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New second-order nonlinear optical polymers containing the same isolation groups: Optimized syntheses and nonlinear optical properties

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Abstract

Based on control experiments, a new series of second-order nonlinear optical polymers with fluorene moieties as isolation spacers were successfully prepared. In the polymers, the chromophore moieties were embedded into the polymer backbone with one position at the donor side, and another point in the π bridge. Different acceptors were used to construct the push–pull structure of chromophore moieties, including nitro groups, sulfonyl groups, 3-phenyl-5-isoxazolone, 1,3-diethylthiobarbituric acid and TCF groups. The tested NLO properties of the polymers demonstrated that the isolation groups with big size do not always benefit the resultant NLO effect. Also, for different acceptors, there should be different suitable isolation groups to balance the good and bad effects caused by the introduced isolation spacers.

Keywords: Nonlinear optics; Synthesis; Second-order NLO materials

1. Introduction

Polymeric second-order NLO materials have attracted great interest in the past decades, due to their huge potential applications in photonic devices and many advantages over inorganic materials, such as their large nonlinear optical (NLO) coefficients, ultrafast response time, and ease of integration. Thanks to the great efforts of scientists, different types of NLO polymers were prepared to meet the three main requirements of the practical applications: large macroscopic optical nonlinearity, high physical and chemical stabilities, and good optical transparency [1–3]. One of the major problems present in this area, perhaps the most important barrier encountered in optimizing organic NLO materials, is how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers. Recently, Dalton et al. provided a good approach to solve this problem by controlling the shape of the chromophore moieties, according to the site isolation principle [4–6].

On the basis of the work reported in the literatures and our previous research [1–6,7], we designed some new NLO polymers, in which different isolation groups were linked to the chromophore moieties. The preliminary results exhibited that for a given chromophore moiety, there should be a suitable isolation group present to boost its microscopic β value to possibly higher macroscopic NLO effect efficiently [8]. Then, considering this problem on another side, if a fixed isolation group was used, how about its effect on the NLO properties of the resultant polymers containing different NLO chromophore moieties? Also, the poling efficiencies and the macroscopic NLO properties of polymers containing dendronized chromophore were expected to be heavily related to the subtle difference in architectural design. Thus, we wondered how about the results if the chromophore moieties were introduced to the polymer backbone with one position at the donor side, and another point in the π bridge. In this paper, a series of nonlinear optical polymers containing fluorene moieties as

