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A study on regulating the conjugate position of NLO chromophores for reducing the dipole moment and enhancing the electro-optic activities of organic materials

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In order to improve the first-order hyperpolarizability (β) of the chromophore and transform it into a high macroscopic electro-optic activity, a series of novel second-order nonlinear optical chromophores with different push–pull electron groups introduced on the thiophene π-conjugate bridge for tuning the shape and dipole moment (μ) of chromophores were designed and synthesized. These chromophores are based on the same thiophene π-conjugated bridge, where the donor (*N*,*N*-diethylaniline) and acceptor (2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile or malononitrile) are linked to positions 2 and 3 of thiophene, respectively, affording a boomerang-like shape instead of a rod-like shape. Besides, an electron-poor group, Br (bromine atom), or an electron-rich group, DEA (*N*,*N*-diethylaniline), as an auxiliary acceptor or donor are linked to position 5 of thiophene. In addition, all chromophores showed good thermal stability as per the results from the DSC and TGA analysis. Through UV-vis analysis and DFT calculation, it has been concluded that chromophores with additional electron-rich groups as auxiliary donors display better intermolecular charge-transfer (ICT) absorption and lower HOMO–LUMO energy gaps (ΔE). Furthermore, the boomerang-like chromophore with the same push–pull structure shows a smaller dipole moment (μ) and β value than the traditional **FTC**. The poling results of guest–host EO polymers **FTC/APC**, **FTC-H/APC**, **FTC-Br/APC** and **FTC-DEA/APC** with the same number density afford r_{33} values of 17 pm V^{-1}, 11 pm V^{-1}, 10 pm V^{-1} and 25 pm V^{-1}, respectively. Although the β value of **FTC-DEA** is smaller than that of **FTC**, the r_{33} value of **FTC-DEA** (25 pm V^{-1}) is 47% greater than that of **FTC** (17 pm V^{-1}) under the same number density. Hence, the above-mentioned results indicated that regulating the conjugate position of chromophores can efficiently decrease the dipole moment of the chromophores, weakening the dipole–dipole interactions and thereby enhancing the macroscopic electro-optical activity of poled polymers. These results indicate the potential application of these novel chromophores in electro-optical devices.

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1. Introduction

Organic second-order nonlinear optical (NLO) materials have attracted much attention over the past two decades because of their potential advantages such as ultrafast response, broad bandwidth, low driving voltage, tunable structures and large electro-optic (EO) coefficients (r_{33}).[1–4] These materials have potential applications in optical switches, optical sensors, telecommunication devices, *etc.*[5–11] The second-order NLO chromophores are the most important part of the electro-optic (EO) material. Hyperpolarizability (β) has been used to characterize the microscopic NLO activities of the chromophore. However, the challenges in preparing excellent electro-optic (EO) materials are the development of NLO chromophores with a large β value[12–15] and the translation of the microscopic NLO activities into macroscopic electro-optic activities.

Generally, the NLO dipolar chromophores have a dipolar structure, where the electron-donor (D) and electron-acceptor (A) groups are end-capped in a π-conjugated bridge (D–π–A structure), with large intramolecular charge transfer (ICT) absorption for enhancing the first-order hyperpolarizability (β).[16–18] However, strong intermolecular dipole–dipole interactions between the chromophores inevitably existed among dipolar chromophores and impeded the poling-induced noncentrosymmetric alignment, leading

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to a lower r_{33} of the material. Moreover, the larger the β value and the greater the concentration the chromophore had, the stronger the dipole–dipole interaction in the material.[19–23] Therefore, in order to achieve higher EO activity and weaken the intermolecular dipole–dipole interactions among chromophores, many efforts had been made to design and synthesize novel NLO chromophores.[24–28] The structure that links chromophores together in a head-to-head and tail-to-tail fashion can effectively block the intermolecular dipole–dipole interactions and realize the preparation of a single-molecule nonlinear film.[29] The chromophore designed by Dalton *et al.* showed a decrease in the dipole moment (μ) and enhanced the electro-optic activity of the material.[30] It can be seen that reducing intermolecular dipole–dipole interactions by reducing the dipole moment (μ) of the chromophore molecule was a very effective method for increasing the electro-optic activity.[30]

Up to now, NLO chromophores conjugated with thiophene have been widely used, and **FTC** has been used as a classic high-performance chromophore in many devices. Therefore, further modification of the **FTC** has been extensively studied to achieve better performance.[31,32] Xu's group designed **FTC** derivatives by introducing sterically hindered groups into the donor and conjugated bridges of the **FTC**. The introduction of hindered groups efficiently prevented the dipole–dipole moment and led to a higher doping content of the chromophore (up to 49 wt%), and the r_{33} value (56 pm V^{-1}) was 43% higher than that of the **FTC** (39 pm V^{-1} with 25 wt% in APC).[33] Based on the previous work on the variety of structures of chromophores, we found that donors and acceptors of **FTC** derivatives were linked to positions 2 and 5 of the thiophene-conjugated bridge, respectively, and this rod-like structure facilitated the ICT absorption but exhibited a large dipole moment, as shown in Chart 1(a). The **FTC** molecules that connect the donors and acceptors to positions 2 and 3 of thiophene, respectively, were rarely reported (Chart 1(b)). We proposed that the dipole moment of this shape might be smaller than that of the rod-like **FTC** molecules, leading to relatively small dipole–dipole interactions and high EO activity of materials. Therefore, we are eager to know if the shape tuning and introduction of auxiliary donors or acceptors at position 5 of thiophene π-conjugated bridge would affect the electron transfer of the chromophore and optical properties and EO performance of the materials.

In this work, we designed and synthesized six dipole chromophores with thiophene as a π-conjugated bridge with different auxiliary groups on the thiophene π-conjugated bridge, such as DEA (*N*,*N*-diethylaniline) groups with the electron-donating ability and Br (bromine atom) with the electron-withdrawing ability,[34] affording **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA.** Major push–pull conjugated structures of all the chromophores used thiophene as a π-conjugated bridge, *N*,*N*-diethylaniline and TCF (2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile) or malononitrile as the donor and acceptor linked to positions 2 and 3 of thiophene, respectively, for tuning the shape and dipole moment. This means that **FTC-DEA** and **MTD-DEA** chromophores have two electron-donating groups. Synthetic chromophores (in Chart 2) showed great solubility in common organic solvents and good compatibility with polymers. ^{1}H NMR, ^{13}C NMR and MS analyses were carried out to demonstrate the successful preparation of these chromophores. Thermal stability, photophysical properties, DFT calculations and EO activities of these chromophores were systematically studied.

2. Results and discussion

2.1 Synthesis and characterization of chromophores

All NLO chromophores were designed with the same electron acceptor (TCF and malononitrile) and the same electron donor (*N*,*N*-diethylaniline group). The synthesis of **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** chromophores is depicted in Schemes 1 and 2. Chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** were prepared according to different strategies. All reactions were performed under nitrogen protection. The TCF acceptor was prepared according to the literature.[35] **FTC-H** and **MTD-H** were obtained in seven steps starting from the commercially available 3-methylthiophene. Aldehyde **11** was obtained in moderate yields by free

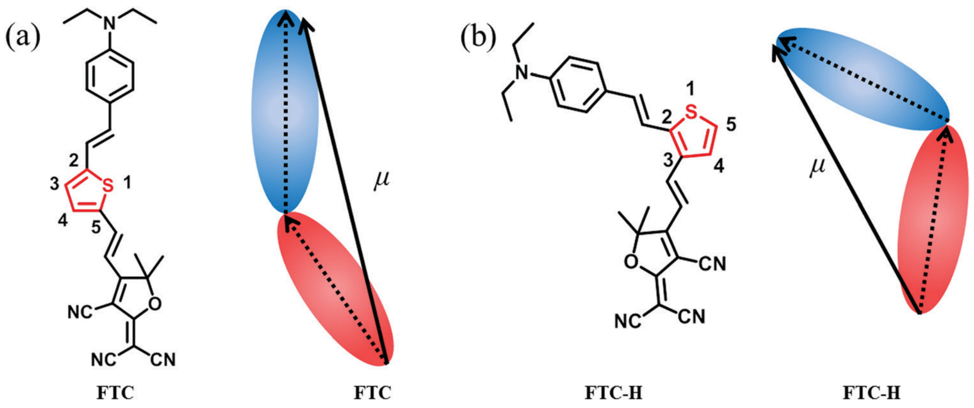


Chart 1 (a) Molecular structure and its dipole moment diagram of **FTC**. (b) Molecular structure and dipole moment diagram of non-traditional **FTC** molecular **FTC-H**.

