 5.57; found: C, 86.13; H, 8.47; N, 5.53;

#### 2.2.2 Synthesis of 9-hexyl-9H-carbazole-3-carbaldehyde (Compound 3a)

DMF (1.64 g, 22.50 mmol) was added to freshly distilled POCl<sub>3</sub> (2.30 g, 15.00 mmol) under an atmosphere of N<sub>2</sub> nitrogen at 0 °C, and the resultant solution was stirred until its complete conversion into a glassy solid. After the addition of 2a (2.51 g, 10.00 mmol) in 1,2-dichloroethane (60 mL) dropwise, the mixture was stirred at room temperature overnight, then poured into a saturation aqueous solution of sodiumacetate (300 mL). After 2 hour stirring at room temperature, the mixture extracted with chloroform (5 × 30 mL), and the organic fractions were collected and dried over anhydrous MgSO<sub>4</sub>. The crude product was purified through a silica gel chromatography eluting with (Acetone: Hexane = 1:5) to afford a yellow oil 3a in 75.6% yield (2.11 g, 7.56mmol). MS, m/z: 279.16. (M+). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.85 (s, 1H), 8.30 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.32 (m, 1H,ArH), 7.19 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.10 (m, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 1.68 – 1.47 (m, 2H), 1.20 – 0.95 (m, 6H), 0.68 (t, *J* = 5.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  191.18, 143.71, 140.91, 128.33, 126.73, 126.42, 123.47, 122.78, 122.73, 120.39, 119.98, 109.12, 108.59, 42.51, 31.21, 28.57, 26.17, 21.89,

13.51. Anal. Calcd (%) for C<sub>19</sub>H<sub>21</sub>NO: C, 81.68; H, 7.58; N, 5.01; found: C, 81.73; H, 7.52; N, 5.12;

#### 2.2.3 Synthesis of (E)-9-hexyl-3-(2-(thiophen-2-yl) vinyl)-9H-carbazole (Compound 4a)

NaH (0.59 g, 25.00 mmol) was added to a stirred solution of compound 3a (1.26 g, 5.00 mmol) and 3e (3.47 g, 6.00 mmol) in ether (100 mL) under nitrogen. The solution was stirred for 24 h and then poured into water. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:20) to give compound 4a as yellow solid in 84.3% yield (1.51 g, 4.21 mmol), m.p. : 104.6 °C. MS, m/z: 359.17 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.17 (dd, *J* = 14.0, 8.4 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.91 (m, 1H), 6.83 (d, *J* = 4.5 Hz, 1H), 6.76 – 6.70 (m, 1H), 6.65 (d, *J* = 11.9 Hz, 1H), 6.58 (d, *J* = 11.8 Hz, 1H), 3.97 (t, *J* = 6.8 Hz, 2H), 1.63 (m, 2H), 1.13 (m, 6H), 0.76 (t, J=6.8 Hz,3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.58, 140.28, 139.84, 129.88, 127.62, 127.54, 126.56, 126.15, 125.52, 124.73, 122.84, 122.80, 121.92, 120.68, 120.25, 118.79, 108.61, 108.50, 42.80, 31.17, 28.71, 26.54, 22.36, 13.85. Anal. Calcd (%) for C<sub>24</sub>H<sub>25</sub>NS: C, 80.18; H, 7.01; N, 3.90; found: C, 80.23; H, 7.09; N, 3.85;

#### 2.2.4 Synthesis of (E)-10-hexyl-3-(2-(thiophen-2-yl) vinyl)-10H-phenothiazine (Compound 4b)

The procedure for compound 4a was followed to prepare 4b from 3b and 3e as orange oil in 85.7% yield (0.34 g, 0.86 mmol). MS, m/z: 391.14 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (s, 1H), 7.17 (m, 2H), 7.13 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 3.4 Hz, 1H), 6.92 (dd, J = 8.2, 4.6 Hz, 2H), 6.87 (d, J = 8.1 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 11.9 Hz, 1H), 6.44 (d, J = 11.9 Hz, 1H), 3.95 – 3.81 (m, 2H), 1.84 (m, 2H), 1.54 – 1.41 (m, 2H), 1.34 (m, 4H), 0.91 (t, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.88, 143.51, 142.12, 138.79, 132.80, 132.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 46.50, 30.44, 25.77, 25.49, 21.56, 130.17, 127.06, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 126.50, 126.45, 126.13, 125.47, 124.35, 123.51, 121.66, 121.17, 114.15, 126.50, 30.44, 25.77, 25.49, 21.56, 130.17, 124.18, 126, 126.18,

