RSC Advances

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Novel Electro-optic Chromophores Based on Substituted Benzo[1,2-b:4,5-b']dithiophene π-Conjugated Bridges

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Two novel nonlinear optical (NLO) chromophoreswere designed and synthesized based on substitutedbenzo[1,2-b:4,5-b']dithiophene unit, tricyanofuran (TCF) electron acceptor and two different electron donors. These new chromophores, which exhibited good thermal stability and solubility in common organic solvents, were systematically characterized by thermogravimetric analysis, UV-Vis spectra, density functional theory (DFT) calculations and measurements of electro-optic (EO) coefficients. Compared with the dodecyl group in chromophore BDT1 we previously reported, the isooctane group in BDT2 could act as the suitable isolation group, and as a result, the guest-host system containing 30% of BDT2 in APC displayed the largest EO coefficient of 102 pm/V, which was greatly improved than BDT1 and the analogous thiophene-based chromophore with the same electron donor and acceptor. The solvatochromic analysis and DFT study demonstrated that julolidine group in BDT3 possessed stronger donating ability. However, the 30% BDT3/APC only exhibited the EO coefficient of 82 pm/V, which probably was caused by the diminishment of hyperpolarizability value of BDT3 in the polar polymer matrix. These results indicate the potential of isooctane-substituted benzo[1,2-b:4,5-b']dithiopheneπ-conjugated bridge in chromophore design and NLO materials, and further illustrate the critical role of suitable isolation group and fine-tuning of donor's electron-donating strength in optimizing the nonlinear properties of NLO chromophores.

Introduction

With the rocketing development of information technology, electro-optic (EO) materials, which are widely used in telecommunications such as phased array radar, optical gyroscopes and modulators, have drawn great attention in the past decades[1-10]. Compared to inorganic/semi-conductor EO materials, organic EO materials have many advantages such as large nonlinear optical (NLO) coefficients, ultra-fast response time, large bandwidth, low dielectric constant and good processability[2, 11, 12]. In order to promote the development of EO materials, much effort has been expended in developing NLO chromophores and EO polymers. But to fulfill the requirements for device fabrication and operation, a strong need remains for improving the NLO properties and stability of NLO chromophores, which plays a key role in EO devices at both the microscopic level and macroscopic materials level[13-15].

Organic second-order NLO chromophore molecules are the core component of EO materials and typically consist of a π-conjugated bridge end-capped with strong electron-donating and -accepting groups[2, 11]. Among them, π-conjugated electron bridge helping intramolecular charge-transfer plays an essential role in chromophore structure[11, 14, 16]. For the purpose of improving microscopic first-order hyperpolarizability (β), increasing and optimizing the π-conjugated bridge is a critical aspect. But unfortunately, the added conjugation length often influences the stability of the molecule, which will directly decrease the practical application of NLO chromophoresc[2, 11]. Benzo[1,2-b:4,5-b']dithiophene (BDT) unit containing two thienyl rings is widely used for photovoltaic conjugated polymers due to its large planar conjugated structure, which makes BDT a promising electron bridge[17-19]. Previously, we first introduced this unit into NLO materials and synthesized a novel chromophore BDT1 which showed promising second order NLO features and could meet the requirement of stability for application[20]. However, the guest-host EO materials[21, 22] of BDT1 doped into APC didn't exhibit the desired EO activities.

Suppressing the dipolar-dipolar electrostatic interaction and increasing the microscopic hyperpolarizability are basic strategies to improve the EO activities from the angle of NLO chromophores. Dipolar-dipolar electrostatic interaction between chromophores, which could cause the chromophores' aggregation, is a major obstacle hindering the translation of microscopic hyperpolarizability into macroscopic EO activity[5, 23-30]. Dalton et al.'s and Li et al.'s work demonstrated that the dipole-dipole interactions could be effectively suppressed through introduction of suitable isolation groups[31-35]. And the relative researches also predicted that the ideal shape for chromophore is spherical[2, 36]. On the other hand, the hyperpolarizability is the source of EO

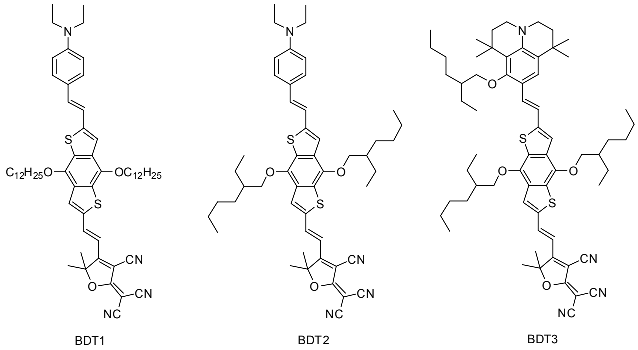

Chart 1. Chemical structures of the chromophores

activity, so improving the chromophores' NLO properties is also an effective approach to improve macroscopic activity, and the hyperpolarizability can be tuned by optimizing the ground-state polarization through modification of the strength of the donor or acceptor.

