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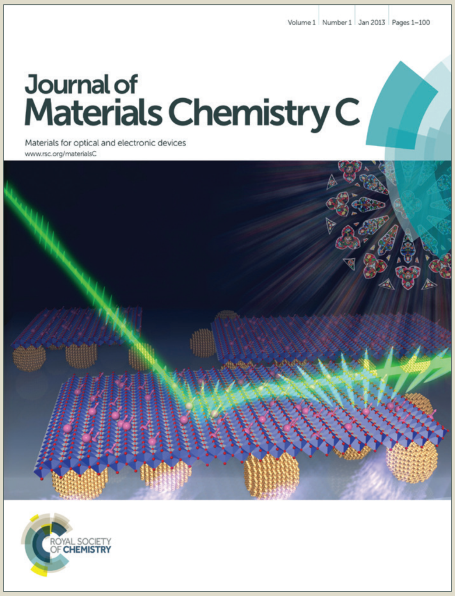

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Synthesis and Optical Nonlinear Property of Y-type Chromophores Based on Double-Donor Structure with Excellent Electro-Optic Activity

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Abstract

New Y-type chromophores FTC-yh1 and FTC-yh2 containing bis(*N,N*-diethyl)aniline as a novel electron-donor, thiophene as π-conjugated bridge and tricyanofuran (TCF) acceptor have been synthesized and systematically investigated in this paper. Density functional theory (DFT) was used to calculate the HOMO-LUMO energy gaps and first-order hyperpolarizability (β) of theses chromophores. These chromophores showed the better thermal stability with their decomposition temperatures all above 240 °C. Most importantly, the high molecular hyperpolarizability of these chromophores can be effectively translated into large electro-optic (EO) coefficients (r_{33}) in poled polymers. The doped films-A containing 25wt % chromophore FTC-yh1 displayed a value of 149 pm/V at 1310 nm, and the doped films-B containing FTC-yh2 showed a value of 143 pm /V at the concentration of 25 wt %. These values are almost four times higher than the EO activity of usually reported traditional single (*N, N*-diethyl) aniline nonlinear optical (NLO) chromophores FTC. High r_{33} values indicated that the double donors of bis(*N,N*-diethyl)aniline unit can efficiently improve the electron-donating ability and reduce intermolecular electrostatic interactions thus enhance the macroscopic EO activity. These properties, together with the good solubility, suggest the potential use of the new chromophores as advanced materials devices.

1. Introduction

Organic electro-optic (EO) materials have attracted considerable attention over the past two decades because of their potential applications in optical communication and optical data processing technologies. [1-4] As an important branch, organic EO polymers have excellent characteristics with large EO coefficients, ultrafast response times, and easy processing, [3,5-8] so they have shown great promise for applications in recent years, such as high speed EO modulators, switches, directional couplers and so on. However, for practical applications, one of the challenges in preparing excellent EO materials is to develop nonlinear optical (NLO) chromophores with large hyperpolarizability (β) and to reduce adverse strong inter-molecular electrostatic interaction among the chromophores molecules.[9,10] Thus, chromophores with large β and weak inter-molecular electrostatic interaction, as the decisive factor, must be designed and prepared.

Generally, the NLO chromophores have the structures of a donor-π-acceptor which usually possess a rod-like structure. So the strong intermolecular dipole-dipole interactions will develop in the polymeric system and further make the poling-induced noncentrosymmetric alignment of chromophores a daunting task. [11] Furthermore, accompanying with the increased concentration of chromophore moieties in the materials, these intermolecular dipole-dipole interactions would become stronger, which would finally lead to a decreased EO activity.[12] Thus, how to decrease these interactions, and efficiently translate the large β values of the organic chromophores into high macroscopic EO activity of polymers, has become one of the major problems in optimizing organic NLO materials.[13-15] To achieve higher EO activity and suppress the dipole interaction among chromophores, rational molecular designs of dipole chromophores have been made from the conjugated push–pull molecules. Many efforts have been carried out to design and synthesize novel NLO chromohores, seeking to engineer NLO molecules both microscopically (β) and macroscopically (r_{33}).[13, 16 17] However, it should be noted that the majority of these works were focused on the conjugated bridge and acceptor structures. [18-25] The electron donors, which are important components of NLO chromophores, have received little attention. Among all the materials studied, the dipolar chromophores bearing *N,N*-dimethyl aniline as donating group have been widely studied due to its large molecular nonlinearity with significantly enhanced thermo-and photostabilities.[20, 8, 25-27].

In this paper, we choose the bis(*N,N*-diethylaniline)unit as a new donating moiety. Due to its high electron-density and low cost,[28] bis(*N,N*-diethylaniline) unit have been widely studied in the dye-sensitized solar cells (DSCs).[4, 28,29] On the one hand, the new donor with two *N, N*-diethylaniline may improve the electron-donating ability thus may enhance the optical nonlinearity. The one of the *N, N*-diethylaniline unit can act as both the additional donor and the isolated group (IG). Applying the site isolation principle, the introduction of some IGs to the chromophore moieties is an effective approach to suppress the dipole interactions among chromophores and improve the poling efficiency, thus achieve much larger macroscopic NLO effects.15, 30 On the other hand, as reported, controlling the shape of the chromophore was proven to be an efficient approach for minimizing this interaction and enhancing the poling efficiency.31 These new chromophores having the double benzene rings with an appropriate angle make the special Y-type structure which is different from the general NLO chromophores showing the rod-like structure. So it may efficiently reduce the intermolecular electrostatic interactions and thus may enhance the macroscopic EO activity. To the best of our knowledge, the novel double donors units rarely appeared in NLO chromophore before.

