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## ARTICLE

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## Systematic Study of the Structure-Property Relationship of a Series of Nonlinear Optical Julolidinyl-based Chromophores with Thieno[3,2-b]thiophene Moiety

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A series of nonlinear optical (NLO) chromophores **a-d** bearing a fused bithiophene, namely thieno[3,2-b]thiophene (TT), as the conjugated bridge or lateral moiety, with the same julolidinyl-based electron donor, but different electron acceptors (*i.e.*, the 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran, TCF, or malononitrile) have been synthesized and investigated. The solvatochromic behavior, thermal stability and electrochemical properties were evaluated to study the structure-property relationships. The solvent dependence of dipole moment ( $\mu$ ), static polarizability ( $\alpha$ ), hyperpolarizability ( $\beta$ ) and bond length alternation (BLA) of all chromophores were carried out by density functional theory (DFT) calculations. Upon using the D-A- $\pi$ -A structure, blue-shift phenomenon and substantially enhanced microscopic NLO properties of chromophore **d** were obtained. The electrooptic coefficient ( $r_{33}$ ) of chromophore **a** (94 pm/V at 1.31  $\mu\text{m}$ ) was four times higher than that of chromophore **b** (~20 pm/V), while the calculated hyperpolarizability ( $\beta$ ) of chromophore **b** was five times larger with respect to chromophore **a**. All the results demonstrated that TT unit is a highly efficient conjugated bridge, and it has some electronic and steric effect on macroscopic electrooptic (EO) activity when it is used as the lateral moiety. Guidelines can be proposed for the design of a new series of guest-host polymers including julolidinyl-based chromophores with TT moiety, which could be useful in organic EO device fabrication.

### Introduction

Organic second-order nonlinear optical (NLO) chromophores have been of considerable interest in ultrafast electrooptic (EO) applications over the last few decades.<sup>1, 2</sup> The designed NLO chromophores were required to simultaneously exhibit large hyperpolarizability ( $\beta$ ), strong thermal and photochemical stability as well as good optical transparency for practical EO device applications.<sup>3-5</sup> To achieve better NLO properties, significant advances in the development of novel organic EO materials have been made through rational molecular design<sup>6-13</sup> to optimize the ground-state polarization of the push-pull type chromophores by fine tuning the combination of electron donor (D), electron acceptor (A) and the  $\pi$ -conjugated bridge ( $\pi$ -bridge).<sup>14-19</sup> The methods like using twisted  $\pi$ -conjugated systems,<sup>20-22</sup> alkali-metal-doped effect,<sup>23</sup> non-covalent charge transfer effect<sup>14</sup> and attaching the halogen atom<sup>24</sup> to the chromophores were all demonstrated to largely increase the EO properties of the materials. Recently, NLO chromophores with julolidinyl group as the stronger electron donor have been

studied and showed more excellent EO properties than chromophores with the classical dialkylamine donor for EO device application.<sup>25-29</sup> Among them, chromophores with julolidinyl-based donor, thiophene-based electron bridge and a strong acceptor (*i.e.*, 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran, TCF) have been developed previously in our group to exhibit appealing NLO properties and good stability.<sup>30,31</sup> However, the  $\beta$  values of these chromophores can still be improved. Thus, the potentially attractive microscopic NLO properties of the julolidinyl-based chromophores are desirable to develop. And the enhanced  $\beta$  values coupled with excellent chemical and thermal stability are needed for practical EO applications.

Considering the best charge transfer (CT) efficiency, polyene-type structure was introduced as the  $\pi$ -bridge between the donor and acceptor. However, chromophores with olefinic fragments always associated with poor thermal stability that restricted their practical applications to a large extent. Thus, the replacement of polyene-type structure by heteroaromatic compounds with lower aromatization energies was a common

alternative to provide a good balance between NLO activity and stability.<sup>32, 33, 34</sup> Five-membered heterocyclic rings have been successfully developed as highly efficient  $\pi$ -bridges for CT.<sup>32</sup> Among them, thiophene has been widely employed in the heterocycle-based  $\pi$ -bridge, and so do some more complex structures like fused rings.<sup>35-41</sup> The thieno[3,2-b]thiophene (TT) unit, because of its good electron transfer ability, was mostly introduced to provide optimized planarity and intramolecular charge transfer (ICT) stability for organic photovoltaic applications.<sup>42, 43, 44</sup> But thieno[3,2-b]thiophene (TT) as the fused ring based  $\pi$ -bridge was rarely used in the NLO chromophores. And the reported chromophores with TT unit didn't show satisfied NLO properties due to the relatively weak donor and acceptor.<sup>45, 46</sup> Moreover, Thus, chromophores with stronger donor/acceptor, and TT based bridge are expected to provide higher NLO responses and better thermal stability.<sup>46-48</sup> However, to the best of our knowledge, few julolidinyl-based chromophores with TT unit were studied, and they were expected with large microscopic and macroscopic NLO properties.

According to the two-level model,<sup>49</sup> chromophores with large dipole moment ( $\mu$ ) and  $\beta$  value always accompanied by long wavelength absorption, leading to the so-called nonlinearity-transparency trade-off and resulting in large optical loss for EO modulator applications.<sup>26</sup> Therefore, one crucial way to search for the blue-shifted chromophores without the loss of nonlinearities is combining the different types of conjugated bridges. This novel concept was proposed to overcome the nonlinearity-transparency trade-off, but only a few studies on this concept were reported in recent years.<sup>50, 51</sup> Consequently, chromophore **d** with combined bridges was designed and synthesized with two successive microwave methods, which were studied by us previously. This new designed D-A- $\pi$ -A structure chromophore finely demonstrated this novel concept. In summary, these chromophores were expected to have large NLO properties as well as high thermal stability and to overcome the nonlinearity-transparency trade-off.

In this work, we focus our attention on the synthesis and characterization of six new chromophores **a-f** (with TT unit) (see Scheme 1 and Scheme 2) bearing different  $\pi$ -bridges and acceptors and a fixed julolidinyl donor. The solvatochromism behaviour and thermal stability of all chromophores were also discussed in detail. Moreover, DFT calculations were carried out to demonstrate the solvent dependence of the static polarizability ( $\alpha$ ),  $\beta$ ,  $\mu$ , electron density, bond length alternation (BLA) and the energy gap ( $\Delta E$ ).<sup>26</sup> Through the theoretical calculation, the  $\beta$  value of chromophores, which contained the julolidinyl-based donor, TCF acceptor and TT-based  $\pi$ -bridge, were much larger than that of chromophores with thiophene-based  $\pi$ -bridge. In this system, chromophores **a-d** were designed for the first time to discuss the effect of the TT unit as the  $\pi$ -bridge or the lateral moiety on the molecular polarization level and NLO responses. Chromophores **e** and **f** were synthesized without TT unit for comparison. Finally, the macroscopic EO activity ( $r_{33}$  value) of chromophores **a** and **b** was studied by doping them into the amorphous polycarbonate (APC). The  $r_{33}$  values of poled film **a/APC** (94 pm/V at 1.31  $\mu\text{m}$ ) was almost four times larger with respect to **b/APC** (~20 pm/V at 1.31  $\mu\text{m}$ ).<sup>52</sup> The experimental measurements and theoretical calculations described herein helped us to recognize the electronic and geometric structures of these chromophores.

## Experimental section

## General methods

All reagents were purchased from commercial sources and were used as received unless otherwise specified. Solvents such as N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were freshly treated and distilled over calcium hydride and sodium, respectively, and stored under nitrogen prior to use. Phosphorus oxychloride ( $\text{POCl}_3$ ) was distilled before use. The dielectric constants of six different solvents are 1,4-dioxane: 2.25, toluene: 2.38, chloroform: 4.81, dichloromethane: 8.93, acetone: 20.7, acetonitrile: 37.5, respectively. The thieno[3,2-b]thiophene electron bridge and the 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) acceptor were prepared according to the literature procedures,<sup>53, 54</sup> respectively. UV-Vis-NIR spectra were obtained using a HITACHI U-2001 spectrometer. The TGA curve was recorded with a TA-instrument Q50 analyzer at a heating rate of 10  $^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a TA5000, 2910MDSC with a heating rate of 10  $^\circ\text{C}/\text{min}$  under the protection of nitrogen. The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.) spectrometer and on EI (Electron Impact Source) with an ApexIII (7.0 tesla) FTICR mass spectrometer (Bruker). Cyclic voltammetry (CV) experiments were performed on Princeton Applied Research Model 283 Potentiostat/Galvanostat. A three-electrode-system is used for the measurement and bulk electrolysis, with a 3 mm glass carbon working electrode, a platinum sheet counter electrode, and a non-aqueous Ag/AgNO<sub>3</sub> reference electrode for organic solution reference electrode for aqueous solution. The electrolyte solution (0.1 M of n-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN for organic solution) was degassed by bubbling with argon for 40 min before measurement. The working electrode was polished with 0.05  $\mu\text{m}$  alumina paste and sonicated for 15 min before use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on an AVANCE 400 (Bruker) spectrometer (400 MHz) using tetramethylsilane (TMS;  $\delta = 0$  ppm) as the internal standard, respectively.