To improve the macroscopic EO activities of BDT-based NLO chromophores and further explore the potential of BDT π-conjugated bridge in NLO materials, we designed and synthesized novel chromophore BDT2 with new isolation groups and BDT3 with stronger electron donor as shown in chart 1. BDT2 adopts the shorter dendritic isooctane groups, which we believe are more suitable for isolating and can make the chromophore closer to spherical shape. In BDT3, the julolidine derivative 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine,which has been proved to be an excellent electron donor[13, 37], is used to improve the electron donating ability. The thermal stability, photophysical properties, density functional theory (DFT) calculations and EO activities of these chromophores were systematically studied and compared. The results further proved that substituted benzo[1,2-b:4,5-b’]dithiophene is a quite promising π-conjugated bridge in chromophore design and that the isooctane group could be a suitable isolation group to improve the EO activities (maximum r_{33} values was up to 102 pm/V), and they also illustrated the critical role of fine-tuning of donor's electron-donating strength in optimizing the nonlinear properties of NLO chromophores.

Experimental

Materials and instruments

All reagents were purchased from commercial sources and were used as received unless stated. DMF, THF, ethyl ether and acetone were freshly distilled prior to use. Compound 3 was synthesized by our group,4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione and the TCF acceptor were prepared according to the literature[18, 38-40]. ^{1}H NMR and ^{13}C NMR spectra were measured on an AVANCE 400 spectrometer (Bruker) using tetramethylsilane (TMS; δ = 0 ppm) as the internal standard (Resolution ^{1}H≤0.45Hz; ^{13}C≤0.2Hz). High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV FTMS spectrometer (Accuracy <1-2ppm). The MS spectra were obtained using MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on GCT Premier (Waters) (Resolution 7000FWHM; Sensitivity 1pg). Melting points were obtained using Beijing X4 melting point tester. The Fourier transform infrared (FT-IR) spectra were recorded on a Varian 3100 FT-IR spectrometer (Resolution 0.20 cm^{-1}; Accuracy < 0.01 cm^{-1}). UV-Vis spectra were obtained using a Varian Cary5000 spectrophotometer (Resolution 0.05 nm; Accuracy ≤±0.1nm). The TGA curve was recorded with a TA-instrument Q50 analyzer with a heat rate of 10 °C/min under nitrogen atmosphere.

Syntheses

Synthesis of Compound 1

4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (4.4 g, 20 mmol), zinc powder (3.3 g, 50 mmol), and water (60 mL) were put into a 250 mL flask, then NaOH (12 g, 0.3 mol) was added into the mixture. After the mixture was stirred and refluxed for 1 h, 1-bromoisooctane (11.6 g, 60 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. The reactant was refluxed for 8 h and then was poured into cold water and extracted by ethyl ether three times. The organic layer was dried over anhydrous $MgSO_4$. After solvent removed, the crude product was purified by column chromatography. Compound **1**(7.1 g, yield 79%) was obtained as pale yellow oil. IR(KBr), ν_{max}/cm^{-1}: 3084, 2959, 2927, 2872 (C-H), 1519 (thienyl), 1439 (benzene ring), 1198 (Ph-O-C). MS, *m/z*: 446.23 (M$^+$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (thienyl, d, *J* = 5.5 Hz, 2H), 7.37 (thienyl, d, *J* = 5.5 Hz, 2H), 4.26 – 4.15 (-O-CH_2-, m, 4H), 1.83 (-CH-, m, *J* = 11.9, 5.8 Hz, 2H), 1.77 – 1.35 (-CH_2-, m, 16H), 1.00 (-CH_3, m, 12H).

Synthesis of Compound 2

Compound **1** (2.23 g, 5 mmol) was dissolved into dry THF (30 mL) in a 100 mL flask. Then n-butyllithium (3.75 mL, 15 mmol, 2.5M) was injected into the solution slowly at -78 °C under an inert atmosphere. The solution was stirred for 30 min at -78 °C and for 30 min at -10 °C. After that, the solution was cooled at -78 °C and excess DMF was injected into the solution slowly. The solution was stirred at -78 °C for 30 min and then warmed to room temperature. After that the reactant was quenched with water (300 mL), extracted with ethyl ether, and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography. Compound **2**(1.80 g, yield 72%) was obtained as orange solid. Mp: 93-94 °C. IR(KBr),ν_{max}/cm^{-1}: 2960, 2930, 2874 (C-H), 1670 (-CHO), 1535, 1452 (aromatic ring), 1215 (Ph-O-C). MS, *m/z*: 502.43 (M$^+$).^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm)10.14 (-CHO, s, 2H), 8.18 (thienyl, s, 2H), 4.28 (-O-CH_2-, d, *J* = 5.3 Hz, 4H), 1.91 – 1.80 (-CH-, m, 2H), 1.74 – 1.34 (-CH_2-, m, 16H), 0.98 (-CH_3, m, 12H).