Considering the mentioned advantages above, we choose the bis(*N,N*-diethylaniline)unit as a new donating moiety. Two new chromophores (in chart 1) with the bis(*N,N*-diethylaniline) unit as a donor were designed and prepared by a facile route from Miche's ketone. They showed great solubility in common organic solvents, good compatibility with polymers, and large EO activity in the poled films. ^{1}H-NMR and ^{13}C-NMR analysis were carried out to demonstrate the preparation of these chromophores. Thermal stability, photophysical properties, DFT calculations and EO activities of these chromophores were systematically studied and were compared with the single-aniline chromophore FTC (chart 1).

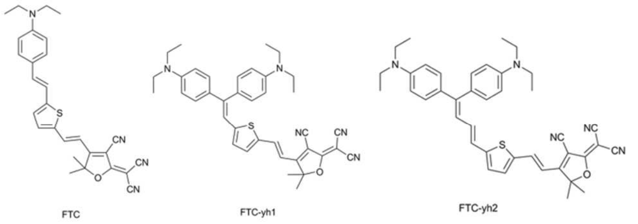
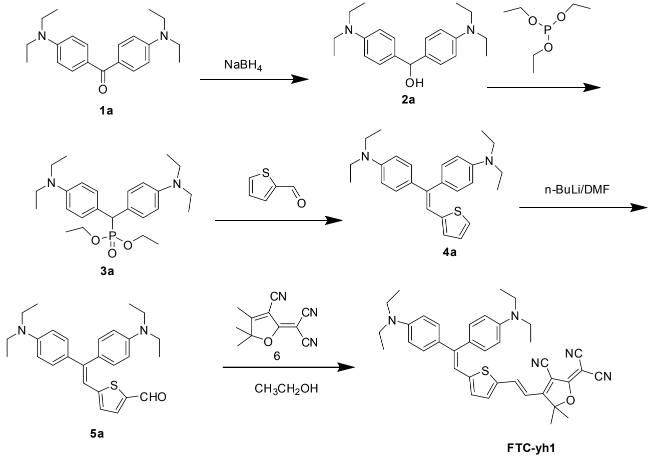


Chart1: the structure of the chromophore of FTC, FTC-yh1 and FTC-yh2

2. Results and discussion

2.1 Synthesis and characterization of chromophores

Synthesis of FTC-yh1, FTC-yh2 and traditional FTC chromophores were depicted in scheme 1, scheme 2 and scheme 3, respectively. Chromophore FTC-yh1 and FTC-yh2 were prepared according to different strategies. FTC-yh1 was obtained in five steps starting from the commercially available Michler's ketone (Scheme 1). Alcohol 2a was obtained in moderate yield by reduction of the Michler's ketone with sodium borohydride in boiling THF and was then directly converted to the phosphonate 3a using a procedure described in the literature.[32] The phosphonate 3a was condensed with 2-Thenaldehyde by Horner-Emmons reaction in which the proper base plays a key role in determining the yield. We found that replacing the commonly used potassium tert-butoxide with sodium hydride produceed 4a with a much improved yield (60%). Treatment of compound 4a with n-BuLi and DMF gave an aldehyde 5a. The target chromophore FTC-yh1 was obtained via Witting reaction of the aldehyde 5a with acceptor TCF in the presence of a catalytic amount of piperidine.



Scheme 1 Chemical structures and synthetic scheme for chromophore FTC-yh1

FTC-yh2 was obtained by five steps in a different way (Scheme 2). The crucial reaction involves the creation of an additional double bond and a functional group on the donor of Michlers Ethylketone for later conversion to aldehyde. The reaction of 1b with diisopropyl (cynaomethyl)-phosphonate using sodium hydride as base resulted in 2b with 65% yield. The reduction with DIBAL-H followed by acid hydrolysis converts the nitrile group on 2b into the corresponding aldehyde 3b with 83% yield. The aldehyde 3b was condensed with 2-thienyltriphenylphosphonate bromide by Witting condensation to gain 4b. As expected, after introduction of the thiophene bridge by Wittig condensation, treatment of compound 4b with n-BuLi and DMF gave an aldehyde 5b. The target chromophore FTC-yh2 was obtained via Knoevenagel condensation reaction of the aldehyde 5b with acceptor TCF in the presence of a catalytic amount of piperidine**.**

Traditional FTC chronophore was obtained in three steps starting from the commercially available aldehyde 1c (Scheme 3). The aldehyde 1c was condensed with 2-thienyltriphenylphosphonate bromide by Witting condensation to gain 2c. As expected, after introduction of the thiophene bridge by Wittig condensation, treatment of compound 2c with n-BuLi and DMF gave an aldehyde 3c. The target chromophore FTC was obtained via Knoevenagel condensation reaction of the aldehyde 3c with acceptor TCF in the presence of a catalytic amount of piperidine**.**

All of the chromophores were fully characterized by ^{1}H-NMR, ^{13}C-NMR, and mass spectroscopy. These chromophores possess good solubility in common organic solvents, such as dichloromethane, chloromethane and acetone.

2.2 Thermal analysis.

NLO chromophores must be thermally stable enough to withstand encountered high temperatures (>200℃) in electric field poling and subsequent processing of chromophore/polymer materials. Thermal properties of the two chromophores were measured by Thermogravimetric Analysis (TGA). Both FTC-yh1 and FTC-yh2 showed excellent stability. The decomposition temperatures (T_d) of chromophores FTC-yh1 and FTC-yh2 were 249 ℃ and 247℃, respectively. While, the traditional single donor FTC showed a T_d of 242 ℃. Therefore, the double donor chromophores have a better thermo-stability than the traditional FTC chromophore. Therefore, the T_d of the two chromophores was high enough for the application in EO device preparation.