12.98. Anal. Calcd (%) for  $C_{24}H_{25}NS_2$ : C, 73.61; H, 6.43; N, 3.58; found: C, 73.71; H, 6.48; N, 3.63;

#### 2.2.5 Synthesis of (E)-10-hexyl-3-(2-(thiophen-2-yl)vinyl)-10H-phenoxazine (Compound 4c)

The procedure for compound 4a was followed to prepare 4c from 3c and 3e as orange oil with 87.3% yield (0.33 g, 0.87 mmol). MS, m/z: 375.27 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (d, J = 4.8 Hz, 1H), 7.02 (m, ArH, 2H), 6.98 (d, J = 3.8 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.81 (m, 2H), 6.74 (d, J = 16.0 Hz, 1H), 6.65 (m, 2H), 6.48 (d, J = 7.9 Hz, 1H), 6.41 (d, J = 8.2 Hz, 1H), 3.51 – 3.45 (m, 2H), 1.67 (m, 2H), 1.43 (m, 6H), 0.94 (t, J = 5.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 144.69, 143.28 , 132.82 , 132.54, 129.96, 127.48 , 125.29 , 123.54 , 122.77, 120.78, 119.35 , 115.40 , 112.00, 111.36 , 111.11 , 44.06 , 31.64 , 26.59 , 24.99, 22.67 , 14.02. Anal. Calcd (%) for C<sub>24</sub>H<sub>25</sub>NOS: C, 76.76; H, 6.71; N, 3.73; found: C, 76.83; H, 6.82; N, 3.67;

#### 2.2.6 Synthesis of (E)-10-(4-methoxyphenyl)-3-(2-(thiophen-2-yl)vinyl)-10H-phenoxazine (Compound 4d)

The procedure for compound 4a was followed to prepare 4d from 3d and 3e as yellow solid with 82.1% yield (1.63 g, 4.10 mmol). m.p. : 146.8 °C. MS, m/z: 397.11 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 5.0 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 3.4 Hz, 1H), 6.89 (d, *J* = 4.6 Hz, 1H), 6.71 (s, 1H), 6.62 (d, *J* = 9.6 Hz, 2H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 11.9 Hz, 1H), 6.30 (d, *J* = 11.9 Hz, 1H), 5.92 (d, *J* = 7.6 Hz, 1H), 5.87 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.16, 143.67, 143.53, 139.61, 134.18, 133.82, 131.24, 129.82, 128.09, 127.58, 126.33, 125.00, 123.87, 123.04, 121.78, 121.07, 115.99, 115.43, 115.15, 113.0, 112.72, 55.00. Anal. Calcd (%) for C<sub>25</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 75.54; H, 4.82; N, 3.52; found: C, 75.61; H, 4.93; N, 3.49;

2.2.7 Synthesis of (E)-5-(2-(9-hexyl-9H-carbazol-3-yl) vinyl) thiophene-2-carbaldehyde (Compound 5a)

Under a N<sub>2</sub> atmosphere, 4a (0.72 g, 2.00 mmol) was dissolved in 150 mL freshly distilled THF and cooled to -78 °C. Approximately 2 equivalents of BuLi in hexanes (16 mL, 4 mmol) was added drop wise over 20 min. Reaction continued at -78 °C for 1 h at which time DMF (0.29 g, 4.00 mmol) was added over 1 min. The reaction was allowed to reach RT while the solution stirred for 1h. The organic phase was extracted by AcOEt, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (Acetone: Hexane = 1:5) to give compound 6c as an orange solid with 76.7% yield (0.59 g, 1.53 mmol). m.p. : 115.8 °C. MS, m/z: 387.17 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (s, 1H), 8.12 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 3.9 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 3.9 Hz, 1H), 4.18 (t, *J* = 7.3 Hz, 2H), 1.76-1.83(m,2H), 1.38 – 1.29 (m, 2H), 1.26-1.28 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 182.33, 153.53, 140.75, 140.40, 137.44, 134.06, 126.73, 125.96, 125.36, 124.58, 123.14, 122.60, 120.29, 119.38, 119.22, 117.76, 108.81, 43.04, 31.43, 28.81, 26.81, 22.43, 13.92. Anal. Calcd (%) for C<sub>25</sub>H<sub>25</sub>NOS: C, 77.48; H, 6.50; N, 3.61; found: C, 77.52; H, 6.46; N, 3.65;

2.2.8 Synthesis of (*E*)-5-(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)thiophene-2-carbaldehyde (Compound 5b) The procedure for compound 5a was followed to prepare 5b from 4b as a red solid in 73.2% yield (0.26 g, 0.63 mmol). m.p. : 126.48 °C. MS, m/z: 419.64 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.81 (s, 1H), 7.59 (d, J = 3.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.13 (m, 2H), 7.05 (d, J = 3.9 Hz, 1H), 6.99 (d, J = 5.5 Hz, 2H), 6.92 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 3.81 (t, J = 7.2 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.46 – 1.35 (m, 2H), 1.33 – 1.23 (m, 4H), 0.88 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.31, 152.72, 145.52, 144.32, 140.96, 137.23, 131.66, 130.07, 127.29, 127.25, 126.51, 125.96, 125.03, 124.96, 123.80, 122.56, 118.79, 115.35, 115.14, 47.52, 31.32, 26.67, 26.47, 22.48, 13.89. Anal. Calcd (%) for C<sub>25</sub>H<sub>25</sub>NOS<sub>2</sub>: C, 71.56; H, 6.01; N, 3.34; found: C, 71.63; H, 6.11; N, 3.27;