The DFT quantum chemical methods using Gaussian 09<sup>58</sup> software package in gas phase and six different solvents were carried out at the B3LYP/6-31G level. Geometry structures of each chromophore were optimized and resulted in a three dimensional D- $\pi$ -A arrangement. The calculated parameters including electron density,  $\mu$ ,  $\alpha$ ,  $\beta$ , BLA and  $\Delta E$ .

## Electric Field Poling and EO Property Measurements

To study the poling and EO activity derived from the chromophores, guest-host polymers were generated by formulating chromophores **a** (20 wt%) and **b** (10 wt%) into amorphous polycarbonate (APC) using dibromomethane ( $\text{CH}_2\text{Br}_2$ ) as the solvent. The resulting solutions were filtered through the 0.2  $\mu\text{m}$  PTFE filter, and then spin-coated onto indium tin oxide (ITO) glass substrates (from thin film devices). Films of doped EO polymers were baked in vacuum oven over night to ensure the removal of the residual solvent. Corona poling was used to pole the films. The poling temperature was 135  $^\circ\text{C}$  for **a/APC** and 145  $^\circ\text{C}$  for **b/APC**. Then, a thin layer of aluminium (50~100 nm) was sputtered onto the films as the top electrode. The  $r_{33}$  values were measured by the Teng-Man simple reflection technique at the wavelength of 1.31  $\mu\text{m}$  using a carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections.<sup>55</sup>

**General procedure for synthesis of compound 1.** Under N<sub>2</sub> atmosphere to a solution of 8-hydroxy-1,1,7,7-tetramethylformyljulolidine (2.73 g, 10 mmol) in anhydrous DMF was added 1-chloroheptane (2.02 g, 15 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.08 g, 15 mmol). The mixture was irradiated under microwaves (140 °C) for 35 min and then poured into water until it was cooled to the ambient temperature. The resulting solutions were filtered and then extracted with ethyl acetate. The combined organic extracts were washed with brine and then dried over MgSO<sub>4</sub> and filtered. After the removal of the solvent, the residue was purified by column chromatography using petroleum ether and ethyl acetate (40 : 1, v/v) as eluent to give the product as an yellow solid (2.96 g, yield: 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 9.96 (s, 1H), 7.59 (s, 1H), 3.96 (t, J = 6.9 Hz, 2H), 3.29 (t, 2H), 3.23 (t, 2H), 1.93 – 1.82 (m, 2H), 1.76 – 1.66 (m, 4H), 1.46 (dd, J = 8.6, 4.1 Hz, 2H), 1.43 (s, 6H), 1.38 – 1.31 (m, 4H), 1.26 (s, 6H), 0.91 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ 187.75, 162.12, 148.20, 126.06, 125.29, 120.71, 117.26, 78.88, 47.46, 46.82, 39.41, 35.70, 32.44, 32.04, 31.74, 30.25, 30.01, 29.73, 25.63, 22.56, 14.01. MALDI-TOF-MS (m/z): calcd: 358.0 ; found: 359.2.

**General procedure for synthesis of compound 2.** A solution of thieno[3,2-b]thiophene (1 g, 7.13 mmol) in dry THF (30 mL) was cooled to -78 °C and was maintained at this temperature under N<sub>2</sub> atmosphere during the dropwise addition of n-BuLi in hexane (2.5 M, 14.26 mmol). After the mixture was stirred at -78 °C for 1 h, it was warmed to -10 °C and held for 30 min. The solution was cooled back to -78 °C again, and kept at this temperature during the dropwise addition of dry DMF (10 mL). The reaction mixture was warmed to the ambient temperature, and then quenched by adding 10 mL of water. The residue was extracted with ethyl acetate (3×50 mL). The combined organic layer was washed sequentially with brine and DI water, and then dried over MgSO<sub>4</sub>, filtered, concentrated and purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (80 : 3, v/v) to give compound 2 as an orange solid (1.02 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 9.96 (s, 1H), 7.93 (s, 1H), 7.69 (d, J = 5.3 Hz, 1H), 7.32 (d, J = 5.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 184.40, 146.56, 146.29, 140.05, 134.74, 129.92, 121.00. EI-MS (m/z): calcd: 167.9 ; found: 168.8.

**General procedure for synthesis of compound 3.** To a solution of compound 2 (1.68 g, 10 mmol) in methanol (20 mL) was added NaBH<sub>4</sub> (0.46 g, 12 mmol) in batches at 0 °C with an ice bath. After the temperature warmed up to room temperature and the solution became clear, diluted hydrochloric acid was added to neutralize the reaction and then keep stirring for 2 h. The solution was extracted with ethyl acetate; the combined organic extracts were washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was directly dried in the vacuum oven for the next step without flash chromatography. The product was a white solid (0.88 g, yield: 75%). <sup>1</sup>H NMR (400 MHz, Acetone, δ ppm) 7.36 (d, J = 5.2 Hz, 1H), 7.19 (d, J = 5.2 Hz, 1H), 7.12 (s, 1H), 4.70 (d, J = 5.9 Hz, 2H), 1.91 (dt, J = 4.3, 2.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Acetone, δ ppm) 149.65, 139.62, 139.40, 127.49, 120.55, 117.40, 60.70. MALDI-TOF-MS (m/z): calcd: 170.0 ; found: 171.0.

**General procedure for synthesis of compound 4.** Into about 20 mL of CHCl<sub>3</sub> was dissolved 0.5 g (2.94 mmol) of compound 3. To this solution was added triphenylphosphine hydrobromide 1.14 g (3.32 mmol). The mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure. The product

was collected and washed with anhydrous ethyl ether, and used without further purification. The yield was 1.4 g (97% yield). The molecular formula without bromine was tested since the bromine is not observed. MALDI-TOF-MS (m/z): calcd: 414.1 ; found: 415.1.

**General procedure for synthesis of compound 5.** To a solution of compound 1 (1.91 g, 5.34 mmol) and compound 4 (2.64 g, 5.34 mmol) in dry THF (20 mL) was added NaH (2.40 g, 100 mmol). The solution was allowed to stir at room temperature for 24 h and then poured into water. The residue was extracted with ethyl acetate (3×50 mL). The combined organic layer was washed sequentially with brine and DI water, and then dried over MgSO<sub>4</sub>, filtered, concentrated and purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (100 : 1, v/v) to give compound 5 as an orange oil (1.32 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.18 (dd, J = 11.9, 6.7 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.05 (s, 1H), 7.01 (s, 1H), 6.52 (s, 1H), 3.91 (t, J = 6.5 Hz, 1H), 3.86 (t, J = 6.5 Hz, 2H), 3.13 – 3.07 (m, 2H), 3.06 – 2.99 (m, 2H), 1.93 – 1.83 (m, 2H), 1.78 – 1.66 (m, 4H), 1.60 – 1.50 (m, 2H), 1.43 (s, 6H), 1.37 (m, 4H), 1.28 (s, 6H), 1.14 (s, 2H), 0.94 – 0.81 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 154.99, 146.19, 141.89, 138.51, 135.71, 132.72, 132.52, 127.58, 127.41, 127.35, 125.46, 125.15, 124.76, 121.48, 118.47, 116.70, 115.24, 72.32, 46.33, 45.85, 39.39, 35.83, 31.66, 31.21, 30.85, 30.42, 29.34, 29.11, 24.95, 21.59, 12.92. MALDI-TOF-MS (m/z): calcd: 493.2; found: 494.2.