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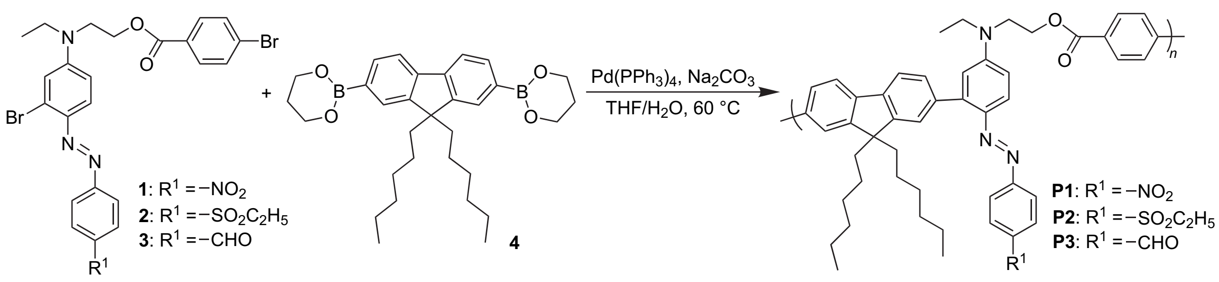
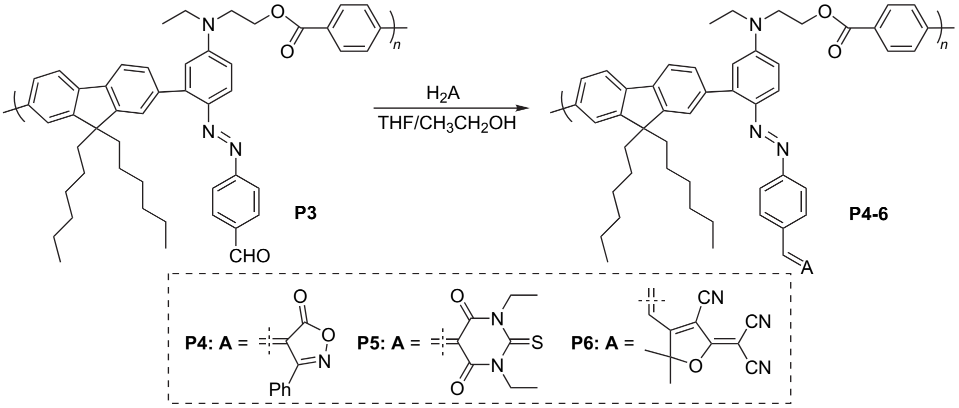
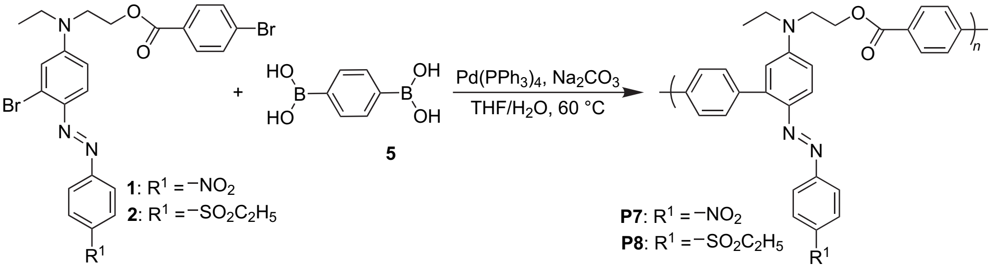


Scheme 1.



Scheme 2.



Scheme 3.

isolation spacers (**P1–P6**) were designed and prepared (Schemes 1 and 2). For comparison, two polymers with phenyl ring as the isolation moiety, **P7** and **P8**, were also synthesized (Scheme 3). The synthetic routes and reaction conditions were optimized, based on several control experiments (we would discuss these points in detail in Section 3). Our examples might give light on the preparation of other functional polymers inaccessible from their corresponding monomers directly. All the polymers were soluble in common solvents and exhibited relatively good NLO properties. Our preliminary results demonstrated that the fixed isolation group does not always benefit the resultant NLO effect. Herein, we would like to report the syntheses, characterization, and NLO properties of these polymers.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. Dichloromethane (CH_2Cl_2) was dried over anhydrous calcium chloride ($CaCl_2$) and distilled before use. Ethanol was dried according to the normal procedure before use. 3-Bromo-*N*-ethyl-*N*-hydroxyethyl-aniline (**S1**), 4-ethylsulfonylaniline (**S3**), 4-amino-benzaldehyde (**S4**), and 3-bromo-bis(2-hydroxyethyl)aminobenzene (**S9**) were synthesized according to the literature methods [9]. 9,9-Dihexylfluorene-2,7-bis(trimethylene borate) (DHFBTMB), 1,4-phenylenediboronic acid (**5**) and phenylboronic acid (**7**) were purchased from Aldrich. Tricyanovinyldihydrofuran (TCF) was synthesized according to the literature method [10]. Chromophore **11** was prepared by the reaction between 4-*N*,*N*-dihydroxyethyl-4′-formylazobenzene and 3-phenyl-5-isoxazolone according to our previous work [11]. All the other reagents were used as-received.