2.3 Optical properties

In order to reveal the effect of double donors on the intromolecular charge transfer (ICT) of dipolar chromophores, UV-Vis absorption spectra of three chromophores (c=1×10^{-5} mol/L) were measured in a series of aprotic solvents with different polarity so that the solvatochromic behavior of these chromophores could be investigated to explore the polarity of chromphores in a wide range of dielectric environments (Figures 1 and 2). The spectrum data are summarized in Table 1. The synthesised chromophores exhibited a similar $\pi \rightarrow \pi^*$ intramolecular charge-transfer (ICT) absorption band in the visible region. FTC-yh1 and FTC-yh2 showed the maximum absorption (λ_{max}) of 725 nm and 750 nm in $CHCl_3$ respectively. With extending a double bond into the chromophore FTC-yh1, the λ_{max} of FTC-yh2 chromophore red shifted by 25 nm to 750 nm. These values are exceptionally large compared to the traditional FTC (λ_{max} of 676 nm in $CHCl_3$) with single aniline donor and the same π-conjugated bridge and acceptor. The double donors shifted the ICT absorption band of the chromophore to the lower energy. As shown in Fig.1 and Fig.2, the peak wavelength of FTC-yh1 and FTC-yh2 showed a bathochromic shift of 71 nm from dioxane to chloroform, displaying the larger solvatochromism compared with the single donor FTC chromophore (55 nm in Table 1). The resulting spectrum data confirmed that the chromophores with double donors were more easily polarizable than the single donor FTC. These analyses implied that the double donors of bis(*N,N*-diethyl)aniline improved the electron-donating capability and increased the polarizability of FTC-yh1 and FTC-yh2.

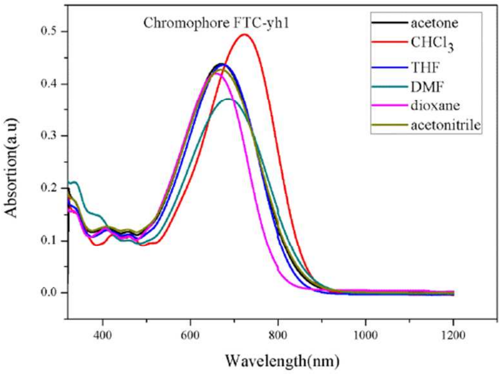


Fig. 1 UV-Vis absorption spectra in different solvents of chromophore FTC-yh1. (c=1×10^{-5}mol/L)

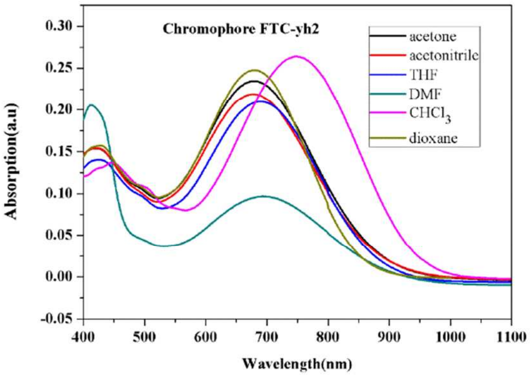


Fig. 2 UV-Vis absorption spectra in different solvents of chromophore FTC-yh2. (c=1×10^{-5}mol/L)

As reported [33], the observed blueshifts (*H* type) or redshifts (*J* type) of dyes in optical absorption spectra are due to the interplay of optical selection rules modified through intermolecular interactions. However, we find that there is no dipole-dipole interaction in the solvents at this low concentration of our chromophores (10^{-5} mol/L). By testing the different concentrations of these three chromophores at $CHCl_3$, we have proved that there was no shift for the shape of the absorption peaks in Fig.3. In our work, the absorption peak shifts in the different solvent were measured for solvatochromism which was related to the polarization and nonlinearity of the chromophores.

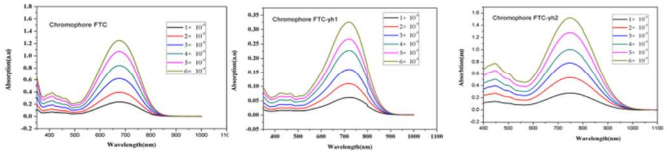


Fig. 3 UV-Vis absorption spectra of different concentrations of three chromophores at $CHCl_3$

2.4 Theoritical calculations

In order to model the ground state molecular geometries, the HOMO-LUMO energy gaps and β values of these chromophores were calculated. The DFT calculations were carried out at the hybrid B3LYP level by employing the split valence 6-31 g (d, p) basis set. [34-36] The data obtained from DFT calculations are summarized in Table 2.

The frontier molecular orbitals are often used to characterize the chemical reactivity and kinetic stability of a molecule and to obtain qualitative information about the optical and electrical properties of molecules.[36, 37, 38] Besides, the HOMO-LUMO energy gap is also used to understand the charge transfer interaction occurring in a chromophore molecule. [38-40] In the case of these chromophores, Fig.4 represents the frontier molecular orbitals of chromophores FTC, FTC-yh1 and FTC-yh2. According to the Fig.4, it is clear that the electronic distribution of the HOMO is delocalized over the thiophene linkage and benzene ring, whereas the LUMO is mainly constituted by the acceptor moieties.[38]

The HOMO and LUMO energy were calculated by DFT calculations as shown in Table 2. For double donor chromophore FTC-yh1 and FTC-yh2, the effect of double donor structure narrows the energy gap between the HOMO and LUMO energy with ΔE values of 1.963 eV and 1.766 eV respectively. By contrast, the ΔE value of FTC is 2.032 eV. It can be concluded that the LUMO energy of chromophore FTC is 0.021 eV larger than that of FTC–yh1 (-3.192 eV vs. -3.123 eV), while the HOMO energy of FTC is 0.048 eV smaller than that of FTC-yh1 (-5.224 eV vs. -5.176 eV). The same trend can be observed in the chromophore FTC-yh2. This may result from that the double donor structure influences the HOMO energy to a greater extent than the LUMO energy. The HOMO-LUMO gaps of FTC-yh1 (1.963 eV) and FTC-yh2 (1.766 eV) are lower than FTC (2.032 eV), and this indicates FTC-yh1 and FTC-yh2 should exhibit better ICT and NLO property than FTC. This is well supported by the facts that the lower is the optical gap, the greater possibility will be the ICT and higher nonlinearity.[38]