Synthesis of Compound 4

Compound **2** (1.10 g, 2.2 mmol), compound **3** (1.01 g, 2 mmol), NaH (1.0 g, 0.04 mol), and dry ethyl ether (50 mL) were put into a 100 mL flask. The reactant was stirred for 24 h at ambient temperature with the flask sealed up. After that, the mixture was poured into ice water (200 mL) slowly. The mixture was then extracted with ethyl ether and dried over $MgSO_4$. After the removal of ethyl ether, the crude product was purified by column chromatography. Compound **4** (0.82 g, yield 58%) was obtained as red oil. ^{1}H NMR ($CDCl_3$) shows that the product is a mixture of trans and cis isomers. On the basis of the integration areas of two –CHO signals, the trans isomer is estimated to be 90% and the cis isomer 10%. IR(KBr), ν_{max}/cm^{-1}: 2959, 2926, 2870 (C-H), 1670 (-CHO), 1599, 1520, 1449 (aromatic ring), 1265 (Ph-O-C). MS, *m/z*: 647.12 (M$^+$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)

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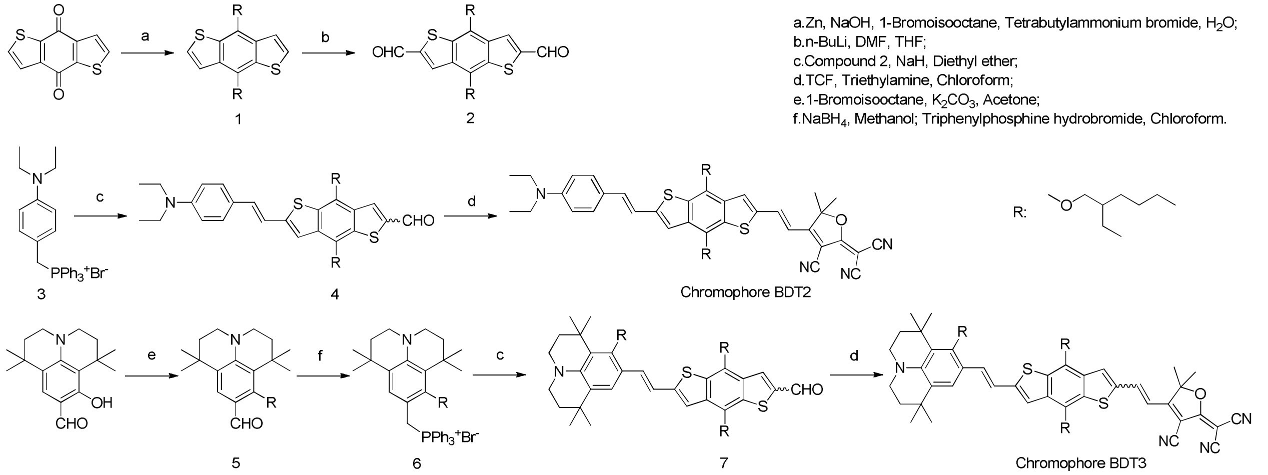


Scheme 1. Synthesis route of BDT2 and BDT3

10.11 (-CHO, s, 0.10H), 10.06 (-CHO, s, 0.90H), 8.15 (thienyl-H, s, 0.10H), 8.11 (thienyl, s, 0.90H), 7.39 (phenyl, d, J = 8.7 Hz, 2H), 7.24 (thienyl, s, 1H), 7.09 (vinylic, d, J = 15.9 Hz, 1H), 6.95 (vinylic, d, J = 15.9 Hz, 1H), 6.66 (phenyl, d, J = 8.7 Hz, 2H), 4.36 – 4.09 (-O-CH_2-, m, 4H), 3.40 (-N-CH_2-, q, J = 7.0 Hz, 4H), 1.88-1.76 (-CH-, m, 2H), 1.69 – 1.39 (-CH_2-, m, 16H), 1.19 (-CH_3, t, J = 7.0 Hz, 6H), 1.03 (-CH_3, t, J =7.6 Hz, 6H), 0.99 – 0.94 (-CH_3, m, 6H).