2.2. Instrumentation

^1H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared

(FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on NaCl pellets. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

*2.3. General procedure for syntheses of chromophores **S5–S7***

4-Nitroaniline (**S2**), 4-ethylsulfonylaniline (**S3**) or 4-aminobenzaldehyde (**S4**) (1.05 equiv or 1.20 equiv) was dissolved in a water solution of 35% hydrochloric acid. The mixture was cooled to 0–5 °C in an ice bath, and then a solution of sodium nitrite (1.05 equiv or 1.20 equiv) in water was added to the above cooled solution dropwise. After stirring below 5 °C for 15 min, a solution of **S1** (1.00 equiv) in ethanol was added slowly. The mixture was left in the ice bath for another 1 h and then some sodium bicarbonate was added to adjust the pH value to about 7.0. The reaction mixture was stirred for another 0.5 h, the red precipitate filtered, and washed with water. The crude product was purified by recrystallization or column chromatography.

*2.3.1. Compound **S5***

S1 (1.00 g, 4.10 mmol), **S2** (0.59 g, 4.28 mmol). Purified by recrystallization from ethanol/water to afford deep red powder (1.46 g, 90.7%). Mp = 140–141 °C. IR (thin film) ν (cm^{-1}): 1515, 1337 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.25 (t, J = 7.5 Hz, 3H, $-CH_2CH_3$), 3.50–3.61 (m, 4H, $-N-CH_2-$), 3.90 (t, J = 5.7 Hz, 2H, $-O-CH_2-$), 6.69 (dd, J = 2.4, 9.3 Hz, 1H, ArH), 7.04 (d, J = 2.1 Hz, 1H, ArH), 7.78 (d, J = 8.7 Hz, 1H, ArH), 7.96 (d, J = 8.7 Hz, 2H, ArH), 8.30 (d, J = 8.7 Hz, 2H, ArH). MS (EI), *m/z* [M^+]: 392.5, calcd: 392.1. UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 480 nm; ε_{max}: 3.13×10^4 $mol^{-1}\,L\,cm^{-1}$.

*2.3.2. Compound **S6***

S1 (1.00 g, 4.10 mmol), **S3** (0.79 g, 4.28 mmol). Purified by recrystallization from ethanol/water to afford orange red powder (1.65 g, 91.7%). Mp = 106–107 °C. IR (thin film) ν (cm^{-1}): 1301, 1130 ($-SO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.29 (m, 6H, $-CH_3$), 3.15 (q, J = 7.2 Hz, 2H, $-SO_2CH_2-$), 3.5–3.65 (m, 4H, $-N-CH_2-$), 3.83 (br s, 2H, $-O-CH_2-$), 6.73 (d, J = 8.7 Hz, 1H, ArH), 7.06 (br s, 1H, ArH), 7.83 (d, J = 8.7 Hz, 1H, ArH), 8.00 (q, J = 8.7 Hz, 4H, ArH). UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 448 nm; ε_{max}: 3.01×10^4 $mol^{-1}\,L\,cm^{-1}$.

*2.3.3. Compound **S7***

S1 (2.00 g, 8.20 mmol), **S4** (1.19 g, 9.83 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (3/1) as an eluent to afford red powder (1.50 g, 50.0%). Mp = 96–98 °C. IR (thin film) ν (cm^{-1}): 1695 ($-CHO$). ^1H NMR ($CDCl_3$) δ (ppm): 1.27 (t, J = 7.5 Hz, 3H, $-CH_3-$), 3.51–3.65 (m, 4H, $-N-CH_2-$), 3.90 (br s, 2H, $-O-CH_2-$), 6.73 (dd, J = 2.7, 9.0 Hz, 1H, ArH), 7.06 (d, J = 2.4 Hz, 1H, ArH), 7.83 (d, J = 9.3 Hz, 1H, ArH), 8.00 (q, J = 9.0 Hz, 4H, ArH), 10.04 (s, 1H, $-CHO$). UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 456 nm; ε_{max}: 5.27×10^4 $mol^{-1}\,L\,cm^{-1}$.