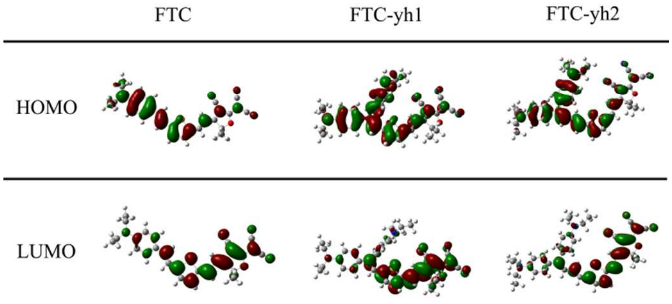


Fig. 4 The frontier molecular orbitals of chromophores FTC, FTC-yh1 and FTC-yh2.

The HOMO-LUMO gap was also investigated by cyclic voltammetry (CV). It showed an energy gap (ΔE) value of 1.353 eV for FTC-yh1 and 1.212 eV for FTC-yh2, while the chromophore FTC exhibited a ΔE value of 1.529 eV.[8] This comparison demonstrated that the double donors narrowed the energy gap indicating the excellent ICT of the double donor chromophores. This result corresponded with the conclusion of UV-Vis spectra analysis and the DFT results.

Further, the theoretical microscopic β was calculated by Gaussian 03. The β value is related to the substituent, molecular configuration, and intramolecular charge-transfer. [41] As the reference reported earlier, the β has been calculated at 6-31g (d, p) level. [42] From this, the scalar quantity of β can be computed from the x, y, and z components according following equation.

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad (1)$$

Where $\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}),\ i, j \in (x, y, z)$

Due to the double donors with the stronger electron-donating ability and better conjugated system, chromophore FTC-yh2 showed a larger β value than the other two chromophores, while the chromophore FTC-yh1 exhibited the smallest β value (713×10^{-30} esu). It may be revealed by the optimized configurations (Fig.5) that chromophore FTC-yh1 possessed a less coplanar geometry compared to the FTC chromophore, due to the double benzene ring with an angle in FTC-yh1. As for the FTC-yh2, on the one hand, with extending a double bound from the FTC-yh1, the steric hindrance between the aromatic groups indeed decreases with the lengthening of the ethylenic spacer.[4] On the other hand, FTC-yh2 has a better conjugation effect which can be verified in the UV-Vis data. Due to the above mentioned, FTC-yh2 with the largest β value is not hard to understand.

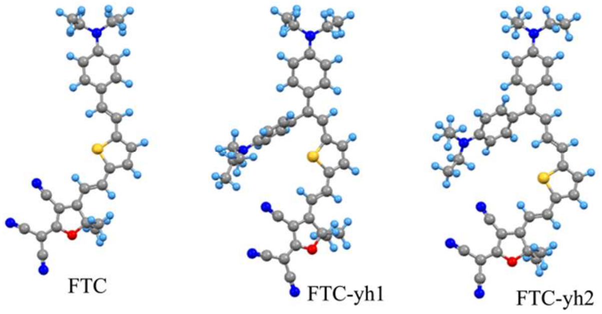


Fig. 5 The optimized structure of chromophore FTC, FTC-yh1 and FTC-yh2

Chromophore FTC-yh1 possessed a little smaller β value, but it showed a larger r_{33} value in the next section. Many factors can affect the r_{33} value. One important factor may be the less electrostatic interaction for FTC-yh1 between the chromophore molecules. Besides, due to the improved coplanar geometry, electrostatic interaction between the chromophore molecules was enhanced which led to FTC-yh2 a little smaller r_{33} than the FTC-yh1.

As above stated, we have not come to an exact ascertainment that our double donors of Y-type chromophores based bis(*N,N*-diethyl)aniline unit is different from the general NLO chromophores. These new chromophores have an obvious advantage in transferring microscopic β to macroscopic electro-optic effect.

2.5 Electric field poling and EO property measurements.

For studying EO property derived from these chromophores, a series of guest-host polymers were generated by formulating the chromophores into amorphous polycarbonate (APC) using dibromomethane as solvent. The resulting solutions were filtered through a 0.2-μm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 80 ℃ overnight to ensure the removal of the residual solvent. The corona poling process was carried out at a temperature of 10 ℃ above the glass transition temperature (T_g) of the polymer. The r_{33} values were measured using the Teng-Man simple reflection technique at the 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. [43]

The r_{33} values of films containing chromophore FTC-yh1 (film-A), FTC-yh2 (film-B) and FTC (film-C) were measured in different loading densities, as shown in Fig.6. Traditional chromophore FTC with the single *N,N*-diethylaniline donor gained the r_{33} value from 12 pm/V (10 wt %) to 39 pm/V (25 wt %), while the r_{33} values of chromophore FTC-yh1 were gradually improved from 30 pm/V (10 wt %) to 149 pm/V (25 wt %). The similar trend of enhancement was also observed for chromophore FTC-yh2, whose r_{33} values increased from 50 pm/V (10 wt %) to 143 pm/V (25 wt %). When the chromophore loading density was up to 25 wt %, the r_{33} value of film B was 143 pm /V. However, as the loading density increasing from 25 wt % to 30 wt %, the film-B displayed a downward trend. To our regret, the film-A with the loading 30 wt % of FTC-yh1, it presents an obvious phase separation.