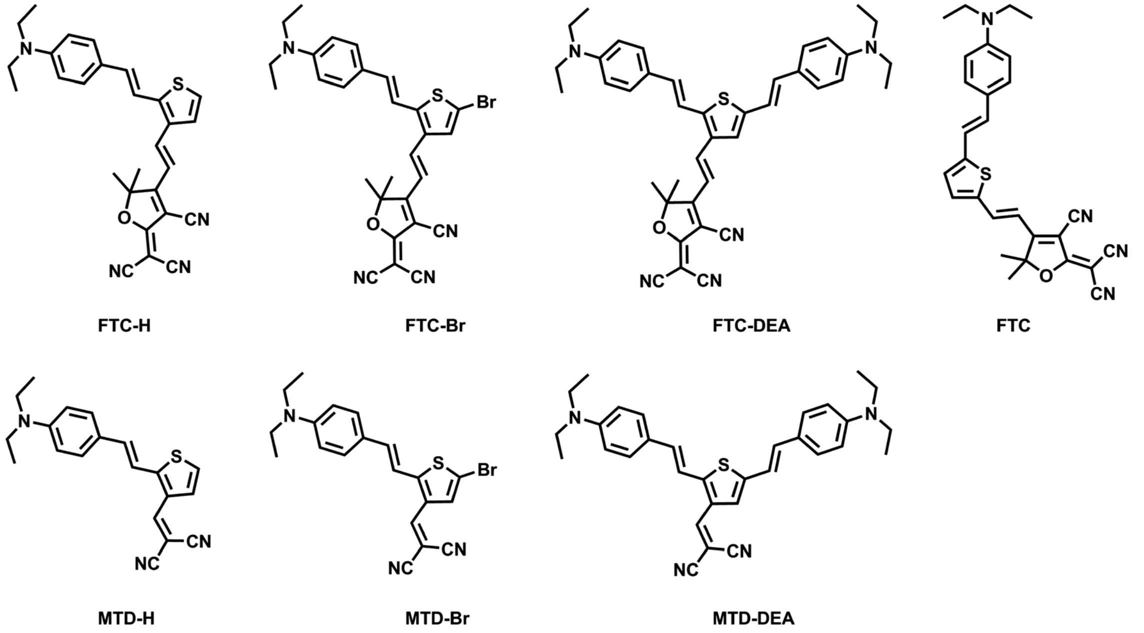
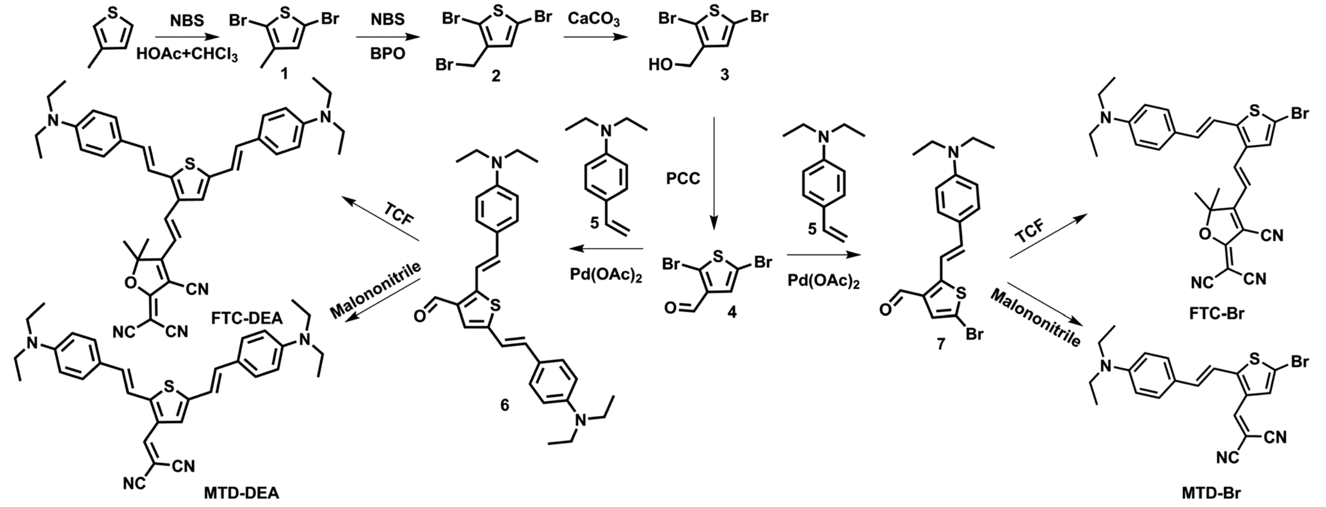


Chart 2 Structure of the chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** and the reference compound **FTC**.

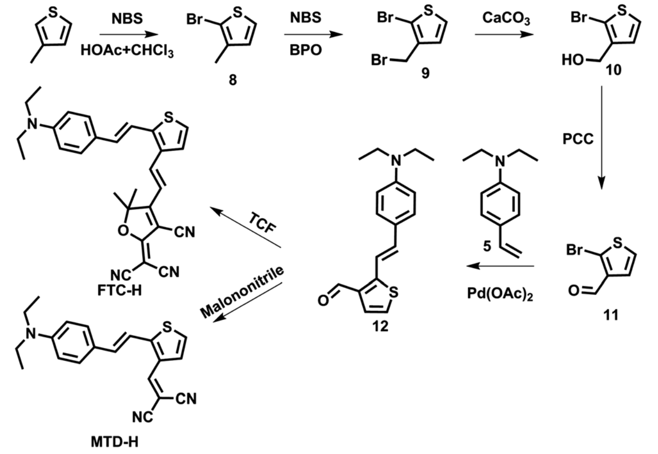


Scheme 1 Chemical structure and synthetic scheme of chromophores **FTC-DEA**, **MTD-DEA**, **FTC-Br** and **MTD-Br**.

radical and oxidation reactions. Compound **12** was synthesized by the palladium-catalyzed Heck reaction. Finally, the two electron acceptors (TCF and malononitrile) were respectively attached to thiophene by the Knoevenagel condensation reaction to finally form the chromophores. **FTC-Br** and **MTD-Br** and **FTC-DEA** and **MTD-DEA** were obtained in seven steps starting from the commercially available 3-methylthiophene. Aldehyde **4** was obtained in moderate yields by free radical and oxidation reactions. Compounds **6** and **7** were synthesized by the palladium-catalyzed Heck reaction after controlling the receptor content. Finally, two electron acceptors (TCF and malononitrile) were attached to **6** and **7** by the Knoevenagel condensation reaction, respectively, to finally form chromophores **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA**. All the chromophores were structurally characterized by ^{1}H-NMR, ^{13}C-NMR, and MS. These chromophores possessed good solubility in common organic solvents, such as dichloromethane, chloromethane and *N*,*N*-dimethylformamide.