**General procedure for synthesis of compound 6 and 7.** A solution of 20 mL DMF was cooled to 0 °C and was maintained at this temperature during the dropwise addition of freshly distilled phosphorus oxychloride (POCl<sub>3</sub>, 0.64 g, 4.2 mmol). The solution was kept for 2 h of stirring at 0 °C and the temperature was kept during the dropwise addition of compound 5 in 10 ml DMF (1.0 g, 2 mmol). The solution was gradually warmed to room temperature and then heated to 90 °C for 3 h. The solution of Na<sub>2</sub>CO<sub>3</sub> (10%, 150 mL) was added to quench the reaction which was then allowed to cool down to room temperature. The reaction mixture was extracted by ethyl acetate (3×50 mL), washed with brine, dried over MgSO<sub>4</sub> and filtered. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (400 : 7, v/v) to give compound 6 as an orange solid (0.57 g, 55%) and to give compound 7 as a red solid (0.31 g, 28%). Compound 6: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 9.63 (s, 1H), 7.62 (s, 1H), 7.32 (d, J = 5.2 Hz, 1H), 7.28 (s, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.04 (s, 1H), 3.94 (t, J = 6.7 Hz, 2H), 3.21 – 3.13 (m, 4H), 1.95 – 1.83 (m, 2H), 1.77 – 1.68 (m, 4H), 1.60 – 1.49 (m, 6H), 1.42 (s, 9H), 1.40 – 1.35 (m, 6H), 1.26 (s, 4H), 0.95 – 0.89 (m, 4H), 0.77 (s, 6H), 0.07 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 191.27, 158.30, 148.56, 144.94, 139.24, 138.21, 136.49, 132.80, 132.61, 127.43, 126.06, 125.78, 124.65, 120.43, 118.90, 118.38, 113.06, 74.86, 46.35, 45.75, 38.62, 34.80, 31.50, 30.78, 30.71, 29.15, 28.91, 28.88, 24.84, 21.67, 13.03. MALDI-TOF-MS (m/z): calcd: 521.2; found: 522.2. Compound 7: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 9.83 (s, 1H), 9.51 (s, 1H), 7.81 (s, 1H), 7.57 (s, 1H), 7.29 (s, 1H), 6.95 (s, 1H), 3.86 (t, 2H), 3.10 (t, 4H), 1.81 (s, 2H), 1.62 (m, 2H), 1.46 (m, 2H), 1.33 (s, 12H), 1.16 (m, 2H), 0.82 (m, 2H), 0.70 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 190.31, 182.37, 158.55, 149.38, 145.46, 144.64, 144.01, 143.66, 138.95, 128.16, 126.04, 125.80, 124.78, 120.53, 119.33, 112.41, 75.33, 46.33, 45.74, 38.43, 34.53, 31.46, 30.74, 30.68, 29.12, 28.89, 28.78, 24.81, 21.56, 13.05. MALDI-TOF-MS (m/z): calcd: 549.2; found: 550.2.

**General procedure for synthesis of compound 8.** A solution of compound 5 (3.95 g, 8 mmol) in dry THF (50 mL) was cooled to -78 °C and was maintained at this temperature under N<sub>2</sub> atmosphere during the dropwise addition of n-BuLi in hexane (2.5 M, 16 mmol). After the mixture was stirred at -78 °C for 1 h, it was warmed to -10 °C and held for 30 min. The solution was cooled back to -78 °C again, and kept at this temperature during the dropwise addition of dry DMF (12 mL). The reaction mixture was warmed to the ambient temperature, and then quenched by adding 10 mL of water. The residue was extracted with ethyl acetate (3×70 mL). The combined organic layer was washed sequentially with brine and DI water, and then dried over MgSO<sub>4</sub>, filtered, concentrated and purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (60 : 1, v/v) to give compound 8 as an orange red solid (2.79 g, 67%). <sup>1</sup>H NMR (400 MHz, Acetone, δ ppm) 9.95 (s, 1H), 8.16 (s, 1H), 7.45 (s, 1H), 7.38 (s, 1H), 7.28 (d, J = 16.1 Hz, 1H), 7.20 (d, J = 16.1 Hz, 1H), 3.84 (t, J = 6.6 Hz, 2H), 3.21 (t, 2H), 3.15 (t, 2H), 1.95 – 1.85 (m, 2H), 1.72 (t, 4H), 1.64 – 1.53 (m, 2H), 1.41 (s, 6H), 1.40 – 1.38 (m, 2H), 1.28 (s, 6H), 0.90 (s, 3H). <sup>13</sup>C NMR (101 MHz, Acetone, δ ppm) 183.99, 157.63, 154.82, 147.42, 145.09, 137.61, 131.00, 129.33, 127.83, 123.78, 123.14, 118.02, 76.26, 48.05, 47.54, 41.26, 37.68, 33.56, 33.14, 32.81, 31.74, 31.07, 30.90, 26.99, 23.51, 14.53. MALDI-TOF-MS (m/z): calcd: 521.2; found: 522.2.

**General procedure for synthesis of chromophore a.** A mixture of compound 6 (2.61 g, 5 mmol) and acceptor 9 (1.09 g, 5.5 mmol) in 20 mL of ethanol was irradiated under microwaves (95 °C) for 15 min. The resulting mixture was removed the solvent and purified through column chromatography using petroleum ether and ethyl acetate (6 : 1, v/v) as eluent to give the product as dark green solids (2.63 g, yield: 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.06 (d, J = 15.0 Hz, 1H), 7.51 (s, 1H), 7.44 (d, J = 5.2 Hz, 1H), 7.30 (d, J = 5.2 Hz, 1H), 7.13 (s, 1H), 6.60 (s, 1H), 6.09 (d, J = 15.0 Hz, 1H), 3.91 (t, J = 6.5 Hz, 2H), 3.24 (s, 4H), 2.00 – 1.87 (m, 2H), 1.78 – 1.66 (m, 4H), 1.61 (s, 9H), 1.55 – 1.47 (m, 2H), 1.40 (s, 12H), 1.26 (s, 2H), 1.04 – 0.86 (m, 4H), 0.64 (s, 6H), 0.07 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 175.68, 172.06, 159.77, 153.00, 145.75, 139.43, 138.75, 138.03, 129.90, 127.82, 126.60, 126.30, 125.69, 124.96, 120.83, 119.06, 118.60, 114.79, 109.77, 95.57, 76.81, 64.54, 46.66, 46.02, 38.13, 31.44, 30.73, 30.55, 29.06, 28.52, 28.04, 25.40, 13.08. MALDI-TOF-MS (m/z): calcd: 702.2; found: 703.2.

**General procedure for synthesis of chromophore b.** A mixture of compound 8 (2.61 g, 5 mmol) and acceptor 9 (1.09 g, 5.5 mmol) were dissolved in ethanol (2 mL) and chloroform (18 mL). The solution was added 2 drops of triethylamine and then was refluxed at 90 °C for 3-5 h and monitored by TLC. After removal of the solvents, the residue was purified by column chromatography eluting with petroleum ether and ethyl acetate (10 : 1, v/v) to give a dark solid (2.45 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.91 (d, J = 15.6 Hz, 1H), 7.56 (s, 1H), 7.30 (s, 1H), 7.13 (s, 1H), 7.03 (d, J = 15.9 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 3.85 (t, J = 6.7 Hz, 2H), 3.24 (t, J = 5.8 Hz, 2H), 3.17 (t, 2H), 1.89 (m, 2H), 1.77 (m, 2H), 1.76 (s, 6H), 1.57 (m, 4H), 1.44 (s, 6H), 1.39 (s, 4H), 1.32 (s, 6H), 0.92 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Acetone, δ ppm) 182.97, 156.59, 153.78, 146.30, 144.30, 143.82, 136.63, 129.97, 128.29, 126.79, 122.74, 122.10, 117.11, 116.85, 75.22, 47.01, 46.50, 40.22, 36.64, 32.52, 32.10, 31.78, 30.71, 30.03, 29.87, 25.96, 22.48, 13.50. MALDI-TOF-MS (m/z): calcd: 702.2; found: 703.1.

**General procedure for synthesis of chromophore c.** A mixture of compound 8 (2.61 g, 5 mmol) and malononitrile (0.46 g, 7 mmol) were dissolved in 15 mL chloroform. The solution was added 2 drops of triethylamine and was stirred at room temperature for 15 min. After removal of the solvents, the residue was purified by column chromatography eluting with petroleum ether and ethyl acetate (20 : 1, v/v) to give a dark solid (1.28 g, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.77 (d, J = 19.1 Hz, 2H), 7.27 (d, J = 12.5 Hz, 2H), 7.12 (s, 1H), 7.02 (d, J = 15.9 Hz, 1H), 3.84 (t, J = 6.6 Hz, 2H), 3.23 (t, 2H), 3.16 (t, 2H), 1.89 (m, 2H), 1.75 (m, 4H), 1.54 (m, 2H), 1.43 (s, 6H), 1.39 (s, 4H), 1.31 (s, 6H), 0.91 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 175.56, 172.08, 159.75, 152.89, 145.51, 139.52, 138.84, 138.22, 129.84, 127.87, 126.58, 126.36, 125.76, 119.13, 118.61, 114.99, 111.89, 110.95, 110.88, 95.56, 76.79, 64.53, 46.73, 46.10, 38.31, 31.53, 30.75, 29.11, 28.62, 28.18, 25.38, 21.56, 13.02. MALDI-TOF-MS (m/z): calcd: 569.2; found: 570.1.