Synthesis of Compound 5

8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine (2.73 g, 0.01 mol), 1-bromoisooctane (2.90 g, 0.015 mol) and K_2CO_3 (3.0 g, 0.022 mol) were added into anhydrous acetone (50 mL). The mixture was stirred and refluxed for 15 h. After the precipitates were filtered out and the solvent was removed, the residue was purified by column chromatography. Compound **5** was gained as pale yellow oil (3.03 g, yield 81%). IR(KBr), ν_{max}/cm^{-1}: 2957, 2930, 2857 (C-H), 1661 (-CHO), 1589, 1516 (benzene ring), 1233 (Ph-O-C). MS, *m/z*: 385.59 (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 9.98 (-CHO, s, 1H), 7.62 (phenyl, s, 1H), 3.90 – 3.80 (-O-CH_2-, m, 2H), 3.32 – 3.26 (-N-CH_2-, m, 2H), 3.25 – 3.19 (-N-CH_2-, m, 2H), 2.00 – 1.89 (-CH-, m, 1H), 1.76 – 1.65 (-NCH_2-CH_2-, m, 4H), 1.61 – 1.19 (-CH_2- and -CH_3, m, 20H), 0.92 (-CH_3, m, 6H).

Synthesis of Compound 7

Compound **5** (3.85 g, 0.010 mol) was dissolved into methanol (40 mL) and well stirred, and then sodium borohydride (0.5 g, 0.013 mol) was added gradually at 0 °C. Then the reactant was stirred for 24 h at ambient temperature. After that, the methanol was removed and water was added. The aqueous solution was neutralized with diluted hydrochloric acid and extracted with dichloromethane. The combined organic layer was dried over $MgSO_4$. Dichloromethane was removed under vacuum to get pale yellow oil. The oil was dissolved into chloroform (40 mL) and triphenylphosphine hydrobromide (3.10 g, 0.009 mol) was added. The reactant was refluxed for 3 h and then chloroform was removed. The precipitates were washed several times with ethyl ether to gain compound **6** as white powder directly for next step. Compound **7** was prepared from compound **2** and compound **6** according to the synthesis of compound **4**. Compound **7** was obtained as red oil (yield 54%). ^1H NMR ($CDCl_3$) shows that the product is a mixture of trans and cis isomers. On the basis of the integration areas of two thienyl-H signals, the trans isomer is estimated to be 82% and the cis isomer 18%. IR(KBr), ν_{max}/cm^{-1}: 2957, 2926, 2858(C-H), 1674 (-CHO), 1504, 1456 (aromatic ring), 1250 (Ph-O-C). MS, *m/z*: 855.75 (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 10.00 (-CHO, s, 1H), 8.08 (thienyl, s, 0.18H), 8.05 (thienyl, s, 0.82H), 7.15 (thienyl, phenyl and vinylic, m, 3H), 6.99 (vinylic, d, J = 15.9 Hz, 1H), 4.25 – 4.01 (-O-CH_2-, m, 4H), 3.78 – 3.61 (-O-CH_2-, m, 2H), 3.15 – 2.99 (-N-CH_2-, m, 4H), 2.00 – 1.87 (-CH-, m, 1H), 1.76 (-CH-, m, 2H), 1.70 – 1.09 (-CH_2- and -CH_3, m, 40H), 0.94 (-CH_3, t, J = 8.2 Hz, 6H), 0.89 – 0.84 (-CH_3, m, 6H), 0.77 (-CH_3, t, J = 6.9 Hz, 6H).

Synthesis of Chromophore BDT2

Compound **4** (0.33g, 0.5mmol) was dissolved into chloroform (20 mL), and then a catalytic account of triethylamine and TCF (0.14 g, 0.75mmol) were added. The mixture was stirred and refluxed for 5 h. After the solvent removed, the crude product was purified by column chromatography. Chromophore BDT2 (0.23 g, yield 56%) was obtained as dark blue solid. Mp: 224-225 °C. IR(KBr),ν_{max}/cm^{-1}: 2960, 2928, 2870 (C-H), 2227 (C≡N), 1601, 1539 (aromatic ring), 1285 (Ph-O-C). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (vinylic, d, J= 15.8 Hz, 1H), 7.81 (thienyl, s, 1H), 7.77 (phenyl, d, J= 8.2 Hz, 2H), 7.68 (phenyl, d, J= 8.2 Hz, 2H), 7.46 (thienyl, s, 1H), 7.41 (vinylic, d, J= 16.0 Hz, 1H), 7.03 (vinylic, d, J= 16.0 Hz, 1H), 6.67 (vinylic, d, J= 15.8 Hz, 1H), 4.27 (-O-CH_2-, d, J= 5.6 Hz, 2H), 4.19 (-O-CH_2-, d, J= 5.5 Hz, 2H), 3.67 (-N-CH_2-, s, 2H), 3.33 (-N-CH_2-, s, 2H), 1.88-1.76 (-CH-, m, 2H), 1.81 (-CH_3, s, 6H), 1.77 – 1.22 (-CH_2- and -CH_3, m, 22H), 1.04 (-CH_3, t, J= 7.4 Hz, 6H), 0.96 (-CH_3, t, J= 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 175.43, 172.31, 148.46, 147.07, 146.25, 143.37, 140.15, 138.50, 136.55, 133.61, 131.15, 130.80, 130.52, 128.65, 128.27, 123.04, 117.73, 116.64, 114.76, 112.04, 111.82, 111.34, 110.85, 97.98, 97.29, 57.12, 44.58, 40.81, 30.44, 29.30, 26.47, 23.94, 23.30, 14.37, 12.85, 11.48. HRMS: for $C_{50}H_{61}N_4O_3S_2$, calcd: 829.41796, found: 829.41653.