2.2 Optical properties

It is generally believed that the NLO properties of organic molecules are greatly influenced by the nature of intramolecular charge-transfer (ICT) absorption properties and electron density distributions of the chromophore. In order to reveal the effect of boomerang-like chromophores and the introduction of auxiliary donor receptors on the ICT absorption properties, UV-vis absorption spectra of the six chromophores ($c = 1 \times 10^{-5}$ mol L^{-1}) were measured in series solvents with different dielectric constants. Therefore, the solvatochromic behavior of these chromophores



Scheme 2 Chemical structure and synthetic scheme of chromophores **FTC-H** and **MTD-H**.

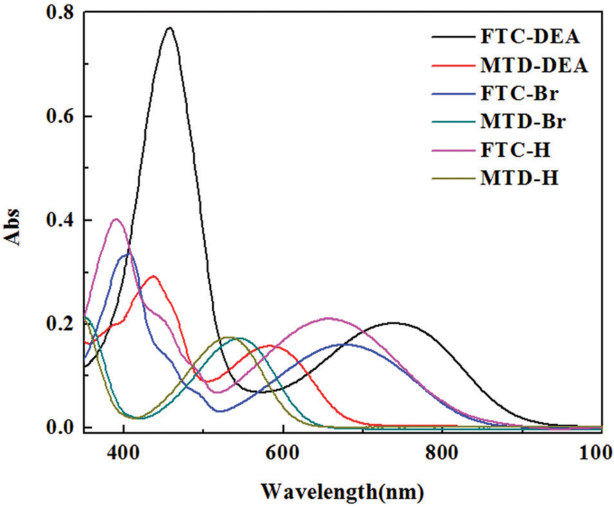


Fig. 1 UV-vis absorption spectra of chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** in chloroform ($c = 1 \times 10^{-5}$ mol L^{-1}).

could be studied to explore the polarity of chromophores in various dielectric environments as shown in Fig. 1 and 2. The spectral data are summarized in Table 1. As shown in Fig. 1, the chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** showed two prominent absorption bands in the visible range. The bands at ~400 nm could be attributed to the π–π* transition of aromatic groups. The absorption bands located in the range of 500–800 nm could be attributed to intramolecular charge transfer (ICT) transitions in D–π–A dipole molecules. All the chromophores displayed similar π–π* ICT absorption bands in the visible region and **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** showed the maximum absorption ($\lambda_{\max}$) of 659 nm, 531 nm, 676 nm, 545 nm, 741 nm and 582 nm in $CHCl_3$, respectively. Compared to the absorption bands of chromophores **MTD-H, MTD-Br** and **MTD-DEA**, the absorption bands of chromophores **FTC-H, FTC-Br** and **FTC-DEA** showed a bathochromic shift, which could be attributed to the TCF acceptor having a higher electron-accepting ability than malononitrile. Comparing the maximum absorption of **FTC-H** and **MTD-H** to that of **FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA**, the introduction of the bromine atom or DEA at position 5 of thiophene could shift the ICT absorption band of the chromophore to a lower energy level, which indicated that the introduction of auxiliary donors and acceptors into the chromophores of the TCF receptor and the malononitrile acceptor have the same effect. Especially, the maximum absorption wavelength of **FTC-DEA** ($\lambda_{\max}$ = 714 nm) showed a bathochromic shift than **FTC** ($\lambda_{\max}$ = 676 nm), which illustrated that the introduction of the electron-rich group DEA as an auxiliary donor could effectively shift the ICT absorption band of the chromophore to a lower energy level.

Besides, the solvatochromic behavior is also an important aspect for studying the polarity of chromophores. In solvents of different polarities including dioxane (DO), toluene, dichloromethane (DCM), chloroform (CF) and *N*,*N*-dimethylformamide (DMF), the series of chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** showed very obvious optical features in terms of solvatochromism, as shown in Fig. 2. All the chromophores displayed a broad ICT absorption band. All the spectra displayed a red-shift of $\lambda_{\max}$ from a nonpolar solvent to a polar solvent (DO to CF) and a blue-shift from a polar solvent to a strong polar solvent (CF to DMF). The solvatochromic behavior suggested that the dipolar chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** could enter the zwitterionic region beyond the limit of the cyanine. In Table 1, dipolar chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** showed bathochromic shifts of 52 nm, 27 nm, 53 nm, 32 nm, 97 nm and 39 nm from dioxane to chloroform, respectively. This confirmed that chromophores **FTC-H, FTC-Br** and **FTC-DEA** were more easily polarizable than chromophores **MTD-H, MTD-Br** and **MTD-DEA**. Particularly, **FTC-DEA** (97 nm) has the largest solvatochromic behavior and is much larger than **FTC** (55 nm), which indicated that the introduction of additional electron donors assisted the enhancement of ICT absorption. It also illustrated that **FTC-DEA** was the most easily polarized, which generally indicates the large molecular first-order hyperpolarizability. The $\Delta\lambda$ values of **FTC-H** and **FTC-Br** are basically the same. This indicated that the introduction of a bromine atom has little effect on the ICT absorption properties.

2.3 Thermal stability

Thermal stability is very important for the chromophore application during the NLO device preparation. Most of the processes need high temperatures: the poling temperature should be higher than the glass transition temperature of the polymer during the poling process. Therefore, the NLO chromophore must be thermally stable enough to withstand the encountered high temperatures (usually need to withstand temperatures above 200 °C). The thermal stability of all the chromophores was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) at the same heating rate of 10 °C min^{-1} under nitrogen, as shown in Fig. 3 and 4, respectively. The TGA curves of all the chromophores showed the 5 wt% weight loss temperature (T_d), which are listed in Table 1. It was found that all the chromophores