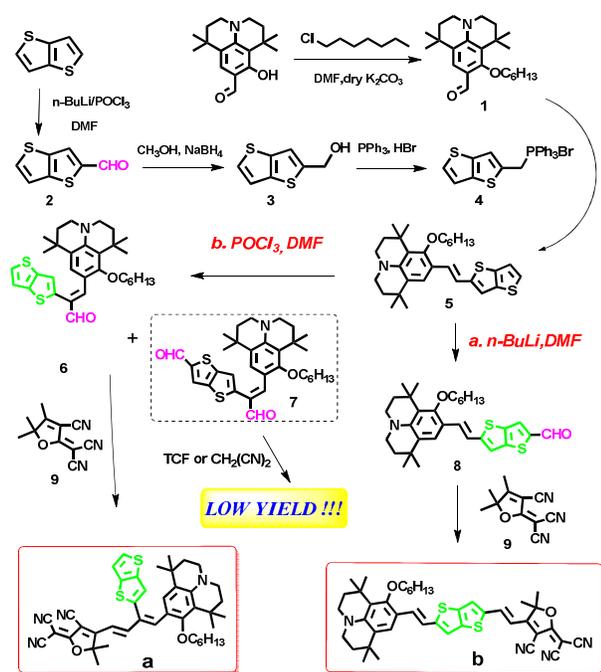
**General procedure for synthesis of chromophore d.** A mixture of compound 8 (2.61 g, 5 mmol), compound 4 (isophorone, 0.83 g, 6 mmol), sodium ethoxide (7 mmol, 0.17 g sodium dissolved in 2 mL anhydrous ethanol) in 10 mL anhydrous ethanol was irradiated under microwaves (95 °C) for 30 min. Then the reaction finished and cooled to the room temperature. After the solvent was evaporated, the residue and malononitrile (0.46 g, 7 mmol) was dissolved in 10 mL anhydrous ethanol was irradiated under microwaves (95 °C) for 20 min. Then the reaction finished and cooled to the room temperature. After the solvent was evaporated, the residue was purified by column chromatography use petroleum ether and ethyl acetate (10 : 1, v/v) as eluent to give the product as black solids (2.41 g, yield: 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.27 (s, 1H), 7.25 (s, 1H), 7.21 (d, J = 15.7 Hz, 1H), 7.13 (d, J = 15.9 Hz, 1H), 7.07 (s, 1H), 6.99 (d, J = 15.9 Hz, 1H), 6.80 (s, 1H), 6.72 (d, J = 15.6 Hz, 1H), 6.62 (s, 1H), 3.85 (t, J = 6.7 Hz, 2H), 3.19 (t, 2H), 3.12 (t, 2H), 2.59 (s, 2H), 2.43 (s, 2H), 1.92 – 1.82 (m, 2H), 1.75 (m, 4H), 1.55 (s, 4H), 1.43 (s, 6H), 1.38 (m, 4H), 1.31 (s, 6H), 1.08 (s, 6H), 0.91 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 170.32, 168.65, 159.71, 156.39, 153.50, 150.58, 142.52, 141.91, 137.56, 130.90, 130.71, 128.85, 127.41, 122.85, 122.60, 120.59, 116.50, 113.17, 113.07, 112.39, 78.28, 75.34, 47.48, 46.98, 45.69, 42.94, 42.64, 39.18, 36.70, 32.75, 32.35, 32.00, 31.91, 31.30, 30.28, 30.17, 29.70, 28.03, 27.81, 26.02, 25.28, 22.67, 14.08. MALDI-TOF-MS (m/z): calcd: 689.2; found: 689.8.

**General procedure for synthesis of chromophore e.** A mixture of compound 1 (1.79 g, 5 mmol), compound 4 (isophorone, 0.83 g, 6 mmol), sodium ethoxide (7 mmol, 0.17 g sodium dissolved in 2 mL anhydrous ethanol) in 10 mL anhydrous ethanol was irradiated under microwaves (95 °C) for 30 min. Then the reaction finished and cooled to the room temperature. After the solvent was evaporated, the residue and malononitrile (0.46 g, 7 mmol) was dissolved in 10 mL anhydrous ethanol was irradiated under microwaves (95 °C) for 20 min. Then the reaction finished and cooled to the room temperature. After the solvent was evaporated, the residue was purified by column chromatography use petroleum ether and ethyl acetate (80 : 3, v/v) as eluent to give the product as dark purple solids (1.99 g, yield: 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.35 (s, 1H), 7.29 (d, J = 16.0 Hz, 1H), 6.78 (d, J = 15.7 Hz, 1H), 6.77 (s, 1H), 3.79 (t, J = 6.7 Hz, 2H), 3.26 (t, 2H), 3.19 (t, 2H), 2.58 (s, 2H), 2.46 (s, 2H), 1.92 – 1.79 (m, 2H), 1.79 – 1.66 (m, 4H), 1.56 – 1.47 (m, 2H), 1.42 (s, 6H), 1.39 – 1.34 (m, 4H), 1.31 (s,

6H), 1.06 (s, 6H), 0.92 (t, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 169.07, 157.96, 156.09, 145.02, 134.84, 127.33, 123.48, 123.05, 121.03, 114.68, 113.97, 76.45, 47.62, 47.05, 43.09, 39.82, 39.50, 36.23, 32.36, 32.38, 32.09, 32.03, 30.87, 30.31, 30.09, 29.81, 28.21, 26.17, 22.76, 14.19. MALDI-TOF-MS ( $m/z$ ): calcd: 525.4; found: 526.4.

**General procedure for synthesis of chromophore f.** A mixture of compound **1** (1.78 g, 5 mmol) and acceptor **9** (1.09 g, 5.5 mmol) in 20 mL of ethanol was irradiated under microwaves (95 °C) for 15 min. The resulting mixture was removed the solvent and purified through column chromatography using petroleum ether and ethyl acetate (10 : 1, v/v) as eluent to give the product as dark green solids (2.02 g, yield: 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 7.73 (d,  $J = 15.6$  Hz, 1H), 7.42 (s, 1H), 6.73 (d,  $J = 15.8$  Hz, 1H), 3.79 (t,  $J = 7.3$  Hz, 2H), 3.42 (t,  $J = 6.2$  Hz, 2H), 3.35 (t, 2H), 1.97 – 1.87 (m, 2H), 1.76 (s, 6H), 1.75 – 1.72 (m, 2H), 1.43 (s, 6H), 1.34 (dd,  $J = 7.3, 3.4$  Hz, 4H), 1.30 (s, 6H), 0.91 (t, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 174.07, 160.68, 149.17, 143.87, 130.91, 128.85, 128.32, 124.39, 122.44, 115.50, 113.35, 112.54, 111.90, 107.18, 96.06, 71.79, 65.55, 47.94, 47.28, 38.88, 35.12, 32.50, 32.09, 31.75, 29.72, 29.31, 27.12, 25.62, 22.57, 13.99. MALDI-TOF-MS ( $m/z$ ): calcd: 538.3; found: 539.1.