Synthesis of Chromophore BDT3

BDT3 was prepared from compound **7** and TCF according to the synthesis of BDT2. BDT3 was obtained as dark green solid (yield 48%). ^{1}H NMR (Acetone) of the product shows two sets of similar signals, indicating that the product is a mixture of trans and cis isomers. On the basis of the integration areas of two thienyl-H signals, the trans isomer is estimated to be 55% and the cis isomer 45%. Mp: 103-105 °C.IR (KBr), ν_{max}/cm^{-1}: 2957, 2930, 2870 (C-H), 2228 (C≡N), 1539, 1479 (aromatic ring), 1288 (Ph-O-C).^{1}H NMR (400 MHz, Acetone) δ (ppm) 8.32 (vinylic, d, *J* = 16.1 Hz, 1H), 8.20 (thienyl, s, 0.45H), 8.19 (thienyl, s, 0.55H), 7.58 (vinylic, d, *J* = 13.4 Hz, 0.45H), 7.51 (thienyl, s, 0.55H), 7.43 (phenyl, s, 1H), 7.49 (thienyl, s, 0.45H), 7.37 (vinylic, d, *J* = 16.1 Hz, 0.55H), 7.24 (vinylic, d, *J* = 16.2Hz, 1H), 6.96 (vinylic, d, *J* = 16.0, 1H), 4.42 – 4.17 (-O-CH$_2$-, m, 4H), 3.81 (-O-CH$_2$-, dd, *J* = 18.6, 7.6 Hz, 2H), 3.28 – 3.15 (-O-CH$_2$-, m, 4H), 1.94 (-CH$_3$, s, 6H), 1.91 – 1.81 (-CH-, m, 3H), 1.80 – 1.25 (-CH$_2$- and -CH$_3$, m, 40H), 1.05 (-CH$_3$, t, *J* = 7.3 Hz, 6H), 0.97 – 0.93 (-CH$_3$, m, 6H), 0.89 – 0.85 (-CH$_3$, m, 6H). HRMS: for $C_{64}H_{84}N_4O_4S_2$, calcd: 1036.59285, found: 1036.59080.

Film preparation

For r_{33} measurements, guest–host polymers films were prepared by doping the chromophores into amorphous polycarbonate (APC, T_g = 190 °C). The chromophores (20-30 mg) were mixed with APC (100 mg) in dibromomethane (1.0-1.1 mL) as the solvent. Stirred for 12 h, the solutions were filtered through a 0.22 μm Teflon membrane filter and spin-coated onto indium tin oxide (ITO) glass substrates at room temperature with the spinning rate of 600 rpm to produce the films, which were then baked overnight at the room temperature under vacuum, yielding thin films of optical quality with thickness of around 3 μm. The poling process was carried out at a temperature of about 10°C above the T_g of the polymers.

Figure 1. Thermogravimetric analyses of the chromophores

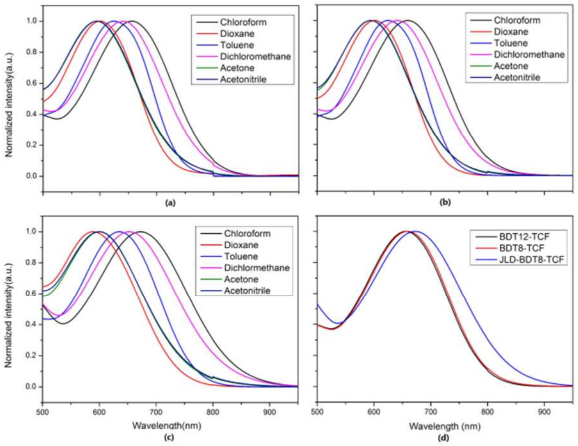
Results and discussion

Synthesis and characterization

The synthetic approach for the new chromophores BDT2 and BDT3 based on substituted BDT π-conjugated bridges is depicted in Scheme 1. 4,8-Dihydrobenzo[1,2-b:4,5-b′]dithiophen-4,8-dione reacted with 1-bromoisooctane after reduced by zinc and sodium hydroxide to obtain compound **1**. Compound **2** was obtained through formylation of compound **1** with *n*-BuLi and DMF. 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine was alkylated with 1-bromoisooctane in the presence of potassium carbonate to obtain compound **5**. Both donors were reduced by sodium borohydride followed by a reaction with triphenylphosphonium bromide to form Wittig Salts, which reacted with compound **2**, finally followed a Knoevenagel condensation with TCF acceptor to obtain target chromophores. The structures of the chromophores were confirmed by ^{1}H NMR, HRMS, and UV-Vis spectroscopic analysis, and the data obtained were in full agreement with the proposed formulations.