### $\textbf{2.2.9 Synthesis of } (E) \textbf{-5-} (2-(10 \textbf{-hexyl-} 10 \textbf{H}\textbf{-phenothiazin-} 3\textbf{-yl}) \textbf{vinyl}) thiophene \textbf{-2-carbaldehyde} (Compound 5c) \\ \textbf{-10} \textbf{-10$

The procedure for compound 5a was followed to prepare 5c from 4c as as a red solid with 75.6% yield (0.27 g, 0.66 mmol). m.p. : 126.90 °C. MS, m/z: 403.56 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.81 (s, 1H), 7.61 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 6.93 (d, J = 3.4 Hz, 2H), 6.86 (dd, J = 8.3, 1.5 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.69 – 6.59 (m, 2H), 6.47 (d, J = 8.3 Hz, 1H), 6.40 (d, J = 8.3 Hz, 1H), 3.49 – 3.43 (m, 2H), 1.65 (m, 2H), 1.38 (m, 6H), 0.92 (t, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  182.23, 153.17, 145.22, 144.74, 140.95, 137.14, 134.22, 132.46, 132.15, 128.81, 125.66, 124.05, 123.69, 121.31, 118.09, 115.45, 112.31, 111.57, 111.11, 44.20, 31.53, 26.56, 25.10, 22.60, 13.94. Anal. Calcd (%) for C<sub>25</sub>H<sub>25</sub>NO<sub>2</sub>S: C, 74.41; H, 6.24; N, 3.47; found: C, 74.49; H, 6.19; N, 3.53;

## 2.2.10 Synthesis of (E)-5-(2-(10-(4-methoxyphenyl)-10H-phenoxazin-3-yl)vinyl) thiophene-2-carbaldehyde (Compound 5d)

The procedure for compound 5a was followed to prepare 5d from 4d as yellow solid with 73.1% yield (0.62 g, 1.46 mmol). m.p. : 158.5 °C. MS, m/z: 425.11 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (s, 1H), 7.59 (d, *J* = 3.9 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.12 – 7.07 (m, 2H), 7.04 (d, *J* = 3.9 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.83 (d, *J* = 1.9 Hz, 1H), 6.69 – 6.66 (m, 2H), 6.65 (s, 1H), 6.64 – 6.54 (m, 1H), 5.97 – 5.91 (m, 1H), 5.88 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  182.29, 159.41, 153.02, 144.06, 143.59, 140.71, 137.34, 135.31, 133.74, 132.01, 131.38, 130.42, 129.08, 125.74, 123.50, 123.29, 121.46, 118.04, 116.18, 115.31, 113.39, 112.98, 112.31, 55.44. Anal. Calcd (%) for C<sub>26</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 73.39; H, 4.50; N, 3.29; found: C, 73.42; H, 4.53; N, 3.26;

## 2.2.11 Synthesis of 2-(3-cyano-4-((*E*)-2-(5-((*E*)-2-(9-hexyl-9*H*-carbazol-3-yl) vinyl) thiophen-2-yl) vinyl)-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (Chromophore CBZ)

To a solution of 5a (0.19 g, 0.50mmol) and the 2-dicyanomethylene-3-cyano-4,5,5-dimethyl-2,5-dihydrofuran (TCF) acceptor (0.12 g, 0.60 mmol) in MeOH (60 mL) was added several drops of triethylamine. The reaction was stirred at 78 °C for 5 h. The reaction mixture was cooled. After removal of the solvent under reduced pressure, the crude product was purified by silica chromatography, eluting with (AcOEt: Hexane = 1:5) to give chromophore A as a purple solid in 61.9% yield (0.18 g, 0.31mmol). m.p. : 197.7 °C. MS, m/z: 568.23 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz,  $d_6$ -acetone)  $\delta$  8.45 (s, 1H), 8.16 (d, *J* = 15.9 Hz, 2H), 7.80 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.51 (d, *J* = 6.1 Hz, 2H), 7.48 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.87 (d, *J* = 15.9 Hz, 1H), 4.44 (t, *J* = 7.2 Hz, 2H), 1.70 (s, 6H), 1.43 – 1.36 (m, 2H), 1.33 – 1.25 (m, 6H), 0.86(t, J=8.5Hz,3H). <sup>13</sup>C NMR (100 MHz,  $d_6$ -acetone)  $\delta$  186.12, 178.19, 153.92, 142.51, 141.35, 139.82, 139.06, 135.99, 129.65, 128.97, 127.77, 126.65, 124.76, 124,17, 122.09, 121.28, 120.87, 119.94, 113.11, 112.50, 110.96, 105.84, 102.34, 99.76, 57.49, 44.40, 32.98, 28.05, 26.84, 24.63, 23.67, 15.08 14.86. Anal. Calcd (%) for C<sub>36</sub>H<sub>32</sub>N<sub>4</sub>OS : C, 76.03; H, 5.67; N, 9.85; found: C, 76.13; H, 5.69; N, 9.79;