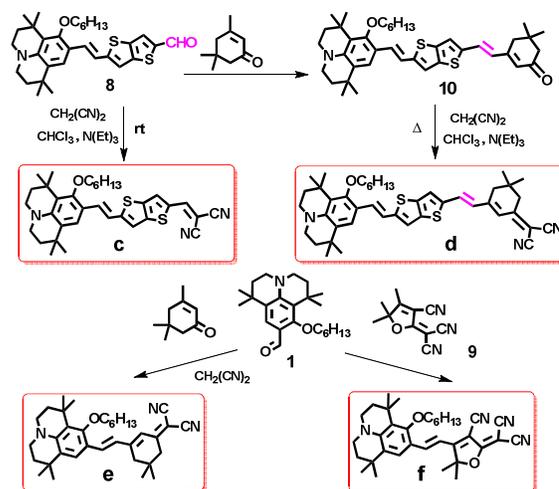
## Results and discussion



**Scheme 1** Synthesis scheme for chromophores **a** and **b**.

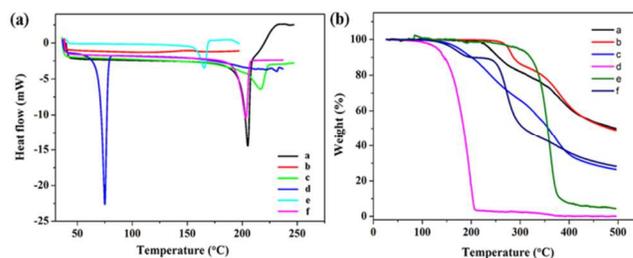
Chromophores **a** and **b** were synthesized as shown in Scheme 1. Compound **2** with one aldehyde group was obtained through two methods of the formylated reaction using *n*-butyllithium (*n*-BuLi) and DMF, and the Vilsmeier reaction with phosphorus oxychloride ( $\text{POCl}_3$ ) and DMF. Both methods can introduce only one aldehyde group by one step approach with high yields (>90 %), when the *n*-BuLi,  $\text{POCl}_3$  and DMF were excess. Compound **2** was then reduced to alcohol **3** and transferred to Wittig salt **4**. Afterwards, compound **1** reacted with Wittig salt **4** following Wittig reaction to obtain compound **5**. Through an

Vilsmeier reaction, TT unit in compound **6** was also found as a dual-function structure and provided steric hindrance and electronic effect.<sup>31</sup> The formation of the unexpected compound **7** with two aldehyde groups, was resulted from the excess  $\text{POCl}_3$  and DMF. Due to the slight electron-withdrawing property of the aldehyde group, it was hard for compound **7** to condense with two acceptors simultaneously with considerable yield. Compound **8** was obtained by deprotonation of compound **5** with *n*-BuLi followed by reaction with DMF. Finally, compounds **6** and **8** were coupled with acceptor **9** to obtain target chromophores **a** and **b**, respectively.



**Scheme 2** Synthesis of chromophore **c**, **d**, **e** and **f**.

To study the influence of acceptor strength and the combined bridge effect on the nonlinearity, chromophores **c** and **d** were designed and shown in Scheme 2. Noticeably, chromophore **d** was synthesized with two successive microwave (MW)-assisted condensation methods introduced by us previously, which demonstrated that MW-assisted heating was an highly efficient method in the synthesis of NLO chromophore. All the chromophores exhibited good solubility in common organic solvents, such as acetone, DMSO,  $\text{CH}_2\text{Cl}_2$ , DMF,  $\text{CHCl}_3$ , and THF. The structures of the compounds were characterized unambiguously with  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MALDI-TOF-MS.



**Fig. 1** The DSC and TGA curves of chromophores **a**-**f** with a heating rate of 10 °C/min in nitrogen.

### Thermal stability

The thermal properties of chromophores **a**-**f** were evaluated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) in nitrogen with the results shown

and tabulated in Fig. 1 and Table 1. All chromophores except chromophore **b** displayed crystalline characteristics with a melting point ( $T_m$ ). Obviously, chromophore **b** was obtained as an thermodynamically stable amorphous glass state solid showing a glass transition temperature ( $T_g$ ) at around 125 °C. The amorphous state of chromophore **b** was mainly attributed to both the longer  $\pi$ -bridge and the stronger TCF acceptor, which disfavoured the close packing of molecules. The strong  $T_m$  peak of chromophore **d** showed that the combined bridge structure could promote chromophore molecules crystallizing.

**Table 1** Thermal properties of chromophore a-f.

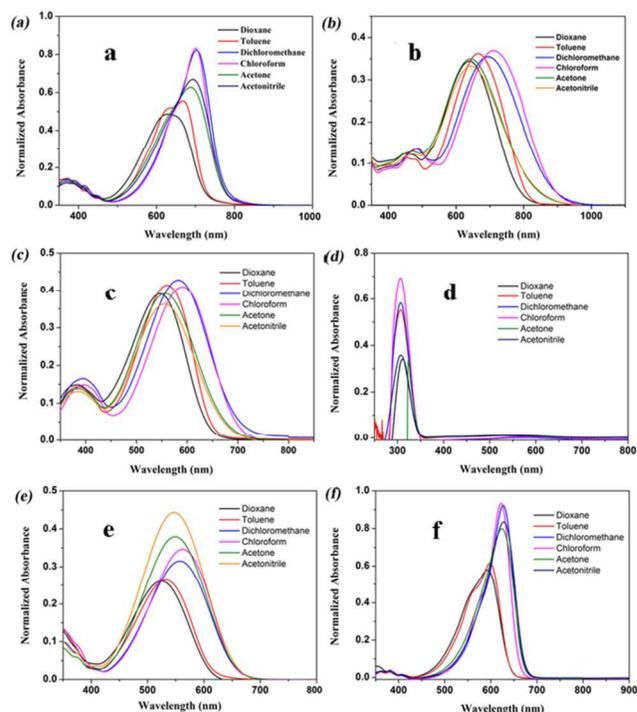
Compd	$T_g/T_m$ (°C)	$T_d$ (°C)
a	205	238
b	125	276
c	217	174
d	75	130
e	166	296
f	203	164

The TGA results did not follow the same trends as DSC results. Chromophore **e** showed the highest decomposition temperature ( $T_d$ ), while chromophore **d** showed the lowest  $T_d$ , which might due to the ‘mismatched’ combination of TT and isophorone units.<sup>33</sup> Chromophore **b** displayed higher  $T_d$  than **a**, suggesting that chromophore with TT unit as the  $\pi$ -bridge can increase the thermal stability compared with the reported polyene-type chromophore (212 °C)<sup>4</sup>. By comparison of chromophores **b** and **c**, it can be concluded that TCF acceptor helped to increase the thermal stability, which was in agreement with  $T_g$  values. As a result, chromophores **a**, **b** and **e** displayed the sufficient thermal stabilities ( $T_d$  is higher than 200 °C) for application in device fabrication.

### UV-Vis-NIR spectroscopy

The solvatochromic behavior of chromophores is strongly influenced by the strength of the donor and acceptor in combination with the  $\pi$ -bridge. To reveal the solvent dependence effect of the  $\pi$ -bridge and acceptor on the electronic structures of chromophores **a-f**, the UV-Vis-NIR absorption spectra were measured in six solvents with different dielectric constants (Fig. 2) and the corresponding optical absorption data were recorded in Table 2. All the chromophores showed intense low-energy ICT absorption bands except for chromophore **d**. Distinctively, chromophore **d** displayed a weak low-energy ICT absorption band and a intense and narrow high-energy ICT band, which was assigned to the  $\pi$ - $\pi^*$  transition of the aromatic moiety. It was presumed that the resonant structures of the combination of the TT unit and isophorone unit disfavoured the ICT from the electron donor to the acceptor.<sup>33</sup> In combination with the poor thermal stability, we called this the ‘mismatched’ phenomenon. With the increase of solvent polarity, all of the chromophores red-shifted initially, reaching the maximum value in chloroform or dichloromethane, and then, chromophores **a**, **e** and **f** exhibited the saturation

behaviors. The cyanine-like characteristic (the neutral and charge-separated limiting resonance forms contributed equally to the ground state) band shape of them indicated that the two limiting resonance forms have approximately the same contribution to the ground state.<sup>25</sup> Chromophores **b** and **c** were polarized distinctly beyond the cyanine limit into the zwitterionic regime in acetone and acetonitrile solvents. While for chromophore **e**, slight blue-shift was observed. Furthermore, chromophores **a** and **f** showed the relative smaller fwhm (full width at half maximum) of the low-energy ICT absorption band and the most intensified absorbance in high polar solvents due to the short polyene  $\pi$ -bridge and the strong TCF acceptor.<sup>26, 56</sup>



**Fig. 2** Solvatochromic behavior of chromophores **a-f** recorded in six solvents ( $10^{-5}$  M) of varying dielectric constants at room temperature.