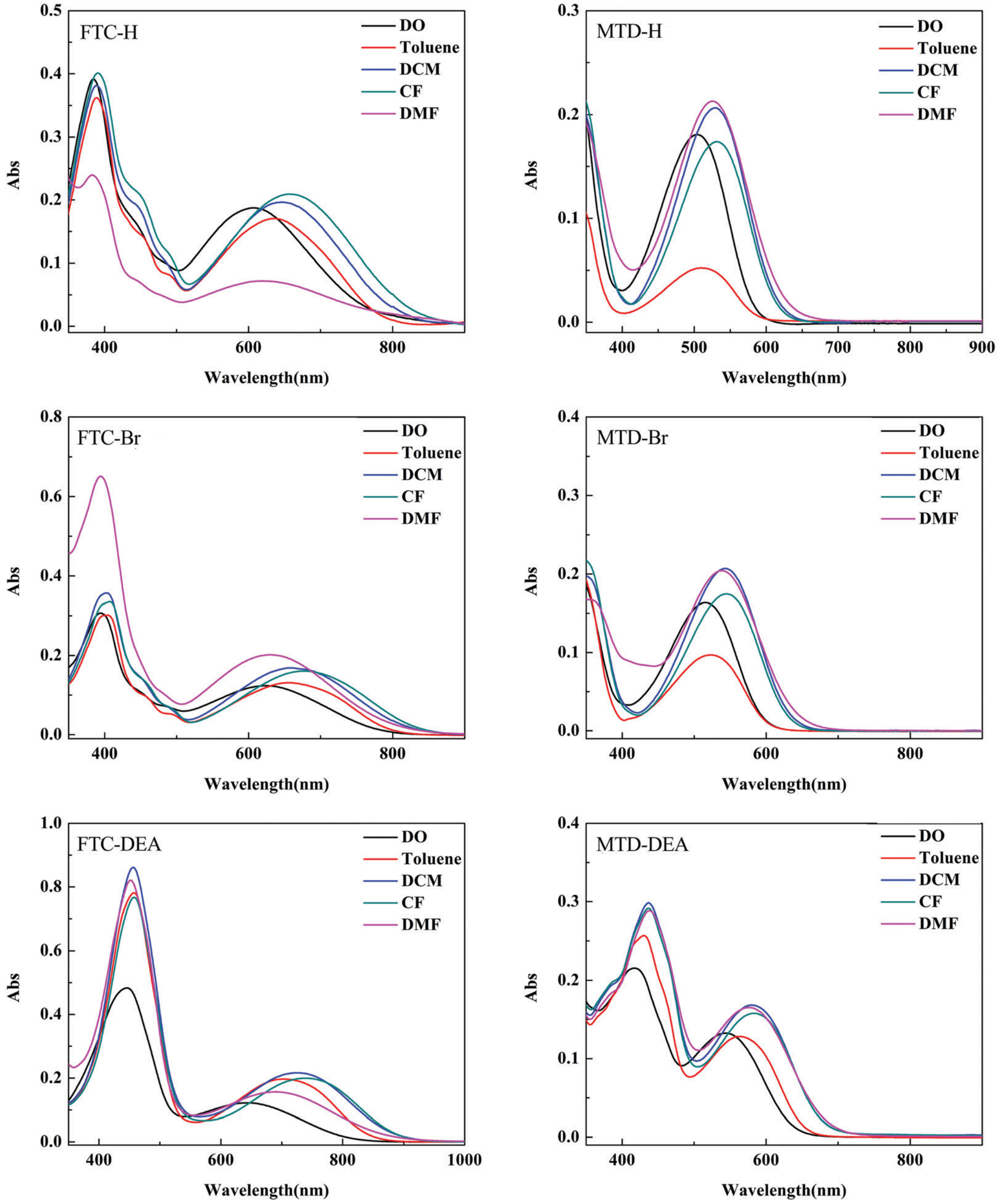


Fig. 2 UV-vis absorption spectra of chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** in different solvents, including dioxane (DO), toluene, chloroform (CF), dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF).

Table 1 Summary of optical and thermal properties of the chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** and the reference compound **FTC**

	λ_{max}[a] (nm)	λ_{max}[b] (nm)	$\Delta\lambda$[c] (nm)	T_d[d] (°C)
FTC	676	621	55	242
FTC-H	659	607	52	258
MTD-H	531	504	27	273
FTC-DEA	741	644	97	268
MTD-DEA	582	543	39	258
FTC-Br	676	623	53	205
MTD-Br	545	513	32	251

[a] λ_{max} was measured in chloroform. [b] λ_{max} was measured in dioxane. [c] $\Delta\lambda = \lambda_{max}$ (in chloroform) − λ_{max} (in dioxane). [d] 5% weight loss temperature determined from TGA in nitrogen at a heating rate of 10 °C min^{-1}.

exhibited excellent stability at decomposition temperatures (T_d) higher than 200 °C, which was high enough for the application in EO device preparation.[36] It is well known that decomposition usually leads to an exothermic or endothermic event, which would be reflected on the DSC curve. Considering that the TGA only reflects the weight loss, the combination of TGA and DSC analysis under the same heating condition may be a more reasonable way to characterize the thermal stability. As shown in Fig. 4, no significant changes were found in the DSC and TGA curves of chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** below 175 °C. Therefore, it could be deducted that chromophores **FTC-H, MTD-H, FTC-Br, MTD-Br, FTC-DEA** and **MTD-DEA** were thermally stable below 175 °C.

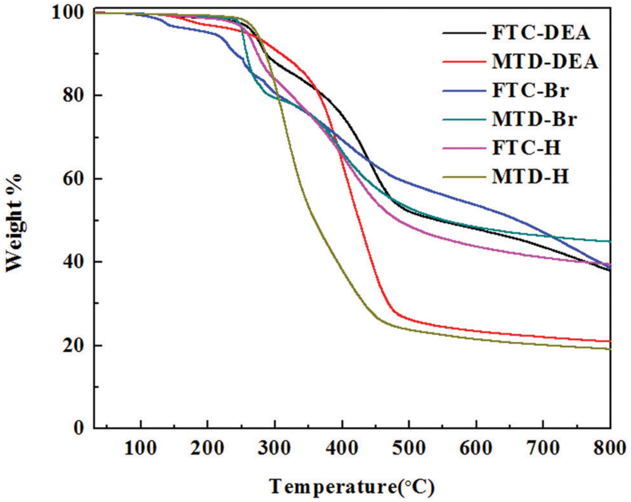


Fig. 3 TGA curves of chromophores at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

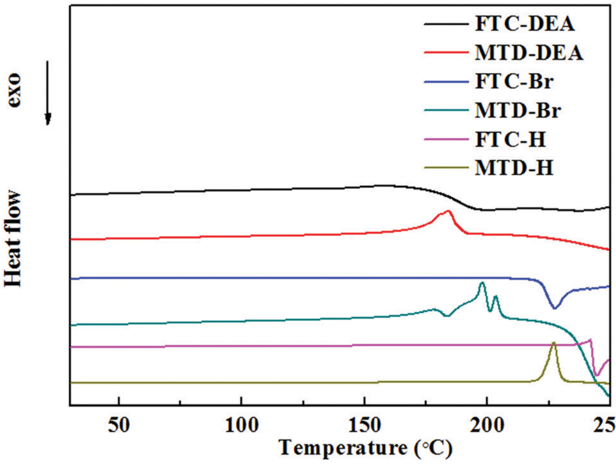


Fig. 4 DSC curves of chromophores at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

All the chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** exhibited satisfactory thermal stabilities. Therefore, the integrated DSC and TGA curves show that the chromophores have high thermal stability and can be widely used in the preparation of electro-optic devices.

2.4 Theoretical calculations

After optimizing the ground state of their molecular geometries, the HOMO–LUMO energy gaps (ΔE), dipole moment (μ), and first hyperpolarizability (β) values of the chromophores have been calculated. The DFT[25,37] calculations were carried out at the hybrid B3LYP[38,39] level by employing the split valence 6-31G(d,p) basis set. All 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 its optical and electrical properties.[40,41] Besides, the HOMO–LUMO energy gap is also used to understand the transfer interaction occurring in a chromophore molecule. Fig. 5 shows the frontier molecular orbitals of chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA**. It is obvious that the electron density distribution of the HOMO level is delocalized over thiophene and the donor, whereas the LUMO level is mainly distributed in the TCF acceptor part.

The HOMO–LUMO energy gaps (ΔE) were also calculated by DFT calculations, as shown in Table 2. The ΔE of chromophores **FTC-H**, **FTC-Br** and **FTC-DEA** were 2.057 eV, 2.034 eV, and 1.836 eV, respectively. According to reports,[42] the energy gap is lower and the degree of intramolecular charge transfer (ICT) absorption is greater, which improves the nonlinearity of the chromophore. According to the data, chromophore **FTC-DEA** showed a lower ΔE than chromophores **FTC-H** and **FTC-Br**. The lower ΔE of **FTC-DEA** indicated better ICT absorption and NLO properties than chromophores **FTC-H** and **FTC-Br**. It also demonstrated that the introduction of the electron-rich group DEA as an auxiliary donor narrowed the energy gap, which is in accordance with the results obtained for optical properties.