Figure 2. Uv-Vis absorption spectra of chromophores (a) BDT1, (b) BDT2 and (c) BDT3 in six different solvents (10^{-5} M) of varying dielectric constants (1,4-dixoane: 2.25; toluene: 2.38; chloroform: 4.81; dichloromethane: 8.93; acetone: 20.7; acetonitrile: 37.5) at room temperature and (d) Uv-Vis absorption spectra of chromophores in chloroform.

Physical properties of the chromophores



Thermal stability

Thermal stability is very important to chromophores' application in NLO devices because most processes of NLO devices' preparation are carried out under high temperature: the temperature should be above glass transition temperature of NLO polymers in poling process; high temperature is needed to drive solvent away in the process of films' preparation (including cladding and coring films); higher temperature would be neededin the process of electrode's preparation. To investigate the thermal stability of the chromophores, thermo gravimetric analysis (TGA) was used. TGA curves of BDT1, BDT2, and BDT3 are shown in Figure 1 and the thermal decomposition temperature (Td, 5% lost) value obtained from TGA were 226 °C,294°Cand 271 °C, respectively. It's easy to see that shortening of the flexible chains in BDT unit can significantly improve the thermal stability of this kind of chromophores to meet the higher requirements of application. We believe that it's the overlong side chains that induce the instability of the conjugated structure of BDT1.

Optical properties

In order to reveal the distinctions of the electronic structures of the chromophores, UV-Vis absorption spectra were measured in a series of aprotic solvents with different polarity so that the solvatochromic behavior of each chromophore could be investigated in a wide range of dielectric environments. The UV-Vis absorption spectra of the chromophores in six different solvents are presented in Figure 2, and the data are summarized in Table 1.The three chromophores in all solvents all exhibited a quite similar broad π-π* intramolecular charge-transfer absorption band. Also, they all showed a bathochromic shift of its absorption maximum initially and then reversed to a hypsochromic shift for more polar solvents like dichloromethane, acetone and acetonitrile, namely inverted solvatochromism. This indicated these three chromophores were all quite dipolar. Compared with spectra of BDT1 and BDT2, which were almost the same due to their same conjugated structure, the spectra of BDT3 exhibited an obvious red-shift. The maximal absorption wavelength (λ_{max}) of BDT1, BDT2, and BDT3 in chloroform were 655 nm, 659 nm and 672 nm, respectively. Compared to BDT2, the λ_{max} of BDT3 red-shifted 13 nm owing to its stronger electron donor. $\Delta\lambda_{max}$ (the difference in dioxane and in chloroform) of BDT1, BDT2 and BDT3 are 54 nm, 58 nm and 83 nm, respectively. According to the reference[14], larger solvatochromic effects mean larger energy shift between different solvents and usually implied better electro-optic performance.

Table 1. UV-Vis absorption and solvatochromic data of the chromophores.

	λ_{max}/(nm)^a	λ_{max}/(nm)^b	λ_{max}/(nm)^c	λ_{max}/(nm)^d	λ_{max}/(nm)^e	λ_{max}/(nm)^f	$\Delta\lambda_{max}$/(nm)^g
BDT1	601	625	655	640	595	595	54
BDT2	601	625	659	641	595	595	58
BDT3	589	635	672	653	599	599	83

$^a\lambda_{max}$ was measured in dioxane. $^b\lambda_{max}$ was measured in toluene. $^c\lambda_{max}$ was measured in chloroform. $^d\lambda_{max}$ was measured in dichloromethane. $^e\lambda_{max}$ was measured in acetone. $^f\lambda_{max}$ was measured in acetonitrile. $^g\Delta\lambda_{max}$ was the difference between $^a\lambda_{max}$ and $^c\lambda_{max}$.