**Table 2** Summary of low-energy optical absorption data

compd	Absorption $\lambda_{max}$ (nm)						$\Delta\lambda_{max}$
	DO	TL	CF	DC	AC	AN	
a	628	668	700	703	688	693	75
b	640	666	712	696	644	643	72
c	546	560	591	583	557	555	45
d	546	565	585	578	547	539	46
e	525	532	562	558	549	547	37
f	593	598	622	627	624	628	35

[a] DO: dioxane; TL: toluene; CF:  $\text{CHCl}_3$ ; DC:  $\text{CH}_2\text{Cl}_2$ ; AC: acetone; AN: acetonitrile

Comparison of chromophores **b** and **c** with different acceptors, the  $\lambda_{max}$  blue-shifted with the decrease of acceptor strength, and the  $\lambda_{max}$  blue-shifted from chromophore **f** to **e**. This suggested that chromophores with stronger acceptor were

easier to polarize. As for the chromophore **d**, the  $\lambda_{\max}$  decreased especially in highly polar solvents, demonstrating that chromophore **d** with the combination of the TT unit and isophorone unit as the  $\pi$ -bridge blue-shifted in comparison with its analogue (chromophore **c**) with single type of  $\pi$ -bridge. The maximal wavelength difference ( $\Delta\lambda_{\max}$ ) of all chromophores in six different solvents were depicted in Table 3. Chromophores **a** and **b** showed larger  $\Delta\lambda_{\max}$  with respect to chromophores **c** and **d**, and chromophores **e** and **f** with shorter  $\pi$ -bridges showed smaller  $\Delta\lambda_{\max}$  values than others. It was suggested that chromophores **a** and **b** were the easiest to be polarized among all the chromophores.

### Electrochemical properties and spectroscopic analysis for $\Delta E$

The electrochemical behavior are closely related to the orbital structures of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the compounds. Thus, the oxidation and reduction potentials tested from electrochemical cyclic voltammetry (CV) measurements can provide important information for the HOMO-LUMO gap ( $\Delta E$ ). All the chromophores exhibited a single reversible or quasi-reversible oxidative wave in a positive energy and a single reversible reductive peak in a negative energy (Fig S1, supporting information). Table 2 showed that the HOMOs were similar for chromophores **b** and **c** because of the same donor part, while the LUMOs were systematically lowered with an increase of the acceptor strength, leading to the decreased  $\Delta E$ . Moreover, due to the increased length of the  $\pi$ -bridge, chromophore **b** showed the smallest  $\Delta E$  (0.85 eV) and the chromophore **f** showed the largest  $\Delta E$  (1.44 eV). The observed electrochemical behavior was in accord with the calculated orbital energy levels and ICT process of HOMO and LUMO for the chromophores studied in the following part.

As shown in Table 3,  $\Delta E$  values of all the chromophores were also calculated through the UV-Vis-NIR absorption spectra by doping them into the APC polymer films. The  $\Delta E$  values of spectra analysis and CV measurements were followed the same trend, and the former was larger with respect to the latter. This can be attributed to the fact that the spectral results were tested in polymer films while the CV results were tested in acetonitrile solutions.

### DFT calculations

**First- and second-order polarizability.** To profoundly understand the microscopic NLO properties of the designed chromophores, DFT calculations were performed at the B3LYP/6-31G level using Gaussian 09 program package.<sup>55</sup> The calculated average static polarizability ( $\alpha$ ) can be obtained using Equation (1) (Table S1, supporting information). The total first hyperpolarizability ( $\beta_{\text{tot}}$ ) of the designed chromophores (Table S2, supporting information) are related to the individual tensor components can be obtained using Equation (2). They were calculated by the finite field method based on the optimized molecular geometries.  $\beta_i$  ( $i=x, y, z$ ) is defined by Equation (3-5),  $\mu$  can be obtained using Equation (6)

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (1)$$

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

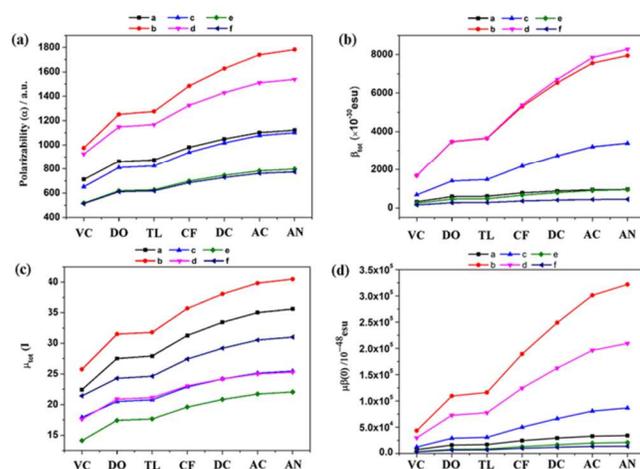
$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (3)$$

$$\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx} \quad (4)$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \quad (5)$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (6)$$

The  $\alpha$  of chromophores **a-f** are shown in Fig. 3(a). It was found that chromophores with longer or similar length of conjugated bridges showed larger or similar  $\alpha$  values. Moreover, the  $\alpha$  values of chromophores in solvents were larger than that in gas phase, and showed the increased tendency with the increase of the solvent permittivity. It was demonstrated that chromophore **b** with the longest conjugated bridge was the most vulnerable to the effects of solvent polarity of all the chromophores.



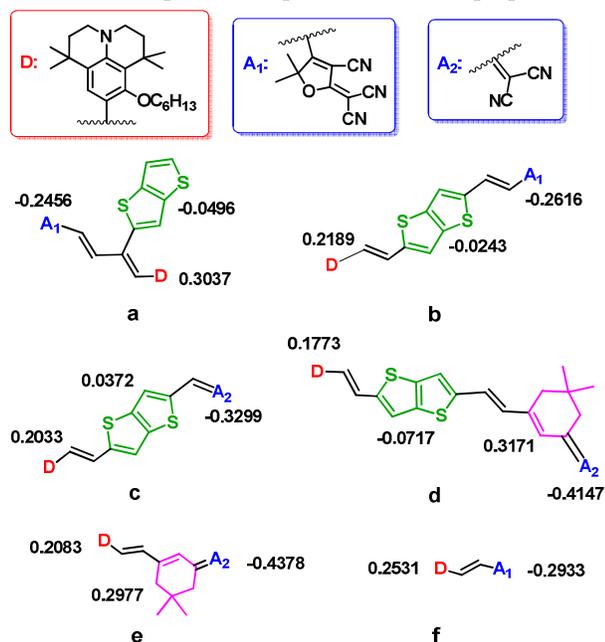
**Fig. 3** The solvent dependence of (a)  $\alpha$ , (b)  $\beta_{\text{tot}}$ , (c)  $\mu$ , (d)  $\mu\beta$  were calculated in gas phase and six solvents. (Table S7-S10, supporting information). VC: Vacuum

Fig. 3(b) showed the calculated  $\beta_{\text{tot}}$  (Table S4, supporting information) in gas phase and solvents. Chromophores **b** and **d** gave the similar  $\beta_{\text{tot}}$ , which was much larger than that of other chromophores. It was demonstrated that chromophores with longer  $\pi$ -bridges and stronger acceptors offered larger  $\beta_{\text{tot}}$ , and was consistent with the trend of  $\alpha$  value. In contrast, chromophore **a** showed lower  $\beta_{\text{tot}}$  value than that of chromophore **c**. This was ascribed to that the existence of the special lateral TT moiety that used as the lateral moiety and could disperse three directional  $\beta_i$  ( $i=x, y, z$ ) tensors and tended to lower the  $\beta_{\text{tot}}$ . All the chromophores showed a similar increasing trend of  $\beta_{\text{tot}}$  to a certain extent as a function of increasing solvent dielectric constant. The slopes were steep for chromophores **b** and **d**, and relatively smooth for chromophores **a**, **e**, and **f**, suggesting that chromophores with longer  $\pi$ -bridges showed larger  $\beta_{\text{tot}}$  values and bigger changes with the increase of dielectric constant. This followed the similar trend of  $\alpha$  value. Especially, chromophore **d** showed the largest calculated  $\beta_{\text{tot}}$  among all six chromophores, and the blue-shifted phenomenon in UV-Vis-NIR spectra was also found for chromophore **d** that

mentioned previously. Thus, it was demonstrated that the combination of different  $\pi$ -bridges could lead to overcoming the nonlinearity-transparency trade-off.

The  $\mu$  of chromophores **a-f** were displayed in Fig. 3(c) and tabulated (Table S3, supporting information). Chromophore **b** showed the largest  $\mu$  due to the strong acceptor and good planarity. Chromophore **a** had larger  $\mu$  with respect to chromophore **f** due to its longer  $\pi$ -bridge. Though chromophore **d** had much larger  $\beta_{\text{tot}}$  than that of chromophore **c**, it showed almost the same  $\mu$  as **c**. It can be explained that the combined  $\pi$ -bridge could not only increase the  $\beta_{\text{tot}}$ , but also decrease the  $\mu$ .