# 2.2.12 Synthesis of 2-(3-cyano-4-((*E*)-2-(5-((*E*)-2-(10-hexyl-*10H*-phenothiazin-3-yl) vinyl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (Chromophore PTZ)

The procedure for chromophore CBZ was followed to prepare chromophore PTZ from 5b as a purple solid in 63.2% yield (0.19 g, 0.32 mmol). m.p. : 200.23 °C. MS, m/z: 600.20 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-acetone)  $\delta$  8.15 (d, J = 15.9 Hz, 1H), 7.68 (d, J = 3.9 Hz, 1H), 7.44 (dd, J = 11.7, 4.4 Hz, 3H), 7.29 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 4.4 Hz, 1H), 7.18 (d, J = 3.2 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H),

6.88 (d, J = 15.9 Hz, 1H), 3.98 (t, J = 6.9 Hz, 2H), 1.89 (s, 6H), 1.52 – 1.39 (m, 2H), 1.27 (m, 6H), 0.86 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-acetone)  $\delta$  177.22, 174.73, 152.18, 146.43, 145.17, 140.44 , 139.71 , 138.06, 132.40, 131.53 , 129.13 , 128.31 , 127.92, 127.76, 125.76 , 125.76 , 124.56 , 123.52 , 120.22 , 116.71 , 116.52, 113.84, 113.04, 112.41 , 111.42 , 99.06, 47.79 , 32.02 , 27.43 , 26.88, 26.05, 22.89, 14.10. Anal. Calcd (%) for C<sub>36</sub>H<sub>32</sub>N<sub>4</sub>OS<sub>2</sub> : C, 71.97; H, 5.37; N, 9.33; found: C, 72.04; H, 5.39; N, 9.29;

## 2.2.13 Synthesis of 2-(3-cyano-4-((*E*)-2-(5-((*E*)-2-(10-hexyl-*10H*-phenoxazin-3-yl) vinyl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (Chromophore POZ)

The procedure for chromophore CBZ was followed to prepare chromophore POZ from 5c as a green solid in in 65.3% yield (0.19 g, 0.33 mmol). m.p. : 201.13 °C. MS, m/z: 585.02 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-acetone)  $\delta$  8.13 (d, J = 15.9 Hz, 1H), 7.66 (d, J = 3.9 Hz, 1H), 7.29 (d, J = 16.1 Hz, 1H), 7.25 (d, J = 3.9 Hz, 1H), 7.09 (d, J = 15.8 Hz, 2H), 6.96 (s, 1H), 6.84 (dd, J = 11.7, 4.2 Hz, 2H), 6.76 – 6.62 (m, 4H), 3.66 (t, J=7.6Hz, 2H), 1.89 (s, 6H), 1.74 – 1.64 (m, 2H), 1.49 (m, 2H), 1.43 – 1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-acetone)  $\delta$  177.23 , 175.04, 152.61, 145.76, 145.31 , 140.47 , 139.43, 138.24, 134.93, 133.08, 132.93 , 130.04 , 128.93, 125.51, 124.81, 122.14, 119.33 , 115.92 , 113.65, 113.08, 112.96, 112.91, 112.57, 112.42, 111.52 , 99.01, 44.05, 32.15, 26.83, 26.11, 25.50 , 23.21 , 14.01 . Anal. Calcd (%) for C<sub>36</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>S : C, 73.95; H, 5.52; N, 9.58; found: C, 74.03; H, 5.58; N, 9.55;

# 2.2.14 Synthesis of 2-(3-cyano-4-((*E*)-2-(5-((*E*)-2-(10-(4-methoxyphenyl)-*10H*-phenoxazin-3-yl) vinyl) thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(*5H*)-ylidene)malononitrile (Chromophore PPZ)

The procedure for chromophore CBZ was followed to prepare chromophore PPZ from 5d as a green solid in 60.8% yield (0.18 g, 0.30 mmol). m.p. : 203.8 °C. MS, m/z: 606.17 (M<sup>+</sup>). <sup>1</sup>H NMR (400 MHz,  $d_6$ -acetone)  $\delta$  8.13