*2.4. General procedure for syntheses of chromophores **1–3***

S5, **S6** or **S7** (1.00 equiv), 4-bromo-benzoic acid (**S8**) (2.00 equiv), dicyclohexylcarbodiimine (DCC) (1.70 equiv), 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (0.20 equiv) were dissolved in dry CH_2Cl_2/THF (2/1 in volume) and stirred at room temperature for 20 h. The precipitate was filtered and the crude product was purified by column chromatography.

*2.4.1. Chromophore **1***

S5 (0.24 g, 0.60 mmol), **S8** (0.25 g, 1.20 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (2/3) as an eluent to afford red powder (0.33 g, 94.2%). Mp = 140–142 °C. IR (thin film) ν (cm^{-1}): 1724 (C=O), 1515, 1337 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.28 (t, J = 7.2 Hz, 3H, $-CH_2CH_3$), 3.54 (q, J = 7.5 Hz, 2H, $-N-CH_2-$), 3.81 (t, J = 6.0 Hz, 2H, $-N-CH_2-$), 4.54 (t, J = 6.0 Hz, 2H, $-O-CH_2-$), 6.76 (dd, J = 3.0, 8.7 Hz, 1H, ArH), 7.16 (d, J = 2.4 Hz, 1H, ArH), 7.58 (d, J = 7.8 Hz, 2H, ArH), 7.80 (d, J = 9.6 Hz, 1H, ArH), 7.86 (d, J = 9.0 Hz, 2H, ArH), 8.00 (d, J = 8.7 Hz, 2H, ArH), 8.33 (d, J = 8.7 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.5, 45.9, 49.0, 62.5, 111.3, 115.5, 119.2, 123.4, 125.0, 128.6, 128.8, 131.4, 131.9, 132.1, 140.4, 148.0, 152.1, 156.7, 166.0. MS (EI), *m/z* [M^+]: 574.4, calcd: 574.0. $C_{23}H_{20}Br_2N_4O_4$ (EA) (%, found/calcd): C, 48.61/47.94; H, 3.62/3.50; N, 9.65/9.72. UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 465 nm; ε_{max}: 3.28×10^4 $mol^{-1}\,L\,cm^{-1}$.

*2.4.2. Chromophore **2***

S6 (0.18 g, 0.41 mmol), **S8** (0.17 g, 0.84 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (2/3) as an eluent to afford orange red powder (0.23 g, 88.2%). Mp = 104–106 °C. IR (thin film) ν (cm^{-1}): 1723 (C=O), 1302, 1128 ($-SO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.28 (m, 6H, $-CH_3$), 3.16 (q, J = 7.8 Hz, 2H, $-SO_2CH_2-$), 3.54 (q, J = 7.5 Hz, 2H, $-N-CH_2-$), 3.80 (t, J = 6.6 Hz, 2H, $-N-CH_2-$), 4.53 (t, J = 6.0 Hz, 2H,

−O−CH$_2$−), 6.75 (dd, $J = 3.0$, 9.3 Hz, 1H, ArH), 7.15 (d, $J = 3.0$ Hz, 1H, ArH), 7.58 (d, $J = 8.7$ Hz, 2H, ArH), 7.80 (d, $J = 9.0$ Hz, 1H, ArH), 7.86 (d, $J = 8.7$ Hz, 2H, ArH), 8.00 (br s, 4H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 5.1, 9.9, 43.2, 46.3, 48.4, 59.9, 108.7, 112.9, 116.6, 120.9, 126.0, 126.2, 126.9, 128.8, 129.0, 129.5, 135.9, 137.6, 149.3, 153.7, 163.4. MS (EI), m/z [M$^+$]: 621.4, calcd: 621.0. $C_{25}H_{25}Br_2N_3O_4S$ (EA) (%, found/calcd): C, 48.33/48.17; H, 4.19/4.04; N, 6.62/6.74; S, 5.06/5.14. UV−vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 442 nm; ε_{max}: 1.80×10^4 mol^{-1} L cm^{-1}.