The theoretical microscopic zero-frequency molecular first-order hyperpolarizability (β) was calculated using Gaussian 09 at the B3LYP/6-31G(d,p) level.[19] The scalar of β can be calculated from the x, y and z components according to the following equation:

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

where

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

The calculated β values of chromophores **FTC-H**, **FTC-Br** and **FTC-DEA** are summarized in Table 2. The variations in the β value of chromophores with different push–pull structures can be clearly observed. The β values of **FTC-H**, **FTC-Br** and **FTC-DEA** are 323 × 10^{-30} esu, 320 × 10^{-30} esu and 379 × 10^{-30} esu, respectively. It can be obviously seen that **FTC-DEA** has the

Table 2 Data from DFT calculations and EO coefficients

Chromophores	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE^a (eV)	β^b (1 × 10^{-30} esu)	μ^c (D)	r_{33} (pm V^{-1})
FTC-H	−5.304	−3.247	2.057	323	4.70	11
FTC-DEA	−4.929	−3.090	1.836	379	6.63	25
FTC-Br	−5.375	−3.341	2.034	320	4.28	10
FTC	−5.488	−3.483	2.005	711	9.11	17

[a] $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$. [b] β values were calculated using Gaussian 09 at the B3LYP/6-31G(d,p) level. [c] μ is the total dipole moment.

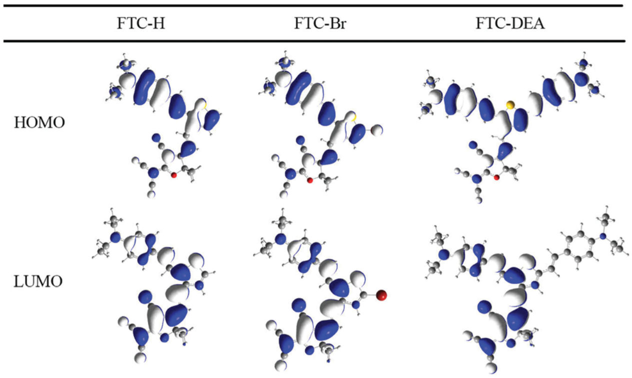


Fig. 5 The frontier molecular orbitals of chromophores **FTC-H**, **FTC-Br** and **FTC-DEA**.

largest β values, and **FTC-H** and **FTC-Br** have very similar values, which indicated that the introduction of the auxiliary donor can effectively increase the nonlinear properties of the molecules and the introduction of an auxiliary acceptor has little effect on the nonlinear properties of the molecules. As stated above, DFT calculations and the UV-vis spectral analysis suggested that the incorporation of the electron-rich group might lead to a higher EO activity. This result corresponds with the UV-vis characterization results.

The DFT calculation results demonstrated that the total dipole moment (μ) of chromophores **FTC-H**, **FTC-Br** and **FTC-DEA** are smaller than that of chromophore **FTC**, which indicated that the introduction of electron donors and electron acceptors at positions 2 and 3 of thiophene, respectively, was beneficial to reduce the dipole moment of the chromophores. The smaller μ may reduce the aggregation of the chromophore **FTC-DEA** in organic materials.[43,44]

2.5 EO activity characterization

For application, the microscopic hyperpolarizability (β) has to be translated into a large macroscopic EO coefficient (r_{33}). For studying the macroscopic nonlinearity of the chromophores **FTC-H**, **FTC-Br** and **FTC-DEA** and the reference chromophore **FTC** in poled polymers, a series of electro-optic films with the same doping content (0.38 mmol g^{-1}) were fabricated by formulating the chromophores into amorphous poly(bisphenol A carbonate) (APC) using dibromomethane as the solvent. The electro-optical coefficient (r_{33}) is proportional to the content of chromophore doping. In order to compare the effect of the chromophore structure on the electro-optic properties of the material, we have selected the same number density to prepare the doped film. The **FTC** content is approximately 18 wt%, and the content of **FTC-H** is 18 wt%, **FTC-Br** is 20 wt% and **FTC-DEA** is 25 wt%.

Contact poling was applied to obtain the noncentrosymmetric alignment. In order to prevent damage to the films, a moderate field of about 100 V μm^{-1} was applied and no breakdown current was observed.

The r_{33} values of the poled films were measured by the Teng–Man simple reflection technique at a wavelength of 1310 nm.[39] The EO coefficients (r_{33}) of the films were 11, 10, 25 and 17 pm V^{-1} for **FTC-H/APC**, **FTC-Br/APC**, **FTC-DEA/APC** and **FTC/APC**, respectively. As shown in Table 2, r_{33} of the guest–host materials appeared to have the same tendency as the calculated β values for **FTC-H/APC**, **FTC-Br/APC** and **FTC-DEA/APC**. It is obvious that **FTC-DEA** with an electron-rich group had the highest EO activity, while the EO coefficient of **FTC-H** and **FTC-Br** were very similar, which indicated that the introduction of the electron-rich group DEA could significantly increase the macroscopic EO activity. For the **FTC**-based structure containing strong electron-acceptors, the introduction of bromo atoms may have little effect on r_{33}. Most importantly, the β value of **FTC-DEA** is less than that of **FTC**, but the value of r_{33} is 47% greater than that of **FTC**. It is probably due to the smaller dipole moment of **FTC-DEA**, leading to the smaller intermolecular dipole–dipole interaction and higher efficiency for translating microscopic NLO activities into the macroscopic EO coefficient. Thus, the boomerang-like chromophores lead to the small dipole moment, which could effectively prevent the dipole–dipole interaction between chromophores, and the introduction of an electron-rich group at position 5 of thiophene could enhance the electro-optic activity. This was favorable for obtaining the organic electro-optic film materials of high electro-optic coefficient.

3. Experimental

3.1 Materials and instruments

All reagents were purchased from Aladdin Co., Ltd, Shanghai, China and used without further purification. The compound 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile (TCF) was prepared according to the literature.[35] The ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker III HD 400 spectrometer. The MS spectra were recorded using a Thermo Fisher ITQ1100 mass spectrometer. The UV-vis spectra were recorded using an Agilent Cary 5000 spectrophotometer. The decomposition temperature of chromophores was analyzed using a Mettler Toledo TGA 2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under the protection of nitrogen. The glass transition temperatures were obtained using NETZSCH 4 under N_2 at a heating rate of 10 °C min^{-1}.

3.2 Syntheses

3.2.1. Synthesis of 2,5-dibromo-3-methylthiophene (compound 1). 3-Methylthiophene (5 g, 50.9 mmol) was dissolved in chloroform and acetic acid (50 mL : 50 mL) in a 250 mL one-necked flask equipped for stirring. *N*-Bromosuccinimide (19.94 g, 112.1 mmol) was added to the solution in one portion, and the solution was stirred for 6 h. The reaction mixture was then poured into water and extracted with chloroform; the organic extracts were washed with water three times and with $NaHCO_3$ (aq.) twice. The organic layer was dried over anhydrous $MgSO_4$, and then the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum) to give compound **1** as a transparent liquid (11.88 g, 91.11% yield). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.77 (1H, s, thiophene-H), 2.15 (3H, s, $-CH_3$).

3.2.2. Synthesis of 2,5-dibromo-3-(bromomethyl)thiophene (compound 2). Compound **1** (2 g, 7.81 mmol) and *N*-bromosuccinimide (1.7 g, 9.55 mmol) were dissolved in carbon tetrachloride (CCl_4, 20 mL). A small amount of benzoyl peroxide was (10 mg, 0.04 mmol) added as an initiator. The mixture was refluxed for 4 h. The reaction mixture was then poured into water and extracted with dichloromethane. The organic extracts were washed with water two times. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum) to give compound **2** as a transparent liquid (2.13 g, 81.3% yield). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.00 (1H, s, thiophene-H), 4.36 (2H, s, $-CH_2-$).

3.2.3. Synthesis of (2,5-dibromothiophen-3-yl)methanol (compound 3). Compound **2** (1 g, 2.99 mmol) was dissolved in 1,4-dioxane (20 mL), and calcium carbonate (0.36 g, 3.6 mmol) and water (10 mL) were added to this. Then the mixture was stirred and refluxed for 12 h and was monitored by TLC. When the reaction was completed, 1 M HCl was added to the mixture to remove excess calcium carbonate and extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum : ethyl acetate = 10 : 1) to give compound **3** as a white solid (0.67 g, 82.7% yield). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.00 (1H, s, thiophene-H), 4.54 (2H, d, E = 3.3 Hz, $-CH_2-$), 2.03 (1H, s, –OH).