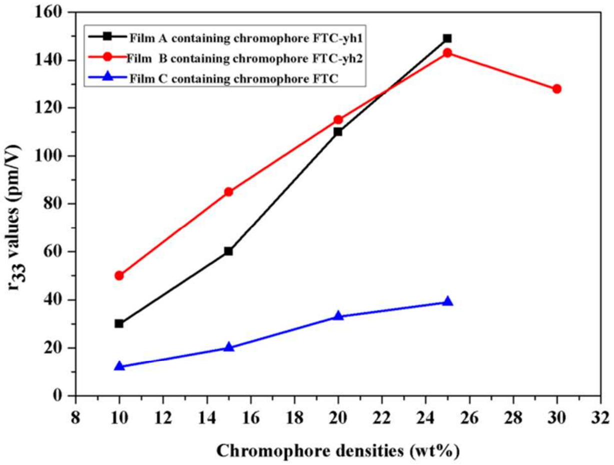


Fig. 6 EO coefficients of NLO thin films as a function of chromophore loading densities.

Through the outcome above, we can obviously see that the chromophores with bis(*N,N*-diethylaniline)unit as donor have nearly 4 times higher r_{33} value than the chromophore FTC, illustrating that the double donors of the chromophores significantly increase their macroscopic EO activity. This may be explained that one of the donors could be also acted as the isolation group. As reported,[44] the introduction of some isolation groups to the chromophore moieties to further control the shape of the chromophore could be an efficient approach to minimize interactions between the chromophores. So the double donor chromophores have an obvious advantage in translating β into r_{33} and thus increased the macroscopic EO activity.

As shown in the Fig.6, when the concentration of chromophore in APC is low, film B displayed a larger r_{33} value than the film A. As the chromophore loading increased, this trend is inversed. This can be explained, when at a low-density range, the intermolecular dipolar interactions are relatively weak. FTC-yh2 had a larger β and was easily poled which displayed a larger r_{33} value. As the chromophore loading increased, FTC-yh2 with a better coplanar geometry presented a stronger negative effect of inter-chromophore dipole–dipole displayed a smaller r_{33} value.

In order to verify the effect of chromophore structure on the NLO activity, the order parameter (Φ) was calculated by measuring UV-Vis absorption spectra (see Fig. 7). After the corona poling, the dipole chromophores in the polymer were aligned, and the absorption curve decreased due to birefringence. From the absorption changes, the order parameter (Φ) for films can be calculated from the absorption changes according to the following equation: $\Phi = 1 - A_1/A_0$, in which A_1 and A_0 are the respective absorptions of the polymer films after and before corona poling. The order parameter (Φ) of poled films at a loading density of 10 wt% was calculated. The Φ value of film-A (FTC-yh1/APC) is 17%, while that of film-B (FTC-yh2/APC) is 28% (Fig. 7). The difference in the order parameter indicates that film-B containing chromophore FTC-yh2 has weaker interchromophore electrostatic interactions and is more easily poled than film-A. At the same time, with an extended double bound into the FTC-yh1, FTC-yh2 has an advantage of molecular rotation and thus makes it move more easily under the electric field. This result corresponded with the conclusion of UV-Vis spectra analysis.

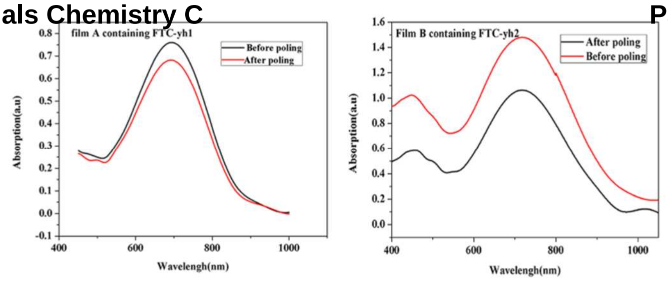


Fig. 7 UV-Vis absorption spectra of E–O polymers before and after poling.

3. Experimental

3.1. Materials and instrumentation

^{1}HNMR spectra were determined by an Advance Bruker 400(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℃/ min 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 two platinum wires as the working and counter electrodes, respectively, and a saturated calomel electrode as the reference electrode in the presence of 1 mM n-tetrabutylammoniumperchlorate as the supporting electrolyte. All chemicals, commercially available, are used without further purification unless stated. The DMF and THF were freshly distilled prior to its use. The 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor was prepared according to the literature.[45]

3.2. Synthesis

3.2.1 Synthesis of compound 3a

Alcohol 2a was obtained in moderate yield by reduction of the Michler's ketone with sodium borohydride in boiling THF and was then directly converted to the phosphonate 3a using a procedure described in the literature. [32]

^{1}H-NMR (400 MHz, Acetone-d_6): δ = 7.34 (dd, J_{HH} = 8.5 Hz, J_{HP} = 1.5 Hz, 4 H, Ar-H), 6.62 (d, J = 8.6 Hz, 4 H, Ar-H), 4.21 (d, J = 25.0 Hz, 1 H, CH), 3.75 – 4.08(m, 4 H, CH_2O), 3.34 (m, 8 H, CH_2N), 1.33 (t, J = 7.0 Hz, 6 H, 2 Me), 1.20 (t, J = 7.0 Hz , 6 H, 2 Me), 1.12 (t, J = 7.0 Hz, 6 H, 2 Me).

MALDI-TOF: m/z calcd for $C_{25}H_{38}N_2O_3P$: 446.26 $[M]^+$; found: 446.27.