(d, J = 15.9 Hz, 1H), 7.66 (d, J = 4.0 Hz, 1H), 7.33 (m, 3H), 7.25 (d, J = 4.0 Hz, 1H), 7.22 (d, J = 8.9 Hz, 2H), 7.09 (d, J = 16.0 Hz, 1H), 7.03 (s, 1H), 6.92 (d, J = 9.9 Hz, 1H), 6.84 (d, J = 15.9 Hz, 1H), 6.67 (m, 3H), 5.93 (t, J = 7.9 Hz, 2H), 3.90 (s, 3H), 1.88 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  181.98, 159.75, 152.81, 144.34, 143.82, 139.20, 138.10, 136.84, 136.02, 133.78, 132.99, 131.44, 130.67, 129.29, 127.52, 124.09, 123.39, 121.85, 118.01, 116.40, 115.48, 113.64, 113.27, 112.34, 110.96, 110.18, 108.81, 105.03, 99.33, 96.92, 55.57, 29.66, 26.47, 24.26. Anal. Calcd (%) for C<sub>37</sub>H<sub>26</sub>N<sub>4</sub>O<sub>3</sub>S : C, 73.25; H, 4.32; N, 9.23; found: C, 73.36; H, 4.38; N, 9.17;

Scheme 1

#### 3. Results and discussion

#### 3.1 Synthesis and characterization

Scheme 1 shows the synthetic approach to the chromophores CBZ, PTZ, POZ and PPZ. Starting from the amine donor intermediates compound **1a-c**, chromophores CBZ, PTZ, POZ and PPZ were synthesized in good overall yields through simple five step reactions: The free N-H group on the donors was protected by the alkyl or aryl group to improve either the solubility or stability. Treatment of compound **2a-d** with POCl<sub>3</sub> and DMF gave an aldehydes **3a-d**. After introduction of the thiophene bridge by a Wittig condensation, compounds **4a-d** were prepared with a high yield. Treatment of compound **4a-d** with n-BuLi and DMF gave aldehyde **5a-d**, the final condensations with the TCF acceptor give chromophores CBZ, PTZ as purple solids and chromophores POZ, PPZ as green solids. All of the chromophores were fully characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, elemental analysis and mass spectrometry. These chromophores possess good solubility in common organic solvents, such as dichloromethane, chloromethane and acetone.

#### 3.2 Thermal stability

The thermal stability of the chromophores was investigated using thermogravimetric analysis (TGA) as shown in Figure 2 and Table 1. All the chromophores exhibited good thermal stabilities with the decomposition temperatures (T<sub>d</sub>) higher than 210 °C (216 °C-298 °C). Chromophore TPA has the highest decomposition temperature (298 °C) [41], followed by PPZ (252 °C), FTC (242 °C) [30], PTZ (232 °C), POZ (223 °C) and CBZ (216 °C). The enhanced thermal stability of the chromophores TPA and PPZ over PTZ, POZ, CBZ and FTC is due to the replacement of alkyl chain to benzene ring on the donor nitrogen. All the thermal stabilities of five chromophores were high enough for the application in EO device preparation [36].

Fig. 3

Table 1

#### 3.3 Optical properties

In order to reveal the effect of different electron donors on the charge-transfer (CT) absorption properties of the six chromophores, UV-Vis absorption spectra of the six chromophores were measured in a series solvent with different dielectric constants as shown in Figure 3 and 4. The spectral data are summarized in Table 1. The absorption maxima ( $\lambda_{max}$ ) of chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC are 606, 620, 610, 665, 660 and 675 nm, respectively. The five aryl chromophores CBZ, TPA, PTZ, POZ and PPZ were blue-shifted in their absorption spectra, compared to the alkyl chromophore FTC, probably due to delocalization of the nitrogen lone

pair into the other phenyl rings of the donor. Although chromophore POZ showed a slight 10 nm blue-shift, its charge-transfer band is slightly broader than that of chromophore FTC (Figure 3), which extends to about 900 nm. This could indicate that the CT state is populated over a wide range of energy levels, suggesting energy gaps  $\Delta E$ (optical) of chromophore POZ is still smaller than that of chromophore FTC. Chromophores POZ and PPZ were red-shifted in their absorption spectra, compared to the other three aryl chromophores CBZ, TPA and PTZ, due to the gradually increased  $\pi$ -donor strength which induced by additional electron donor O atom. The S atom is quite a weak electron donor, so the  $\lambda_{max}$  of chromophore PTZ is similar to chromophores CBZ and TPA. Although chromophore PTZ showed a slight blue-shift, its charge-transfer band is slightly broader than that of chromophore TPA. This could also indicate that  $\Delta E$  (optical) of chromophore PTZ is still smaller than that of chromophore TPA. Chromophore PPZ including the *N*-(4-methoxyphenyl) substituent showed a slight blue-shift in its absorption spectrum, compared to chromophore POZ including the *N*-butylchain. This may be ascribed to the *N*-(4-methoxyphenyl) substituent, which is particular to the average plane of the chromophore, gave inefficient conjugation as showed by the following theoretical calculations (section 3.4).

The solvatochromic behavior was also an important aspect to investigate the polarity of chromophores. It was found that chromophores POZ, PPZ and FTC showed very large bathochromic shifts of 49 nm, 50 nm and 54nm, respectively, on moving from dioxane to chloroform. Chromophores CBZ, TPA and PTZ showed slightly smaller bathochromic shift of 40 nm, 43 nm and 36 nm respectively, from dioxane to chloroform. This confirms that chromophores POZ, PPZ and FTC are more easily polarizable than chromophores CBZ, TPA and PTZ [42, 43].