Because of the largest  $\mu$  and  $\beta_{\text{tot}}$ , chromophore **b** showed the largest  $\mu\beta$  value (Fig. 3(d), Table S4, supporting information), which had a great potential for the NLO application. Chromophore **d** showed lower  $\mu\beta_{\text{tot}}$  value than **b** due to the lower  $\mu$ . Chromophores **a**, **e**, and **f** showed the similar  $\mu\beta_{\text{tot}}$  values due to the similar  $\beta_{\text{tot}}$ . Above all, the calculation results could provide us useful parameters for reference in designing the novel chromophores and predict their NLO properties.



**Fig. 4** Mulliken atomic charges on various molecular domains for six studied chromophores at the B3LYP/6-31G level. The moieties in color were considered for charge calculation.

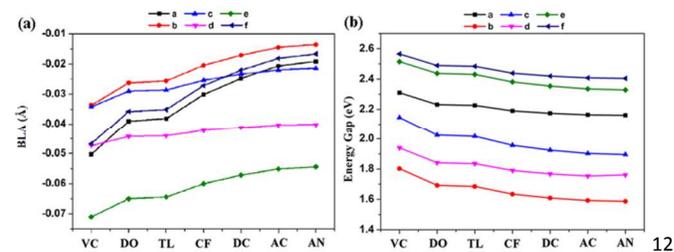
**Calculated Mulliken charges.** Mulliken charge analysis was reported as a useful method to understand the ground state electronic structure and estimate the molecular polarization.<sup>45</sup> Therefore, the Mulliken charges on various molecular domains for the studied chromophores were calculated in gas phase and shown in Fig. 4.

Comparison of chromophores **a** and **b** showed that the TT moiety both lateral moiety and  $\pi$ -bridge exhibited the electronegativity. And the negative charge located in TT moiety as the lateral moiety is higher than that as the  $\pi$ -bridge due to the strong electron-withdrawing stability of TCF acceptor. However, the charge in TT unit for chromophore **c** was

electropositive, resulting in that the strong TCF electron acceptor tended to increase charge separation. In contrast, comparison of chromophores **c** and **d** with chromophores **e** and **f** showed that extending the conjugation length changed the electron property of the TT unit from electropositive to electronegative and disfavored the charge separation. And chromophore **d** showed the approximate D-A- $\pi$ -A structure. These phenomena revealed that the TT unit was regarded as auxiliary acceptor in **d** and as auxiliary donor in **c**. Thus, we speculated that the  $\pi$ -bridges favored to form the D-A- $\pi$ -A structure, and it could favor to overcome the nonlinearity-transparency trade-off. Furthermore, the D-A- $\pi$ -A structure chromophore could be used as a key part in dye-sensitized solar cells (DSSCs).<sup>57</sup>

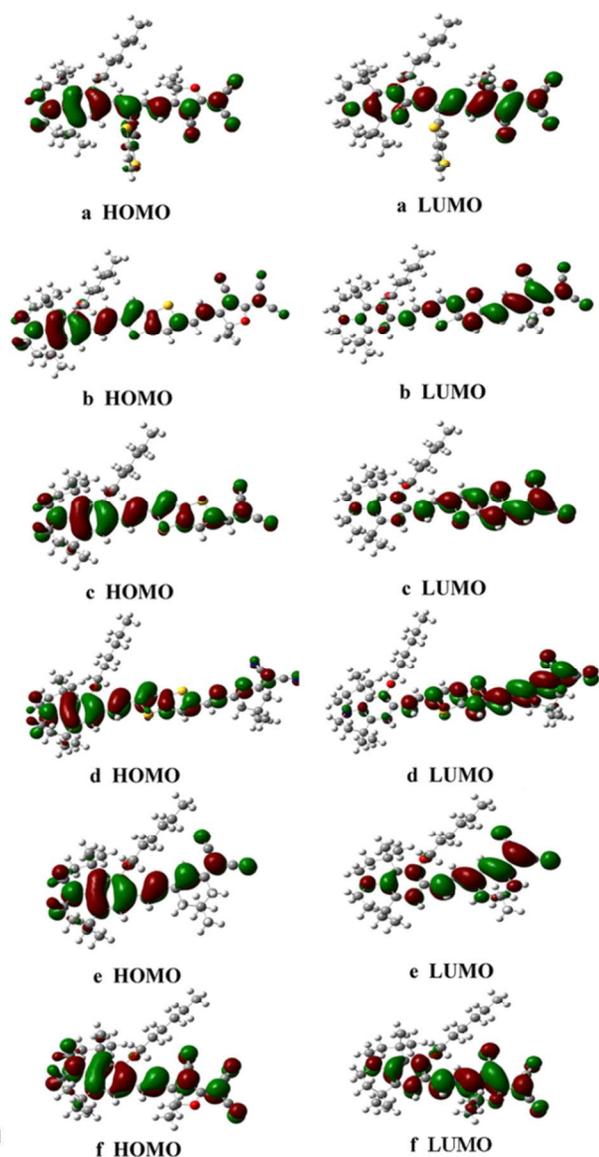
Mulliken charges on various molecular domains for above chromophores were also calculated in six different solvents to study the solvent dependence of the ICT. For the donor and acceptor moieties, ICT of the six chromophores increased with the increase of the dielectric constant of solvents. Distinctively, the TT unit of chromophore **b** showed electron negative firstly and transferred to electron positive with the increasing of the solvent dielectric constant (Table S1'-S6', supporting information). This was in relation to the strong electron-withdrawing ability of TCF acceptor and the strong electron delocalization ability of TT unit. Furthermore, the charge difference of each unit for a given chromophore molecule tend to decrease with the increase of the solvent polarity, suggesting that increasing the solvent polarity could stabilize the charge separation. Therefore, the study of molecular electron structure is a guideline for the chromophore design to tune the quadratic NLO properties.

**Bond-length alternation.** The bond length alternation (BLA) was reported as a key structural parameter that can be correlated with the ground state geometry of the molecule and hyperpolarizability.<sup>25</sup> BLA was defined as the average difference in length between adjacent carbon-carbon single and double bonds in the molecule. Based on the two-state model,<sup>58</sup> there is an optimal structure about the combination of each unit of the chromophore.<sup>25</sup> As reported before, the semiempirical calculations were mainly performed on the push-pull polyene chromophores, while few studies were performed on the heteroaromatic ring based chromophores. For polyene chromophores, tuning the suitable combination of donor and acceptor as well as the  $\pi$ -bridge can optimize the BLA and the  $\beta$ . It showed that the maximum  $\beta$  value can be achieved when the BLA values is intermediate ( $\pm 0.05 \pm 0.01$  Å). Consequently, the BLA values of the  $\pi$ -bridges can be regarded as a measure of ground-state polarization and as an important parameter for NLO response.



**Fig. 5** The calculated (a) BLA and (b) Energy gap values of chromophores a-f in vacuum and six different solvents.

For the heteroaromatic ring based chromophores (a-d) and two polyene chromophores (e and f), as shown in Fig 5(a), the BLA of six chromophores in gas phase and six solvents were calculated (Table S1-S6, supporting information) to study the solvent dependence of BLA and the correlation between the  $\beta_{\text{tot}}$  and BLA. For chromophore **d** with combined bridges, the BLA is between  $-0.04 \text{ \AA}$  and  $-0.05 \text{ \AA}$  and it also shows the largest  $\beta_{\text{tot}}$ , which is in consistent with the BLA model. For chromophore **b** with single TT bridge, the absolute value of BLA shows the minimum value but the  $\beta_{\text{tot}}$  is as large as that of chromophore **d**. We speculated that chromophores used TT unit as the  $\pi$ -bridge were not well suitable for this BLA model. Moreover, all the chromophores showed the similar decaying trend in BLA with an increase of solvent polarity. As the the solvent polarity increased, the occupancy of zwitterionic form arose to the evenly distribution of the two resonance forms. The BLA of chromophore **d** demonstrated that it had larger  $\beta_{\text{tot}}$  value than that of other chromophores according to the BLA model proposed by Marder et al.<sup>59</sup>



**Fig. 6** The HOMO and LUMO frontier molecular orbitals of chromophores a-f.

**Energy gaps ( $\Delta E$ ).** The  $\Delta E$  between HOMO and LUMO of six chromophores were calculated in vacuum and six different solvents. As shown in Fig. 5(b), the  $\Delta E$  of all the chromophores displayed a similar decaying trend as a function of the increasing solvent polarity. Thus, the solvent-dependent behaviors of all the chromophores studied here suggested that increasing the solvent dielectric constant could reduce the  $\Delta E$  of the chromophore molecules and tend to favor ICT. Moreover, the  $\Delta E$  results calculated by DFT method were in consistent with the experimental results using the CV method and the spectral analysis. It also demonstrated that this calculated method can be a good alternative to predict  $\Delta E$ .