3.2.2 Synthesis of compound 4a

To a suspension of diethyl bis(4-(dimethylamino) phenyl) methylphosphonate 3a (1.5 g, 3.36 mmol), and thiophene-2-carbaldehyde (336 mg, 3 mmol) in 20 mL dry THF and NaH (0.14 g, 5.6 mmol) were added and the mixture turned yellow. The mixture was stirred at room temperature for 24 h. Saturated NH_4Cl was added and the resulting mixture was extracted with EtOAc (20 × 3 mL). The combined extracts were washed with water and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography to give a yellow liquid (0.73 g, 60%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 7.18 (d, J = 9.0 Hz, 2 H, Ar-H), 7.14 (s, 1 H, CH), 7.06 (d, J = 5.0 Hz , 1 H , CH), 6.99 (d, J = 8.7 Hz, 2 H, Ar-H), 6.93 (d, J = 3.6 Hz, 1 H, CH), 6.85 (dd, J = 5.0, 3.6 Hz , 1 H, CH), 6.80 (d, J = 8.7 Hz, 2 H, Ar-H), 6.64 (d, J = 9.0 Hz, 2 H, Ar-H) , 3.43(m, 8 H, CH_2N), 1.22 (t, J = 7.0 Hz , 6 H, 2 Me), 1.15 (t, J = 7.0 Hz, 6 H, 2 Me).

^{13}C-NMR (100 MHz, Acetone-d$_6$): δ = 148.56, 148.09, 143.84, 141.69, 132.06, 129.05, 128.85, 127.97, 127.14, 126.61, 125.46, 117.00, 113.07, 112.13, 44.90, 12.99, 12.94.

MALDI-TOF: m/z calcd for $C_{26}H_{32}N_2S$: 404.23 $[M]^+$; found: 404.22.

3.2.3 Synthesis of compound 5a

To a solution of 4a (1.0 g, 2.47mmol) in dry THF (20 mL) was added a 2.4 M solution of n-BuLi in hexane (1.5 mL, 3.7 mmol) dropwise at -78 ℃ under N_2. After this mixture was stirred at this temperature for 1 h, and the dry DMF (0.23 mL, 3.0 mmol) was introduced. The resulting solution was stirred for another 1h at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by water. THF was removed by evaporation. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried by $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 10/1) to obtain a red solid (0.87 g, 82%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 9.74 (s, 1 H, CHO), 7.67 (d, J = 4.0 Hz, 1 H, CH), 7.25 – 7.22(overlap, 3 H, Ar-H, CH), 7.09 (d, J = 4.0 Hz, 1 H, CH), 7.02 – 6.98 (m, 2 H, Ar-H), 6.87 – 6.81 (m, 2 H, Ar-H), 6.67 (m, 2 H, Ar-H), 3.44 (m, 8 H, CH_2N), 1.22 (t, J = 7.0 Hz , 6 H, 2 Me), 1.15 (t, J = 7.0 Hz, 6 H, 2 Me).

^{13}C-NMR (100 MHz, Acetone-d$_6$): δ = 183.06, 153.68, 148.94, 147.41, 142.10, 137.35, 131.75, 129.49, 129.01, 115.86, 113.07, 111.76, 44.90, 12.93.

MALDI-TOF: m/z calcd for $C_{27}H_{32}N_2OS$: 432.24 $[M]^+$; found: 432.22.

3.2.4 Synthesis of chromophore FTC-yh1

A mixture of aldehydic bridge 5a (0.85 g, 1.97 mmol) and acceptor 6 (0.43 g, 2.16 mmol) in ethanol (30 mL) was stirred at 75℃ for 4 h in the presence of a catalytic amount of piperidine. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4:1). A dark solid was obtained (0.45 g, 37%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 7.98 (d, J = 15.7 Hz, 1 H, CH), 7.54 (d, J = 4.2 Hz, 1 H, CH), 7.33 – 7.26 (overlap, 3 H, Ar-H,CH), 7.14 (d, J = 4.2 Hz, 1 H, CH), 7.01 (d, J = 8.7 Hz, 2 H, Ar-H), 6.88 (d, J = 8.7 Hz, 2 H, Ar-H), 6.69 (d, J = 9.0 Hz, 2 H, Ar-H), 6.46 (d, J = 15.7 Hz, 1 H, CH), 3.55 – 3.39 (m, 8 H, CH_2N), 1.79 (s, 6 H, 2 Me), 1.25 (t, J = 7.0 Hz, 6 H, 2 Me), 1.17 (t, J = 7.0 Hz, 6 H, 2 Me).

^{13}C-NMR (100 MHz, Acetone-d$_6$): δ = 177.45, 174.88, 154.58, 154.55, 149.48, 149.27, 149.23, 148.92, 141.19, 139.71, 137.54, 131.81, 131.06, 130.01, 129.11, 125.35, 116.24, 113.47, 113.25, 112.80, 112.06, 111.84, 111.65, 98.62, 97.03, 45.10, 44.96, 26.39, 12.95.

MALDI-TOF: m/z calcd for $C_{38}H_{39}N_5OS$: 613.29 $[M]^+$; found: 613.22.

HRMS (ESI) (M^+, $C_{38}H_{39}N_5OS$): calcd: 614.29481; found: 614.29509.

3.2.5 Synthesis of compound 2b

A 250 mL three-necked flask was charged with NaH (1.5 g, 62.5 mmol) in dry THF (30 mL) under N_2 atmosphere. Disiopropyl (cyanomethyl)-phosphonate (8.05 g, 0.050 mol) was introduced to the mixture dropwise by syringe at 0 °C with an ice bath. After the solution became clear, compound 1b (8.0 g, 0.025 mol) in THF (20 mL) was added. The mixture was refluxed for 24 h. The resulting solution was poured into 100mL ice water and was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, and the residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 50/1) to obtain a yellow solid (5.57 g, 65%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 7.33 – 7.26 (m, 2 H, Ar-H), 7.26 – 7.17 (m, 2 H, Ar-H), 6.78 – 6.73 (m, 2 H, Ar-H), 6.72 – 6.67 (m, 2 H, Ar-H), 5.48 (s, 1 H, CH), 3.46 (m, 8 H, CH_2N), 1.18 (dt, J = 10.4, 7.0 Hz, 12 H, 4 Me).

^{13}C-NMR (100 MHz, Acetone-d$_6$): δ = 163.64, 150.23, 149.81, 132.25, 131.17, 126.73, 124.84, 120.52, 111.76, 111.40, 86.95, 44.93, 44.88, 12.94, 12.88.