Fig. 4

Table 2

#### 3.4 Redox properties and Theoretical calculations

In order to determine the electrochemical properties of the six chromophores, cyclicvoltammetry (CV) measurements were conducted in degassed anhydrous acetonitrile solutions containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF) as the supporting electrolyte. The relative data of  $1 \times 10^{-4}$  mol/L chromophore were recorded, as shown in Table 2 and Fig. 6. The HOMO and LUMO levels of the six chromophores can be calculated from their corresponding oxidation and reduction potentials [47]. The difference between these two values provides the HOMO-LUMO energy difference  $\Delta E$  (CV). The calculation results are summarized in Table 2. The energy gaps between the HOMO and LUMO energy for chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC were 1.83 eV, 1.72 eV, 1.52 eV, 1.40 eV, 1.48eV and 1.43eV, respectively.

From the calculated values reported in Table 2, it can be concluded that the LUMO energy levels are approximately the same for all the compounds. Conversely, chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC showed oxidation potential versus ferrocene/ferrocenium at 0.65 V, 0.59 V, 0.41 V, 0.30 V, 0.37 V and 0.32 V, respectively. The gradual decrease of the oxidation potentials were dictated by the progressively increased strength of the donor group. The HOMO energy levels are systematically lowered with an increase in the donor strength which influences the HOMO to a greater extent than the LUMO level. From the  $\lambda_{max}$ , the cutoff wavelength ( $\lambda_{cut-off}$ ) and the energy gap between the HOMO and LUMO energy of the six chromophores, we could assign the order of electron donor strength under the same accepting strength from TCF as follows: CBZ < TPA < TPZ < PPZ < FTC < POZ.

The DFT calculations were carried out at the hybrid B3LYP level by employing the split valence 6-311g (d, p) basis set [44, 45] to understand the ground-state polarization of the chromophores with different configurations. All molecules were assumed to be in *trans*-configurations. The geometrically optimized structures of the molecules were investigated by calculating the dihedral angles of the donor molecules as shown in Fig. 5. The

geometries of the six chromophores are totally different. The geometry of chromophore CBZ is planar, reveals the aromatic character of the central CBZ heterocycle, which facilitates the delocalization of the nitrogen lone pair into the other phenyl rings. So, the CBZ based chromophore exhibits reduced  $\mu\beta$ . The three benzene rings of the TPA are not in the same plane, the dihedral angle between the other two benzene rings on the N atom of the TPA moiety and the average plane of the average plane of the chromophores was ca. 66.40° and 67.39°, respectively, as shown in picture 1 and 5. The twisted structure may somehow attenuate the delocalization of the nitrogen lone pair into two phenyl rings.

The geometry of PTZ and POZ moieties are not totally planar but are rather slightly bent in the middle to give a butterfly shape. In the optimized structures, the angle between the non-planar phenyl ring of the PTZ/ POZ moiety and the average plane of the chromophores was ca. 9.32  $^{\circ}$  and 25.98  $^{\circ}$ , respectively. As for chromophore PPZ, the two benzene rings exhibited almost planar structures with small torsion angles (1.34 $^{\circ}$ ), the *N*-(4-methoxyphenyl) substituent located on the nitrogen atom made a large dihedral angle of about 90 $^{\circ}$  with average plane of the chromophore. This large dihedral angle caused large steric hindrance that suppressed aggregations among molecules.

Fig. 5

#### Fig. 6

The frontier molecular orbitals are often used to obtain information about the optical and electrical properties of molecules [46]. Fig. 5 depicts the electron density distribution of the HOMO and LUMO structures which indicated the density of the ground and excited state electron is asymmetrical along the dipolar axis of the chromophores.

The molecular quadratic hyperpolarizability  $(\mu\beta)$  of the chromophores obtained from DFT calculations are calculated as shown in Table 2. When used carefully and consistently, this method of DFT has been shown to give relatively consistent descriptions of first-order hyperpolarizability for a number of similar chromophores [8, 45, 47].