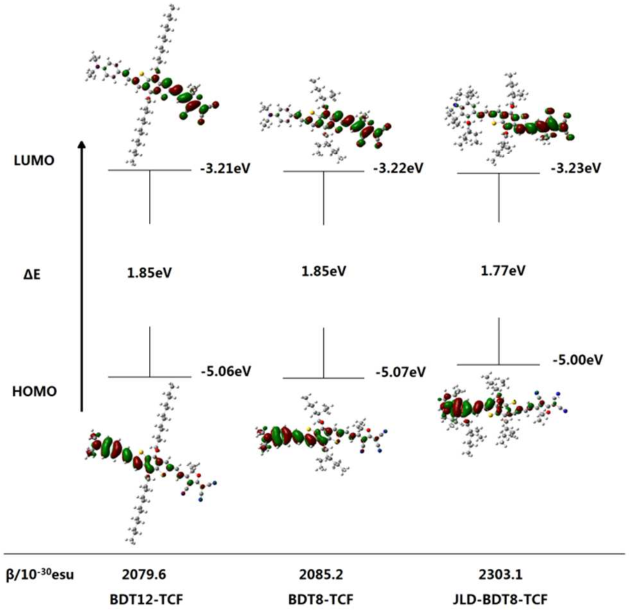
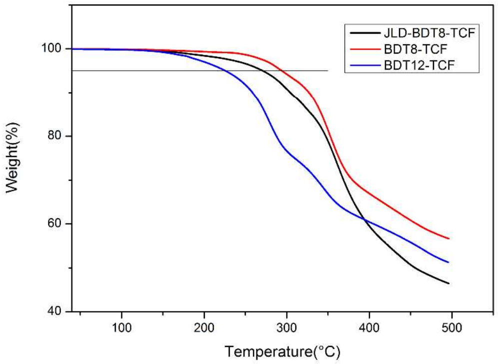


Figure 3. HOMO, LUMO energy level, HOMO-LUMO energy gap and hyperpolarizability of the chromophores using DFT calculations



Theoretical calculations

For further comparison, we have performed the quantum chemical calculations within a framework of GAUSSIAN03 using the split valence B3LYP 6-31G (d,p) basis set[41-43]. The density functional theory (DFT) calculations were carried out to show the electron density of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the chromophores and the β value[44] of the chromophores in vacuum. The theoretical calculation of BDT3 was based on trans isomer. The data obtained from DFT calculation are summarized in Figure 3 and Table 2.

In Figure 3, it's easy to see that the electrons of HOMO was localized predominantly at the donor and electron-bridge, while in the excited state that of LUMO was localized predominantly at the acceptor and electron-bridge, which indicated these chromophores had good intramolecular charge-transfer ability and BDT was an excellent electron-bridge. The compositions of the HOMOs and LUMOs of these chromophores in the ground state were also calculated using the Multiwfn program with Ros e Schuit (SCPA) partition[45] and listed in Table 2. The molecular orbital compositions of BDT1 and BDT2 were nearly the same while the electron donor of BDT3 contributed a lot more to the composition of HOMO, which prominently showed julolidine moiety possesses stronger electron-donating ability compared to aniline moiety. The calculated ΔE (HOMO- LUMO energy gap) of the chromophores also confirmed the results. And as we expected, the β value of BDT1 (2079.6×10^{-30} esu) and BDT2 (2085.2×10^{-30} esu) are very close while that of BDT3 (2303.1×10^{-30} esu) is much larger because BDT1 and BDT2 have the same conjugated structure while BDT3 has a stronger electron donor.

Nonlinear optical property

For application, large hyperpolarizability has to be translated into large EO coefficient (r_{33}). Guest-host EO polymers based on APC as the hosts were prepared to investigate the macroscopic NLO property of these chromophores. The corona poling process was carried out at temperature of about 10 °C above the T_g of the polymers. The r_{33} of the poled films were measured using the Teng-Man simple reflection technique at the wavelength of 1.31

μm[46]. The r_{33} values were calculated by the following equation:

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

Table 2. Molecular Orbital Composition in the Ground State for Chromophores

	BDT1		BDT2		BDT3	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Donor	56.4%	2.2%	56.6%	2.2%	65.7%	2.8%
π bridge	39.9%	50.3%	39.7%	50.4%	31.5%	50.0%
Acceptor	3.7%	47.5%	3.7%	47.4%	2.8%	47.2%

where r_{33} is the EO coefficient of the poled polymer, λ is the optical wavelength, θ is the incidence angle, I_c is the output beam intensity, I_m is the amplitude of the modulation, V_m is the modulating voltage, and n is the refractive indices of the polymer films.