MALDI-TOF: m/z calcd for $C_{23}H_{29}N_3$: 347.29 $[M]^+$; found: 347.23.

3.2.6 Synthesis of compound 3b

To a solution of 2b (3.47 g, 10 mmol) in dry toluene (30 mL) was added a 1 M solution of diisobutylaluminum hydride in hexanes (20 mL, 20 mmol) by syringe at -78 °C with a dry ice/acetone bath. The reaction was stirred at -78 °C for 2 h. After the mixture was warmed to room temperature, NH_4Cl solution was added to quench the reaction. The mixture was stirred for 1h to complete the hydrolysis. The organic solvent was collected and removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/acetone, v/v, 10/1) to yield a red solid (2.9 g, 83%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.47 (d, J = 8.2 Hz, 1 H, CHO), 7.31 (d, J = 8.8 Hz, 2 H, Ar-H), 7.19 (d, J = 8.7Hz, 2 H, Ar-H), 6.65 (d, J = 8.7 Hz, 2 H, Ar-H), 6.62 (d, J = 8.8 Hz, 2 H, Ar-H), 6.39 (d, J = 8.2 Hz, 1 H, CH), 3.40 (dd, J = 13.5, 6.6 Hz, 8 H, CH_2N), 1.20 (dt, J = 8.9, 6.7 Hz, 12H, 4 Me).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 194.86, 164.90, 150.42, 149.76, 134.04, 132.05, 127.59, 124.79, 123.11, 111.72, 111.40, 45.36, 45.29, 13.52,

MALDI-TOF: m/z calcd for $C_{23}H_{30}N_2O$: 350.24 $[M]^+$; found: 350.24.

3.2.7 Synthesis of compound 4b

Under N_2, a mixture of 3b (2.0 g, 5.7 mmol) and 2-thienyl triphenylphosphonate bromide (3.01 g, 6.86 mmol) in dry THF (20 mL) at room temperature, NaH (0.82 g, 34.2 mmol) was added. The mixture turned yellow and was stirred at room temperature for 24 h. Saturated NH_4Cl was added and the resulting mixture was extracted with EtOAc (20 × 3 mL). The combined extracts were washed with water and dried over MgSO4. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography on silica gel (hexane/acetone, v/v, 50/1) to obtain a yellow solid (1.47 g, 60%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.8 Hz, 2 H, Ar-H), 7.21 (d, J = 10.6 Hz, 1 H, CH), 7.14 (d, J = 8.7 Hz, 2 H, Ar-

H), 7.05 (d, J = 3.9 Hz, 1 H, CH), 7.02 – 6.98 (m, 1H, CH), 6.94 – 6.83 (m, 1 H, CH), 6.68-6.60 (m, overlap, 5 H, Ar-H, CH), 6.42 – 6.28 (m, 1 H, CH), 3.41 – 3.34 (m, 8 H, CH_2N), 1.22 – 1.14 (m, 12 H, 4Me).

^{13}C-NMR (100 MHz, Acetone-d_6): δ = 147.77, 147.53, 147.05, 146.94, 131.88, 131.78, 129.79, 129.00, 128.83, 127.67, 127.05, 126.88, 126.32, 125.39, 124.92, 123.50, 123.23, 122.44, 119.58, 119.01, 111.31, 111.28, 111.09, 110.96, 78.56, 44.10, 44.07, 13.30, 12.21.

MALDI-TOF: m/z calcd for $C_{28}H_{34}N_2S$: 430.24 $[M]^+$; found: 430.07.

3.2.8 Synthesis of compound 5b

In a similar manner described above, 5b was synthesized from4b as a red solid (82%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.75 (1 H, s, CHO), 7.56 (1 H, d, J = 4.0 Hz, CH), 7.23 (2 H, d, J = 8.8 Hz, Ar-H), 7.12 (2 H, d, J = 8.7 Hz, Ar-H), 7.08 (1 H, d, J = 11.5 Hz, CH), 6.94 (1 H, d, J = 4.0 Hz, CH), 6.72 – 6.66 (3 H, overlap, Ar-H, CH), 6.63 – 6.57 (3 H, overlap, Ar-H, CH), 3.39 (8 H, m, CH_2N), 1.20 (12 H, m, 4 Me).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 206.35, 147.38, 147.10, 146.48, 141.73, 132.07, 131.97, 129.51, 129.01, 127.45, 127.01, 126.85, 124.82, 119.58, 119.41, 111.00, 110.78, 44.32, 12.70.

MALDI-TOF: m/z calcd for $C_{29}H_{34}N_2OS$: 458.24 $[M]^+$; found: 458.28.

3.2.9 Synthesis of chromophore FTC-yh2

In a similar manner described above, 7b was synthesized from 5b as a dark solid (38%).

^{1}H-NMR (400 MHz, Acetone-d_6): δ = 8.12 (d, J = 15.8 Hz, 1 H, CH), 7.64 (d, J = 4.0 Hz, 1 H, CH), 7.22 (d, J = 8.9 Hz, 2 H, Ar-H), 7.11-7.13 (overlap, 3 H, Ar-H,CH), 7.07 (d, J = 11.0 Hz, 1 H, CH), 6.92 (d, J = 15.8 Hz, 1 H, CH), 6.84 – 6.77 (overlap, 3 H, Ar-H, CH), 6.73 (d, J = 11.0 Hz, 1 H, CH), 6.68 (d, J = 8.9 Hz, 2 H, Ar-H), 3.40 (m, 8 H, CH_2N), 1.86 (s, 6 H, 2 Me), 1.20 (m, 12 H, 4 Me).