The  $\mu\beta$  value of chromophore CBZ and TPA was smaller than that of chromophore FTC, due to delocalization of the nitrogen lone pair into the other phenyl rings. The geometry of chromophore CBZ is planar, reveals the aromatic character of the central CBZ heterocycle, which facilitate the delocalization of the nitrogen lone pair into the other phenyl rings. So, the CBZ based chromophore exhibit reduced  $\mu\beta$  compared to chromophore FTC although they both contain one donor N atom donor. The delocalization of the nitrogen lone pair into the other two phenyl rings of chromophore TPA could also result in smaller  $\mu\beta$  than that of chromophore FTC. The  $\mu\beta$  value of chromophore TPA was larger than that of chromophore CBZ due to a narrower energy gap between HOMO and LUMO. With additional electron-rich sulfur heteroatoms into the benzene ring moiety of donor, the PTZ show a little stronger donor strength than TPA. The POZ unit with electron-rich nitrogen and oxygen heteroatoms has stronger electron-donating ability than PTZ because O atom is a much stronger donor than S atom in this case thus results in larger  $\mu\beta$ . With two additional oxygen heteroatoms into the benzene ring moiety of donor, the chromophore PPZ showed an even larger  $\mu\beta$ . This indicates that by introducing additional heteroatoms into the donor could provide abundant opportunities for further modifications of chromophores thus influence nonlinear optical properties of chromophores

#### 3.5 Electro-Optic performance

In order to investigate the translation of the microscopic hyperpolarizability into a macroscopic EO response, the polymer films doped with 25wt% chromophores into amorphous polycarbonate (APC) were prepared using

dibromomethane as solvent. The resulting solutions were filtered through a 0.2- $\mu$ m PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked at 80 °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<sub>g</sub>) of the polymer. The r<sub>33</sub> values of poled films were measured by Teng–Man simple reflection method at a wavelength of 1310 nm using a carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections [48, 49].

The  $r_{33}$  values were calculated by the following equation [50]:

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

Where  $r_{33}$  is the EO coefficient of the poled polymer,  $\lambda$  is the optical wavelength, h is the incidence angle,  $I_c$  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.

The poled films of CBZ/APC, TPA/APC, PTZ/APC, POZ/APC, PPZ/APC and FTC/APC afforded  $r_{33}$  values of 13, 19, 23, 49, 61 and 39 pmV<sup>-1</sup> at 1310 nm, respectively. In these chromophores, the  $r_{33}$  values were gradually improved from 13 pm/V to 61 pm/V, illustrating that the increases donor strength of the chromophores significantly increase their macroscopic EO activities. The additional donor oxygen or sulfur heteroatom may strengthen the electron-donating power of the donor. The stronger the electron-donating power of the donor leads to higher  $\lambda_{max}$ ,  $\mu\beta$ , and  $r_{33}$  values [51]. Besides, solvatochromic behaviour indicated that chromophores POZ, PPZ and FTC are more easily polarizable than chromophores CBZ, TPA and PTZ. Therefore, in corona poling, chromophores POZ, PPZ and FTC may obtain orientation more easily in contrast with chromophore CBZ, TPA and PTZ. Except for larger  $\mu\beta$ , the much larger  $r_{33}$  value of films POZ/APC and PPZ/APC over film FTC/APC may also be explained by favourable poling efficiency which related to chromophore property, chromophore-host compatibility and so on. The long alkyl chain in chromophores POZ can provides effective site isolation to

decrease the strong electrostatic interactions among chromophores. As for chromophores PPZ, the N-(4-methoxyphenyl) substituent located on the nitrogen atom at the donor which almost perpendicular to the average plane of the chromophore was intended to prevent the strong electrostatic interactions between chromophores. The undesired antiparallel packing between chromophores is expected to decrease during the poling process [51]. Although the  $\mu\beta$  value of chromophore PPZ is only 19% larger than that of chromophore POZ, the r<sub>33</sub>value is almost 25% larger due to a better isolation effect. Moreover, the chromophore CBZ. Besides, the r<sub>33</sub>values of this new aryl chromophore can even be higher than those obtained from their alkyl D- $\pi$ -A analogue chromophore FTC. So the chromophore PPZ has not only a larger  $\mu\beta$  but also advantages in translating  $\mu\beta$  into the macroscopic EO activity due to additional donor oxygen heteroatom and isolation effect of *N*-(4-methoxyphenyl) substituent.

#### 4. Conclusion

Six second-order nonlinear optical chromophores containing an identical  $\pi$ -bridge and electron acceptors but different, aromatic amine electron-donating groups have been synthesized and systematically characterized. To further study the effect of different electron donating groups of second-order nonlinear optical chromophores on nonlinearity performance, three chromophores based on novel donors (PTZ, POZ, and PPZ) were synthesized to compare with chromophores based on traditional donors (CBZ, TPA and FTC). Theoretical and experimental investigations suggest that donor group's efficacy in PTZ, POZ, and PPZ chromophore was higher than that of structurally similar CBZ and TPA chromophore. Cyclicvoltammetry (CV) measurements and DFT calculations show that chromophores PTZ, POZ, and PPZ have reduced energy gap, much larger molecular quadratic hyperpolarizability ( $\mu\beta$ ) than that of chromophores CBZ and TPA. The high molecular hyperpolarizability of these

chromophores can be effectively translated into electro-optic (EO) coefficients ( $r_{33}$ ) in poled polymers. The  $r_{33}$  value of chromophores PTZ and POZ were even higher than their alkyl D- $\pi$ -A analogue chromophores FTC. These two chromophores showed excellent thermal stability with an onset decomposition temperatures higher than 220 °C. High  $r_{33}$  values, high thermal stability, together with good solubility, showed that the novel donors which contain nitrogen and oxygen heteroatoms show promising applications in nonlinear optical (NLO) chromophore devices.