Table 3. EO coefficients (pm/V) of chromophores doped in APC with different loading densities

loading density	BDT1	BDT2	BDT3
20wt%	57	87	68
30wt%	66	102	82

The EO coefficients of the EO poled films with loading densities (chromophores into APC) of 20wt% and 30wt% were measured and listed in Table 3. With the same loading density, the r_{33} values of the poled EO films doped with BDT2 were the largest, BDT3 came second, and BDT1 were the lowest. Compared with BDT1, the r_{33} of BDT2 increased over 50% with the alteration of the dodecane groups. That's because the dendritic isooctane groups can increase the steric hindrance between the chromophores to suppress the intermolecular dipolar-dipolar electrostatic interaction. And the shortening of the chains on BDT probably makes the chromophore easier to move during the poling process and as well. The maximum r_{33} 102 pm/V was obtained from 30wt% BDT2/APC. Compared to analogous thiophene-based FTC-type chromophore (20-50 pm/V), the r_{33} increased more than doubled and can absolutely meet the requirement. In BDT3, the introduction of stronger electron donor obviously increased the hyperpolarizability, but unexpectedly, the films doped with BDT3 with the maximum β value didn't achieve the maximum r_{33} value. Alex K. Y. Jen et al once reported that the electro-optic polymer based on poly(methylmethacrylate) and the isophorone-derived tetraene chromophore with julolidine as donor obtained low EO coefficient because the hyperpolarizability of the chromophore decreased much more obviously than similar chromophores based on aniline donor in polar medium[6]. This could also explained well why films doped with BDT3 obtained lower EO coefficient, which was probably owing to the diminishment of hyperpolarizability value of BDT3 in the polar polymer matrix and these results illustrated the critical role of fine-tuning of donor's electron-donating strength in optimizing the nonlinear properties of NLO chromophores.

Conclusions

Two novel chromophores BDT2 and BDT3 were designed and synthesized through modification of BDT1 which we reported previously. These chromophores were all very soluble in common solvents and were systematically characterized by MS, NMR and UV-Vis absorption spectra. Compared with BDT1 with overlong side chains that induce the instability of the conjugated structure of BDT1, the thermal stabilities of BDT2 and BDT3 were both improved and could meet higher requirements for application. Meanwhile, DFT calculations were carried out to analyze the chromophores. Because BDT1 and BDT2 have the same conjugated structure, their UV-Vis absorption spectra, HOMO-LUMO gap and calculated first-order hyperpolarizability were nearly the same. BDT3 showed stronger bathochromic behavior on the UV-Vis absorption spectra, and owned smaller energy gap and higher first-order hyperpolarizability in vacuum due to its stronger electron donor julolidine moiety. EO polymers were prepared by the chromophores doped into APC and their r_{33} values were measured. The r_{33} values of EO polymers based on BDT2 and BDT3 were larger than the ones based on BDT1 due to the variation of the flexible chains on the BDT unit because the dendritic isooctane groups are more suitable isolation groups than dodecyl groups and can suppress the dipolar-dipolar electrostatic interactions more effectively. The materials based on BDT3 with the maximum β value in vacuum didn't achieve the maximum r_{33} value probably due to the diminishment of β value in the polar polymer matrix. The maximum r_{33} 102 pm/V was obtained from 30wt% BDT2/APC. Compared to analogous thiophene-based FTC-type chromophore, the r_{33} increased more than doubled. The substituents on BDT unit significantly influence the properties of this type of chromophores and dendritic isooctane group is a quite suitable isolation group. These results indicate the importance of suitable isolation groups and fine-tuning of donor's electron-donating strength in optimizing the nonlinear properties of NLO chromophores. BDT unit with suitable isolation groups can be very helpful in chromophore design and promising in NLO materials.

Acknowledgments

We are grateful to the Directional Program of the Chinese Academy of Sciences (KJCX2.YW.H02), Innovation Fund of Chinese Academy of Sciences (CXJJ-11-M035) and National Natural Science Foundation of China (No. 11104284 and No. 61101054) for the financial support.

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† Electronic Supplementary Information (ESI) available: [NMR and HRMS spectra of resulted compounds]. See DOI: 10.1039/b000000x/

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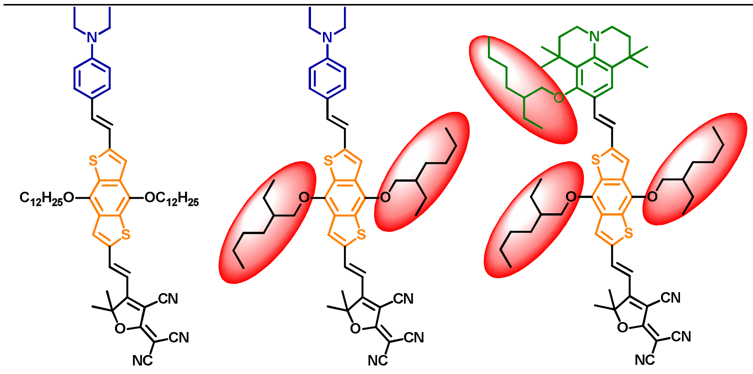

BDT1 **BDT2** **BDT3**

Max r_{33} 102pm/V by BDT2 at 1310 nm

Electro-optic coefficient of BDT-based chromophores was improved to 102pm/V with suitable isolation groups and electron donor.