3.2.4. Synthesis of 2,5-dibromothiophene-3-carbaldehyde (compound 4). Compound **3** (0.4 g, 1.47 mmol) was dissolved in dichloromethane (15 mL) and pyridinium chlorochromate (0.38 g, 1.76 mmol) was added. Then the mixture was stirred at room temperature for 12 h and was monitored by TLC. The solvent was removed, and the residue was purified by column chromatography (petroleum : dichloromethane = 5 : 1) to give compound **4** as a light yellow solid (0.359 g, 91.2% yield). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.79 (1H, s, –CHO), 7.34 (1H, s, thiophene-H).

3.2.5. Synthesis of *N*,*N*-diethyl-4-vinylaniline (compound 5). In an ice bath, methyltriphenylphosphonium bromide (3.02 g, 8.47 mmol) and potassium *tert*-butoxide (1 g, 8.83 mmol) were mixed in freshly dried tetrahydrofuran (THF, 40 mL). The yellow suspension was stirred for 30 min. Then 4-(diethylamino)benzaldehyde (1 g, 5.65 mmol) in THF (10 mL) was slowly added dropwise into the mixture and stirred at room temperature for 5 h and was monitored by TLC. Methanol was added and the solution was filtered. After the removal of the solvent, the residue was purified by column chromatography (ethyl acetate : petroleum = 1 : 30) to give compound **5** as a yellow oil (1.62 g, 61% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (2H, d, J = 8.5 Hz, Ar-H), 6.69 (1H, dd, J_1 = 17.5 Hz, J_2 = 11.2 Hz, $-CH{=}CH_2$), 6.60 (2H, d, J = 8.4 Hz), 5.49 (1H, d, J = 17.4 Hz, $-CH{=}CH_2$), 4.96 (1H, d, J = 10.8 Hz, $-CH{=}CH_2$), 3.37 (4H, q, J = 7.1 Hz, $-CH_2-N-CH_2-$), 1.17 (6H, t, J = 7.1 Hz, $-CH_3$).

3.2.6. Synthesis of 2,5-bis((*E*)-4-(diethylamino)styryl)thiophene-3-carbaldehyde (compound 6). To a solution of compound **4** (0.1 g, 0.37 mmol), compound **5** (0.16 g, 0.913 mmol) and Bu_4NBr (0.24 g, 0.745 mmol) in dry DMF (5 mL), triethylamine (0.077 g, 0.757 mmol), $Pd(OAc)_2$ (0.017 g, 0.076 mmol) and triphenylphosphine (0.0193 g, 0.074 mmol) were added. The mixture was stirred under a N_2 atmosphere at 100 °C for 24 h and was monitored by TLC. After cooling to room temperature, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with brine, and dried with anhydrous Na_2SO_4. Then the solvent was removed to give a crude product, which was then purified by silica gel column chromatography (ethyl acetate : petroleum = 1 : 6) to give compound **6** as a dark red solid (0.07 g, 26.5% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 10.11 (1H, s, –CHO), 7.69 (1H, d, J = 15.8 Hz, $-CH{=}CH-$), 7.41 (2H, d, J = 8.8 Hz, $-CH{=}CH-$), 7.34 (2H, d, J = 8.7 Hz, Ar-H), 7.17 (1H, s, thiophene-H), 7.07 (1H, d, J = 15.8 Hz, $-CH{=}CH-$), 6.91 (1H, d, J = 15.9 Hz, $-CH{=}CH-$), 6.81 (1H, d, J = 16.0 Hz, $-CH{=}CH-$), 6.66 (4H, dd, J = 8.8, 3.1 Hz, Ar-H), 3.44–3.35 (8H, m, $-CH_2-$), 1.20 (12H, dd, J = 11.9, 6.9 Hz, $-CH_3$).

3.2.7. Synthesis of (*E*)-5-bromo-2-(4-(diethylamino)styryl)-thiophene-3-carbaldehyde (compound 7). To a solution of compound **4** (0.69 g, 2.56 mmol), compound **5** (0.3 g, 1.71 mmol) and Bu_4NBr (0.66 g, 2.05 mmol) in dry DMF (5 mL), anhydrous potassium carbonate (0.3 g, 2.17 mmol), $Pd(OAc)_2$ (0.06 g, 0.267 mmol) and triphenylphosphine (0.132 g, 0.503 mmol) were added. The mixture was stirred under a N_2 atmosphere at 100 °C for 24 h and was monitored by TLC. After cooling to room temperature, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with brine, and dried with anhydrous Na_2SO_4. The solvent was removed to give a crude product, which was then purified by silica gel column chromatography (ethyl acetate : petroleum = 1 : 6) to give compound **7** as a dark red solid (0.2 g, 32% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (1H, s, –CHO), 7.58 (2H d, J = 15.6 Hz, $-CH{=}CH-$), 7.37 (2H, d, J = 8.8 Hz, Ar-H), 7.28 (1H, s, thiophene-H), 6.96 (1H, d, J = 15.9 Hz, $-CH{=}CH-$), 6.64 (2H, d, J = 8.4 Hz, Ar-H), 3.39 (4H, q, J = 7.1 Hz, $-CH_2-$), 1.19 (6H, t, J = 7.1 Hz, $-CH_3$).

3.2.8. Synthesis of 2-bromo-3-methylthiophene (compound 8). 3-Methylthiophene (5 g, 50.9 mmol) was dissolved in chloroform and acetic acid (50 mL : 50 mL) in a 250 mL one-necked flask equipped with stirring. *N*-Bromosuccinimide (9.07 g, 51 mmol) was added to the solution in one portion, and the solution was stirred for 5 min. The reaction mixture was then poured into water and extracted with chloroform; the organic extracts were washed with water three times and with $NaHCO_3$ (aq.) twice. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum) to give compound **8** as a transparent liquid (7.41 g, 82% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (1H, d, J = 5.6 Hz, thiophene-H), 6.78 (1H, d, J = 5.6 Hz, thiophene-H), 2.20 (3H, s, $-CH_3$).

3.2.9. Synthesis of 2-bromo-3-(bromomethyl)thiophene (compound 9). Compound **8** (2 g, 11.3 mmol) and *N*-bromosuccinimide (2.01 g, 11.3 mmol) were dissolved in carbon tetrachloride (CCl_4, 20 mL). A small amount of benzoyl peroxide (10 mg, 0.04 mmol) was added as an initiator. The mixture was refluxed for 4 h. The reaction mixture was then poured into water and extracted with dichloromethane; the organic extracts were washed with water two times. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum) to give compound **9** as a transparent liquid (2.26 g, 78.3% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.24 (1H, m, thiophene-H), 7.00 (1H, d, J = 5.7 Hz, thiophene-H), 4.45 (2H, s, $-CH_2-$).

3.2.10. Synthesis of (2-bromothiophen-3-yl)methanol (compound 10). Compound **9** (1 g, 3.91 mmol) was dissolved in 1,4-dioxane (20 mL), and calcium carbonate (0.47 g, 4.69 mmol) and water (10 mL) were added to this. Then the mixture was stirred and refluxed for 12 h and was monitored by TLC. When the reaction was completed, 1 M HCl was added to the mixture to remove excess calcium carbonate and extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed to obtain a crude product, which was then purified by silica gel column chromatography (petroleum : ethyl acetate = 10 : 1) to give compound **10** as a white solid (0.64 g, 84.8% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, J = 5.8 Hz, thiophene-H), 7.01 (1H, d, J = 5.6, 1.3 Hz, thiophene-H), 4.61 (2H, J = 2.2 Hz, $-CH_2-$), 2.01–1.65 (1H, m, –OH).