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Cmpd	$T_d(^{\circ}\mathbb{C})$	$\lambda_{max}^{a}(nm)$	$\lambda_{max}^{\ \ b}(nm)$	$\Delta\lambda^{c}$ (nm)		
CBZ	216	606	566	40		
TPA	298	620	577	43		
PTZ	232	610	574	36		
POZ	223	665	615	50		
PPZ	252	660	611	49		
FTC	242	675	621	54		

Table 1 Thermal and optical properties data of the chromophores.

 $^{a}\lambda_{max}$  was measured in chloroform.  $^{b}\lambda_{max}$  was measured in dioxane.  $^{c}\Delta\lambda$  was the difference between  $^{a}\lambda_{max}$  and  $^{b}\lambda_{max}$ .

Table 2 Summary of DFT, electro-chemical data and EO coefficients of chromophores

Cmpd	$\Delta E(CV)^{a}(eV)$	$E_{ox}^{b}(V)$	$E_{red}^{c}(V)$	$\mu\beta^{d}(10^{-48}esu)$	r <sub>33</sub> (pm/V)
CBZ	1.83	0.653	-1.185	3805.75	13
TPA	1.72	0.590	-1.136	6776.72	19
PTZ	1.52	0.408	-1.115	7075.97	23
POZ	1.40	0.304	-1.099	8523.60	49
PPZ	1.48	0.372	-1.113	10167.05	61
FTC	1.43	0.321	-1.109	7737.78	39

 $\Delta E(CV)^a$  was calculated from their corresponding oxidation and reduction potentials. <sup>b</sup> Referenced to ferrocene standard.  $\mu\beta^d$  is calculated from DFT quantum mechanical methods.

#### Captions

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

Scheme 1 Chemical structures and synthetic routes for chromophores CBZ, PTZ, POZ and PPZ.

Fig. 1 Optimized structures of the six donors.

Fig. 2 TGA curves of chromophores CBZ, PTZ, POZ and PPZ with a heating rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere.

Fig. 3 UV-Vis absorption spectra of chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC in chloroform.

Fig. 4 UV-Vis absorption spectra of chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC in five kinds of aprotic solvents with varying dielectric constants ( $\varepsilon$ ).

**Fig. 5** Optimized structures and frontier molecular orbitals HOMO and LUMO of chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC calculated by DFT calculations at the hybrid B3LYP level by employing the split valence 6-311g (d, p) basis set.

**Fig. 6** Cyclic voltammograms of chromophores CBZ, TPA, PTZ, POZ, PPZ and FTC recorded in  $CH_3CN$  solutions containing 0.1 M  $Bu_4NPF_6$  supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>.

ĊN ĊN ĊN CN CN CN Ò. ò ò CN си CN TPA PTZ CBZ 0 CN CN CN ,CN CN ,CN ò FTC сN 0 CN CN PPZ POZ

Scheme 1



Chromophores CBZ, PTZ, POZ and PPZ

Fig. 1











Fig. 4



Optimized structure	HOMO	LUMO
CBZ 0°		
TPA 66.40°		
PTZ		
POZ 9.32°		
PPZ		
FTC		

Fig. 5

re CBZ - Chromophore TPA 0.00 0.000 0.00 Current(A) Current(A) 0.00000 0.000 -0.0000 -0.0000 -0.0000 -0.0000 -0.0000 -0.000 -0.00004 1.0 -1.0 -0.5 0.0 Potential vs Fc/Fc\*(v) -0.5 0.0 ntial vs Fc/Fc\*(v) 0.5 1.0 -1.0 Po -1.5 0.5 0.000 oor PT7 ore PO 0.00000 0.00000 0.00000 -0.00000 -0.00000 -0.00000 0.0000 0.0000 0.0000 -0.0000 Current(A) Current(A) -0.0000 -0.00004 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 Potential vs Fc/Fc°(v) — Chromophore PPZ 0.0000 0.0000 0.0000 0.0000 0.00001 -0.00001 -0.00002 0.0000 0.00001 0.00000 -0.00001 -0.00002 -0.00003 Current(A) Current(A) -0.000 -0.5 0.0 Potential vs Fc/Fc<sup>+</sup>(v) -0.5 0.0 ential vs Fc/Fc\*(v) 0.5 -1.0 0.5 1.0 -1.0 Po

#### Highlight

- 1. Six chromophores with different donors had been synthesized and systematically investigated.
- 2. The donor strength and structure-nonlinearity relationship were systematically investigated.
- 3. The  $r_{33}$  value of the film from the *N*-(4-methoxyphenyl)phenoxazine is four times higher than that of the carbazole derived chromophore.