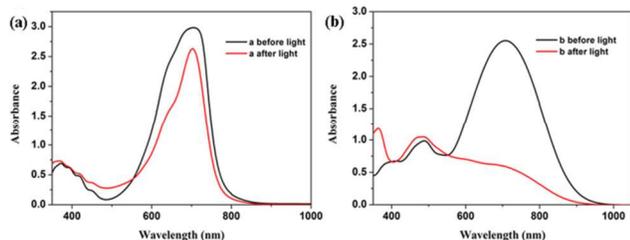
**Frontier molecular orbitals.** Frontier molecular orbitals (FMOs) of chromophores a-f were calculated to show the relationship between the structures and properties. As shown in Fig. 6, for all the chromophores, the HOMOs were delocalized on the julolidinyl-based donors and  $\pi$ -bridges while the LUMOs were localized in the conjugated bridges and concentrated on the acceptors. The results indicated that increasing the length of the  $\pi$ -bridges allowed an efficient ICT from the donor to the acceptor. Moreover, for chromophore **a**, the optimized perpendicular spatial configuration of the TT unit disfavored the ICT on main axis. It was worth highlighting that the TT unit contributed roughly equal to both HOMOs and LUMOs of chromophore **b**, which promoted the ICT. Thus, chromophores with longer  $\pi$ -bridges and stronger acceptors were supposed with lower  $\Delta E$ , which was in accord with the experimental results.

### EO property

According to the experimental and calculated results of chromophores a-f mentioned above, chromophores **a** and **b** were chosen to evaluate the EO activity for such reasons. Firstly, both of them showed good thermal stability. Secondly, chromophore **b** exhibited largest  $\beta_{\text{tot}}$  and  $\mu\beta_{\text{tot}}$  values according to the DFT calculations. Then, they both showed good photophysical properties. Finally, the influence of TT unit as the lateral moiety or  $\pi$ -bridge of the chromophore could be studied. Thus, amorphous polycarbonate (APC) guest-host polymer films incorporating 20 wt% of chromophores **a** and **b** were prepared. Both two EO polymers showed the similar  $T_g$  around  $140 \text{ }^\circ\text{C}$  and the poling temperature was about  $5 \text{ }^\circ\text{C}$  higher than  $T_g$ . Another two critical parameters determining the  $r_{33}$  values were poling voltage and time. The optimum condition was poled at  $145 \text{ }^\circ\text{C}$  for 18 min under the electric field of 11.5 kV. After that, the films were cooled to room temperature rapidly followed by removing the poling voltage. A thick film of aluminium (around 100 nm) was sputtered on the poled films, and then the EO coefficients of them were measured by Teng-Man method at a wavelength of  $1.31 \text{ }\mu\text{m}$ . The maximum  $r_{33}$  value of 94 pm/V for chromophore **a** was achieved. However,

chromophore **b** didn't show the large  $r_{33}$  value because of the poor compatibility in APC films. Then, 10 wt% of the chromophore **b** was doped into APC to make the guest-host polymer film following the same abovementioned procedures. The optimum condition was poled at 155 °C for 25 min under the electric field of 11 kV. The maximum  $r_{33}$  value was only around 20 pm/V. Chromophore **b** was calculated with largest  $\mu$  and  $\beta_{\text{tot}}$  value, however, these values and the good planarity also make it easy to form the antiparallel aggregation, leading to the sharply attenuated  $r_{33}$  value. As to chromophore **a**, the TT unit in this molecule affected both the steric effect and the electron effect, resulting in the decreased intermolecular dipole-dipole interactions. We speculated that the steric effect could play a major role in the macroscopic NLO properties, while the electron effect could play a crucial role in the microscopic NLO properties.

### Photochemical stability



**Fig. 7** The UV-Vis-NIR absorption spectra of the solutions were irradiated with a 450 nm light. The spectra before and after irradiating with a 450 nm light of  $\text{CHCl}_3$  solutions for chromophore **a** (a) and chromophore **b** (b).

To investigate the photochemical stability of chromophores **a** and **b**, they were separately dissolved in chloroform solutions ( $5 \times 10^{-5}$  M), and then irradiated of 450 nm light for an hour. As shown in Fig. 7 (a) and (b), after irradiating, the UV-Vis-NIR absorption spectra of chromophore **b** dropped more extensively than that of chromophore **a**. It also demonstrated that chromophore **a** showed better photostability and EO properties than that of chromophore **b**. This might be attributed to the lower  $\Delta E$  of chromophore **b** (0.85 eV) than that of chromophore **a** (1.11 eV), which made chromophore **b** was more sensitive to light and oxygen than chromophore **a**. This was in consistent with the experimental and calculated  $\Delta E$  results, which showed that chromophore **b** had lower  $\Delta E$  than chromophore **a**. Consequently, for chromophore with large microscopic NLO properties as **b**, how to improve the poling efficiency and solubility and photochemical stability in host polymer films and efficiently translate the large microscopic NLO properties to macroscopic  $r_{33}$  values is an urgent challenge. Such as optimizing the structure by introducing the bulk groups to the donor or acceptor part was an alternative under study.

### Conclusions

A series of julolidinyl-based chromophores based on different types of  $\pi$ -bridges, including TT unit and the isophorone unit, and TCF or dicyanomethylene acceptors, have been synthesized and investigated. The structure-property relationship of the studied chromophores was explored using experimental and calculated data. Electrochemical and solvatochromic behaviour analysis as well as DFT calculations were also carried out to show the microscopic NLO properties of the chromophores. Chromophore **b** displayed larger  $\mu\beta_{\text{tot}}$  value and narrower energy gap than those of chromophore **a**, whereas its  $r_{33}$  value displayed almost three times smaller with respect to chromophore **a**. This might be attributed to the better photochemical stability and the steric structure of the TT unit of chromophore **a**, leading to the increased poling efficiency. Chromophore **d** with combination of TT unit and isophorone unit as the  $\pi$ -bridge was calculated as D-A- $\pi$ -A structure. It preferred to display blue-shifted phenomenon of ICT absorption and large microscopic NLO properties that helped to overcome the nonlinearity-transparency trade-off. However, this new 'mismatched' combination of  $\pi$ -bridge made chromophore **d** display the sharply decreased thermal stability and weak low-energy absorption because of the inefficient ICT. Thus, searching for the 'matched' combination of  $\pi$ -bridge bridges with good thermal stability is a big challenge. Moreover, good thermal stability and NLO properties made chromophores **a** and **b** with great potential for a new generation organic EO devices. Thus, the improvement of translating the large  $\beta$  value into bulk EO activity of materials is a big challenge we need to overcome in the near future.

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### Notes and references

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**Table 3** Measured and calculated parameters from the electrochemical and the absorption spectroscopic experiments

Compd	Electrochemical Analysis					Spectroscopic Analysis	
	$E_{ox}^a, V$	$E_{red}^a, V$	$E_{HOMO}^b (eV)$	$E_{LUMO}^b (eV)$	$\Delta E^c (eV)$	$\lambda_{onset}^d, nm$	$\Delta E^e (eV)$
a	0.21	-0.90	-4.60	-3.49	1.11	870	1.42
b	0.03	-0.82	-4.42	-3.57	0.85	948	1.31
c	0.01	-1.15	-4.40	-3.24	1.16	753	1.65
d	0.001	-1.13	-4.39	-3.26	1.13	766	1.62
e	0.06	-1.16	-4.45	-3.23	1.22	717	1.73
f	0.35	-1.09	-4.47	-3.30	1.44	715	1.73

<sup>a</sup> Potentials vs Ag/Ag<sup>+</sup> in 0.1M TBAPF<sub>6</sub>/MeCN solution. <sup>b</sup>  $E_{HOMO} = -e[4.39V + E_{ox}]$  and  $E_{LUMO} = -e[4.39V + E_{red}]$ . <sup>c</sup>  $\Delta E = E_{HOMO} - E_{LUMO}$ . <sup>d</sup> Estimated from the onset of the absorption at low concentration chromophores in solid film in APC. <sup>e</sup>  $\Delta E = 1240/\lambda_{onset}$ .