3.2.11. Synthesis of 2-bromothiophene-3-carbaldehyde (compound 11). Compound **3** (0.9 g, 4.66 mmol) was dissolved in dichloromethane (20 mL), and pyridinium chlorochromate (1.21 g, 5.59 mmol) was added. Then the mixture was stirred at room temperature for 12 h and was monitored by TLC. Following the removal of the solvent, the residue was purified by column chromatography (petroleum : dichloromethane = 5 : 1) to give compound **11** as a light yellow solid (0.58 g, 92.14% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (1H, s, –CHO), 7.36 (1H, d, J = 5.8 Hz, thiophene-H), 7.29 (1H, d, J = 5.8 Hz, thiophene-H).

3.2.12. Synthesis of (*E*)-2-(4-(diethylamino)styryl)thiophene-3-carbaldehyde (compound 12). To a solution of compound **11** (0.1 g, 0.523 mmol), compound **5** (0.14 g, 0.785 mmol) and Bu_4NBr (0.2 g, 0.628 mmol) in dry DMF (5 mL), anhydrous potassium carbonate (0.09 g, 0.628 mmol), $Pd(OAc)_2$ (0.012 g, 0.0535 mmol) and triphenylphosphine (0.014 g, 0.0534 mmol) were added. The mixture was stirred under a N_2 atmosphere at 100 °C for 24 h and was monitored by TLC. After cooling to room temperature, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried with anhydrous Na_2SO_4. After removing the solvent, a crude product was obtained, which was then purified by silica gel column chromatography (ethyl acetate : petroleum = 1 : 6) to give compound **12** as a dark red solid (0.06 g, 41.2% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 10.17 (1H, s, –CHO), 7.43 (2H, d, J = 8.9 Hz, Ar-H), 7.37 (1H, d, J = 5.4 Hz, $-CH{=}CH-$), 7.13 (1H, s, thiophene-H), 7.09 (1H, s, thiophene-H), 7.02 (1H, d, J = 5.4 Hz, $-CH{=}CH-$), 6.68 (2H, d, J = 8.8 Hz, Ar-H), 3.41 (4H, q, J = 7.1 Hz, $-CH_2-$), 1.21 (6H, t, J = 7.1 Hz, $-CH_3$).

3.2.13. Synthesis of 2-(4-((*E*)-2-(2,5-bis((*E*)-4-(diethylamino)-styryl)thiophen-3yl)vinyl)-3-cyano-5,5-dimethylfuran-2(5*H*)-ylidene)-malononitrile (compound FTC-DEA). Compound **6** (0.15 g, 3.27 mmol), acceptor TCF (0.078 g, 3.92 mmol) and NH_4OAc (0.0025 g, 0.0327 mmol) were dissolved in anhydrous ethanol (3 mL). The reaction mixture was stirred and refluxed for 6 h and was monitored by TLC. The solvent was removed, and the residue was purified by column chromatography (petroleum : tetrahydrofuran = 2.5 : 1) to give compound **FTC-DEA** as a blue black solid (0.087 g, 41.6% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (1H, d, J = 15.7 Hz, $-CH_2{=}CH_2-$), 7.36 (2H, d, J = 8.8 Hz, Ar-H), 7.30 (2H, d, J = 8.8 Hz, Ar-H), 7.16 (1H, d, J = 15.5 Hz, $-CH_2{=}CH_2-$), 7.00–6.90 (2H, m, $-CH_2{=}CH_2-$ and thiophene-H), 6.83 (1H, d, J = 15.9 Hz, $-CH_2{=}CH_2-$), 6.76 (1H, d, J = 15.9 Hz, $-CH_2{=}CH_2-$), 6.65 (4H, dd, J = 8.6, 6.1 Hz, Ar-H), 6.35 (1H, d, J = 15.6 Hz, $-CH_2{=}CH_2-$), 3.41 (8H, p, J = 7.0 Hz, $-CH_2-$), 1.68 (6H, s, $-CH_3$), 1.21 (12H, q, J = 6.9 Hz, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.03, 173.72, 152.08, 148.85, 142.17, 137.88, 134.86, 133.78, 131.55, 129.31, 128.20, 125.49, 123.04, 120.47, 115.50, 112.37, 112.29, 111.83, 111.71, 97.09, 94.39, 55.34, 44.57, 34.23, 30.35, 26.21, 12.74, 12.68. MS (EI^+) *m*/*z* calcd for $C_{40}H_{41}N_5OS(M^+)$: 639.30, found: 639.3.

3.2.14. Synthesis of 2-((2,5-bis((*E*)-4-(diethylamino)styryl)-thiophen-3-yl)methylene)malononitrile (compound MTD-DEA). Compound **6** (0.15 g, 3.27 mmol), acceptor malononitrile (0.03 g, 4.9 mmol) and NH_4OAc (0.0025 g, 0.0327 mmol) were dissolved in anhydrous ethanol (3 mL). The reaction mixture was stirred and refluxed for 6 h and was monitored by TLC. After the removal of the solvent, the residue was purified by column chromatography (petroleum : ethyl acetate = 10 : 1) to give compound **MTD-DEA** as a black solid (0.074 g, 44.5% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, s, $-CH_2{=}CH-$), 7.66 (1H, s, thiophene-H), 7.41 (2H, d, J = 8.5 Hz, Ar-H), 7.34 (2H, d, J = 8.1 Hz, Ar-H), 7.08 (2H, s, $-CH_2{=}CH_2-$), 6.93 (1H, d, J = 15.9 Hz, $-CH_2{=}CH_2-$), 6.81 (1H, d, J = 15.9 Hz, $-CH_2{=}CH_2-$), 6.67 (4H, d, J = 8.1 Hz, Ar-H), 3.56–3.23 (8H, m, $-CH_2-$), 1.21 (12H, q, J = 7.1 Hz, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 161.69, 154.18, 148.41, 147.36, 135.51, 131.31, 129.14, 128.77, 127.69, 122.26, 120.89, 114.90, 113.66, 111.14, 44.03, 29.17, 19.15, 12.12. MS (EI^+) *m*/*z* calcd for $C_{32}H_{34}N_4S(M^+)$: 506.25, found: 506.3.

3.2.15. Synthesis of 2-(3-cyano-4-((*E*)-2-(2-((*E*)-4-(diethyl-amino)styryl)thiophen-3-yl)vinyl)-5,5-dimethylfuran-2(5*H*)-ylidene)-malononitrile (compound FTC-H). Compound **12** (0.1 g, 0.35 mmol) and accepter TCF (0.092 g, 0.463 mmol) were dissolved in anhydrous ethanol (2.5 mL). The reaction mixture was stirred and refluxed for 6 h and was monitored by TLC. Following the removal of the solvent, the residue was purified by column chromatography (petroleum : dichloromethane = 1 : 4.5) to give compound **FTC-H** as a black green solid (0.07 g, 43.2% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (1H, d, J = 14.6 Hz, $-CH_2{=}CH_2-$), 7.42 (2H, s, Ar-H), 7.27 (1H, s, thiophene-H), 7.14 (1H, s, thiophene-H), 7.06 (1H, d, J = 15.8 Hz, $-CH_2{=}CH_2-$), 6.67 (2H, s, Ar-H), 6.51 (1H, d, J = 15.9 Hz, $-CH_2{=}CH_2-$), 3.42 (4H, s, $-CH_2-$), 1.73 (6H, s, $-CH_3$), 1.21 (6H, t, J = 6.7 Hz, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.48, 173.62, 138.42, 128.57, 123.99, 111.41, 96.78, 44.04, 31.20, 29.16, 28.79, 26.69, 25.68, 25.02, 22.15, 13.56, 12.02. MS (EI^+) *m*/*z* calcd for $C_{28}H_{26}N_4OS(M^+)$: 466.18, found: 466.2.