^{13}C-NMR (100MHz, Acetone-d_6): δ = 177.48, 175.02, 154.32, 149.81, 148.99, 148.77, 140.47, 139.05, 138.83, 134.96, 133.00, 132.86, 130.53, 130.26, 129.93, 128.49, 126.87, 123.03, 122.83, 113.37, 113.15, 112.67, 112.00, 111.82, 98.98, 97.61,45.02, 44.79, 26.21, 12.88.

MALDI-TOF: m/z calcd for $C_{40}H_{41}N_5OS$: 639.30 $[M]^+$; found: 639.26.

HRMS (ESI) (M^+, $C_{40}H_{41}N_5OS$): calcd: 640.31046; found: 640.30990.

3.2.10 Synthesis of compound 2c

In a similar manner described above, 2c was synthesized from 1c as a yellow solid (68%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.9 Hz, 2 H, Ar-H), 7.11 – 7.07 (m, 1 H, CH), 7.01 (d, J = 16.1 Hz, 1H, CH), 6.96 (d, J = 3.4 Hz, 1 H, CH), 6.85 (d, J = 16.1 Hz, 1 H, CH), 6.64 (d, J = 8.9 Hz, 2 H, Ar-H), 6.47 (d, J = 3.4 Hz, 1 H, CH), 3.41 – 3.31 (m, 4 H, CH_2N), 1.17 (t, J = 7.1 Hz, 6 H, 2 Me).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 148.10, 144.72, 130.66, 129.48, 128.22, 127.95, 127.03, 125.05, 124.67, 123.34, 117.69, 112.45, 112.06, 44.88, 13.21.

3.2.11 Synthesis of compound 3c

In a similar manner described above, 3c was synthesized from 2c as a red solid (86%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H, CHO), 7.66 (d, *J* = 3.9 Hz, 1H, CH), 7.40 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.12 (d, *J* = 15.9 Hz, 1H, CH), 7.07 (d, *J* = 3.9Hz, 1H, CH), 7.00 (d, *J* = 15.9 Hz, 1H, CH), 6.68 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.43 (m, 4H, CH_2N), 1.22 (t, *J* = 7.0 Hz, 6H, 2 Me).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.12, 153.45, 147.45, 139.24, 136.25, 132.73, 129.24, 127.63, 123.73, 122.21, 114.71, 110.74, 43.46, 11.64.

3.2.12 Synthesis of chromophore FTC

In a similar manner described above, chromophore FTC was synthesized from 3c as a dark solid (41%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.77 (d, *J* = 15.7 Hz, 1 H, CH), 7.38 (d, J = 8.6 Hz, 2 H, Ar-H), 7.37 (d, *J* = 3.9 Hz, 1 H, CH), 7.09 (d, *J* = 15.7 Hz, 1H, CH), 7.01 (d, *J* = 3.9 Hz, 1 H, CH), 6.68 (d, J = 8.6 Hz, 2 H, Ar-H), 6.57 (d, *J* = 15.2 Hz, 1 H, CH), 3.52 – 3.29 (m, 4 H), 1.73 (s, 6 H), 1.28 – 1.14 (m, 6 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 182.03, 172.86, 153.58， 148.02, 142.13, 140.08, 139.33, 137.39, 129.07, 111.61, 110.91, 110.21, 108.85, 104.96, 99.53, 96.90, 44.81, 44.55, 24.42, 12.58.

MALDI-TOF: m/z calcd for $C_{28}H_{28}N_4OS$: 468.20 $[M]^+$; found: 468.33.

Conclusions

In this research, two NLO chromophores based on the bis(*N,N*-diethylaniline) donors have been synthesized and systematically investigated. These chromophores with double donors present Y-type and exhibit good thermal stability and large molecular hyperpolarizabilities, which can be effectively translated into very large EO coefficients in poled polymers. The doped film-A containing chromophore FTC-yh1 displayed a maximum r_{33} value of 149 pm /V at the doping concentration of 25 wt %, while film-B containing chromophore FTC-yh2 showed a maximum r_{33} value of 143 pm/ V at 25 wt %. Those consequences indicate that these chromophores with double *N, N*-diethylaniline donors could efficiently reduce the interchromophore electrostatic interactions and enhance the macroscopic optical nonlinearity. This novel donor chromophore showed promising applications in NLO chromophore synthesis. We believe that these novel Y-type chromophores can be used in exploring high-performance organic EO and photorefractive materials where both thermal stability and optical nonlinearity are of equal importance.

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Notes and references

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Table1. Summary of Thermal and Optical Properties and EO Coefficients of Chromophores FTC, FTC-yh1and FTC-yh2

	T_d^a (□)	$\lambda^b{}_{max}$(nm)	$\lambda^c{}_{max}$(nm)	$\Delta\lambda^d$ (nm)	$r^e{}_{33}$(pm/V)
FTC	242	676	621	55	39
FTC-yh1	249	725	654	71	149
FTC-yh2	247	750	679	71	143

[a] T_d was determined by an onset point, and measured by TGA under nitrogen at a heating rate of 10 □ /min.

[b] λ_{max} was measured in $CHCl_3$.

[c] λ_{max} was measured in dioxane.

[d] $\Delta\lambda=\lambda^b{}_{max}-\lambda^c{}_{max}$

[e] r_{33} values were measured at the wavelength of 1310 nm.

Table2. Data from DFT calculations

Chromophores	E_{HOMO}/eV	E_{LUMO}/eV	ΔE^a/eV	ΔE^b/eV	$\beta_{max}{}^c/10^{-30}$esu
FTC	-5.224	-3.192	2.032	1.529.	883
FTC-yh1	-5.176	-3.213	1.963	1.353	713
FTC-yh2	-5.038	-3.272	1.766	1.212	995

$\Delta E = E_{LUMO} - E_{HOMO}$,

[a] Results was calculated by DFT

[b] Results was from cyclic voltammetry experiment

[c] β values were calculated using gussian03at B3LYP/6-31 g(d) level and the direction of the maximum value is directed along the charge transfer axis of the chromophores.