3.2.16. Synthesis of (*E*)-2-((2-(4-(diethylamino)styryl)thiophen-3-yl)methylene)malononitrile (compound MTD-H). Compound **12** (0.1 g, 0.35 mmol), accepter malononitrile (0.03 g, 0.42 mmol) and ammonium acetate (0.03 g, 0.035 mmol) were dissolved in anhydrous ethanol (2.5 mL). The reaction mixture was stirred and refluxed for 6 h and was monitored by TLC. Following the removal of the solvent, the residue was purified by column chromatography (petroleum : dichloromethane = 1 : 1) to give compound **MTD-H** as a black green solid (0.054 g, 46.5% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (2H, d, J = 4.9 Hz, –CH$_2$═CH$_2$– and thiophene-H), 7.42 (2H, d, J = 8.2 Hz, Ar-H), 7.17 (1H, d, J = 5.4 Hz, –CH$_2$═CH$_2$–), 7.10 (2H, s, thiophene-H), 6.67 (2H, d, J = 6.7 Hz, Ar-H), 3.42 (4H, q, J = 6.9 Hz, –CH$_2$–), 1.21 (6H, t, J = 7.1 Hz, –CH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.37, 136.12, 128.69, 125.23, 123.54, 114.55, 113.31, 111.05, 110.95, 44.02, 12.07. MS (EI$^+$) m/z calcd for $C_{20}H_{19}N_3S$(M$^+$): 333.13, found: 333.1.

3.2.17. Synthesis of 2-(4-((*E*)-2-(5-bromo-2-((*E*)-4-(diethylamino)styryl)thiophen-3-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (compound FTC-Br). Compound **7** (0.157 g, 0.431 mmol), accepter TCF (0.103 g, 0.518 mmol) and NH$_4$OAc (0.002 g, 0.0431 mmol) were dissolved in anhydrous ethanol (3 mL). The reaction mixture was stirred and refluxed for 5 h and was monitored by TLC. Following the removal of the solvent, the residue was purified by column chromatography (petroleum : ethyl acetate = 3.5 : 1) to give compound **FTC-Br** as a black solid (0.103 g, 46% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.38 (1H, d, J = 16.0, –CH$_2$═CH$_2$–), 7.39 (2H, d, J = 8.9, Ar-H), 7.24 (1H, s, thiophene-H), 7.18 (1H, d, J = 15.7, –CH$_2$═CH$_2$–), 6.95 (1H, d, J = 15.7, –CH$_2$═CH$_2$–), 6.66 (2H, d, J = 8.9, Ar-H), 6.37 (1H, d, J = 15.7, –CH$_2$═CH$_2$–), 3.41 (4H, q, J = 7.1, –CH$_2$–), 1.70 (6H, s, –CH$_3$), 1.20 (6H, t, J = 7.1, –CH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 175.44, 173.63, 173.17, 138.46, 136.91, 128.83, 128.60, 126.36, 111.47, 110.84, 96.83, 44.01, 29.81, 27.62, 25.70, 25.55, 23.87, 12.10. MS (EI$^+$) m/z calcd for $C_{28}H_{25}BrN_4OS$(M$^+$): 544.09, found: 544.1.

3.2.18. Synthesis of (*E*)-2-((5-bromo-2-(4-(diethylamino)styryl)thiophen-3-yl)methylene)malononitrile (compound MTD-Br). Compound **7** (0.157 g, 0.431 mmol), accepter malononitrile (0.103 g, 0.518 mmol) and NH$_4$OAc (0.002 g, 0.0431 mmol) were dissolved in anhydrous ethanol (3 mL). The reaction mixture was stirred and refluxed for 5 h and was monitored by TLC. After the removal of the solvent, the residue was purified by column chromatography (petroleum : tetrahydrofuran = 8 : 1) to give compound **MTD-Br** as a black solid (0.087 g, 51% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (2H, t, J = 23.5, –CH$_2$═CH$_2$–), 7.40 (2H, s, Ar-H), 7.10 (1 H, s, thiophene-H), 7.01 (1H, s, –CH$_2$═CH$_2$–), 6.67 (2H, s, Ar-H), 3.42 (4H, d, J = 6.8, –CH$_2$–), 1.22 (6H, t, J = 7.0, –CH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 157.35, 148.38, 146.76, 136.65, 128.93, 128.68, 127.24, 125.26, 121.24, 120.60, 114.25, 112.98, 111.15, 44.11, 12.01. MS (EI$^+$) m/z calcd for $C_{20}H_{18}BrN_3S$(M$^+$): 411.04, found: 411.0.

3.3 Preparation of guest–host films and their poling process

In order to study the EO properties, guest–host films were formulated by doping chromophores **FTC-H**, **FTC-Br**, **FTC-DEA** and **FTC** (0.38 mmol g^{-1}) into poly(bisphenol A carbonate) (APC) using dibromomethane as the solvent. The solution had a solid content of 5.5 wt% and was filtered through a 0.2 μm PTFE filter and spin-coated onto an indium tin oxide (ITO) glass substrate. All the films were baked in a vacuum oven at 80 °C overnight to ensure the removal of the residual solvent. A thin layer of aurum was deposited on the films as the top electrode using the vacuum evaporation method. The thickness of the Au electrode was about ~300 nm. The films were polarized by contact poling. The poling conditions are as follows: at a temperature of about 145 °C, a moderate field of about 100 V μm^{-1} was applied. The r_{33} values were measured using the Teng–Man simple reflection technique at a wavelength of 1310 nm.[39]

4. Conclusions

A series of second-order nonlinear optical chromophores **FTC-H**, **MTD-H**, **FTC-Br**, **MTD-Br**, **FTC-DEA** and **MTD-DEA** were developed by tuning the shape to adjust the dipole moment of the chromophores, in which the major conjugated push–pull structure was located at positions 2 and 3 of the thiophene bridge and auxiliary donors or acceptors were also introduced at position 5 of the thiophene bridge, for improving the electro-optic activity of materials. The chromophores can be successfully synthesized by ^{1}H NMR, ^{13}C NMR and MS characterization. From the results of UV-vis analysis, it could be found that the chromophores with auxiliary groups (Br and DEA group) at position 5 of thiophene showed different degrees of bathochromic shift. **FTC-DEA** showed greater ICT absorption properties than the reference chromophore **FTC**, illustrating that it was a suitable auxiliary donor. Thermal analysis also indicated that all the chromophores showed excellent thermal stabilities. As we proposed, the DFT calculation analysis indicated that the new structure had a smaller dipole moment than the rod-like chromophore **FTC** ($\mu_{\mathbf{FTC}}$ = 9.11, $\mu_{\mathbf{FTC\text{-}H}}$ = 4.70, $\mu_{\mathbf{FTC\text{-}Br}}$ = 4.28 and $\mu_{\mathbf{FTC\text{-}DEA}}$ = 6.63). The EO coefficients (r_{33}) of the films were 11 pm V^{-1}, 10 pm V^{-1}, 25 pm V^{-1} and 17 pm V^{-1} for **FTC-H/APC**, **FTC-Br/APC**, **FTC-DEA/APC** and **FTC/APC**, respectively. Interestingly, although the β of **FTC-DEA** was smaller than that of **FTC**, the r_{33} of **FTC-DEA** (25 pm V^{-1}) was 47% greater than that of **FTC** (17 pm V^{-1}) at the same number density. This indicated that the boomerang-like molecular structure containing the auxiliary donor was beneficial for efficiently transforming the first-order hyperpolarizability of the chromophore into the electro-optic coefficient of the material, thereby increasing the macroscopic EO activity. In a word, adjusting the conjugated structure of chromophores was an efficient way for tuning the dipole moment and optimizing the EO activity.

Conflicts of interest

There are no conflicts to declare.

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