2.4.3. Chromophore *3*

S7 (0.90 g, 2.40 mmol), **S8** (0.96 g, 4.80 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/2) as eluent to afford red powder (1.15 g, 85.8%). Mp = 108−109 °C. IR (thin film) ν (cm^{-1}): 1722 (C=O), 1694 (−CHO). ^{1}H NMR (CDCl$_3$) δ (ppm): 1.26 (t, $J = 6.6$ Hz, 3H, −CH$_3$), 3.52 (q, $J = 6.6$ Hz, 2H, −N−CH$_2$−), 3.80 (t, $J = 5.1$ Hz, 2H, −N−CH$_2$−), 4.51 (t, $J = 5.1$ Hz, 2H, −O−CH$_2$−), 6.75 (d, $J = 8.7$ Hz, 1H, ArH), 7.14 (br s, 1H, ArH), 7.56 (d, $J = 8.1$ Hz, 2H, ArH), 7.80 (d, $J = 9.6$ Hz, 1H, ArH), 7.86 (d, $J = 8.1$ Hz, 2H, ArH), 8.00 (br s, 4H, ArH), 10.06 (s, 1H, −CHO). ^{13}C NMR (CDCl$_3$) δ (ppm): 12.5, 45.8, 49.0, 62.6, 111.3, 115.5, 119.1, 123.5, 128.6, 128.7, 131.0, 131.4, 132.1, 136.7, 140.4, 151.7, 156.8, 166.0, 192.0. MS (EI), m/z [M$^+$]: 557.2, calcd: 557.0. $C_{24}H_{21}Br_2N_3O_3$ (EA) (%, found/calcd): C, 51.60/51.54; H, 3.96/3.78; N, 7.41/7.51. UV−vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 448 nm; ε_{max}: 1.98×10^4 mol^{-1} L cm^{-1}.

2.5. General procedure for syntheses of polymers *P1–P3* and *P7–P8*

A mixture of compound **1**, **2** or **3** (1.00 equiv), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**4**) (1.00 equiv) or 1,4-phenylenediboronic acid (**5**) (1.00 equiv), sodium carbonate (10.0 equiv), THF (monomer concentration is about 0.06 M)/water (2/1 in volume), and Pd(PPh$_3$)$_4$ (3 mol%) were carefully degassed and charged with nitrogen. Then the reaction mixture was stirred at 60 °C for 25 h. After the solution was cooled to ambient temperature, it was dropped into methanol to remove monomer. The obtained solid was dissolved in THF and the insoluble solid was filtered out. The filtrate was concentrated and further precipitated by addition to methanol, and the obtained solid was washed with a lot of acetone. The resultant polymer was collected and then dried under vacuum at 40 °C overnight.

2.5.1. Compound *P1*

1 (0.092 g, 0.16 mmol), **4** (0.080 g, 0.16 mmol). Dark red powder (0.094 g, 78.3%). $M_w = 18\,200$, $M_w/M_n = 1.65$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1722 (C=O), 1518, 1337 (−NO$_2$). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6−0.8 (−CH$_3$), 0.9−1.2 (−(CH$_2$)$_4$−), 1.2−1.4 (−CH$_3$), 1.9−2.1 (−C−CH$_2$−), 3.6−3.8 (−N−CH$_2$−), 3.8−4.0 (−N−CH$_2$−), 4.5−4.7 (−O−CH$_2$−), 6.8−7.0 (ArH), 7.4−7.6 (ArH), 7.6−7.9 (ArH), 8.0 (ArH), 8.1 (ArH), 8.2 (ArH). UV−vis (THF, 0.01 mg/mL) λ_{max} (nm): 477.

2.5.2. Compound *P2*

2 (0.075 g, 0.12 mmol), **4** (0.060 g, 0.12 mmol). Orange red powder (0.071 g, 74.7%). $M_w = 15\,500$, $M_w/M_n = 1.56$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1723 (C=O), 1300, 1121 (−SO$_2$). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6−0.8 (−CH$_3$), 0.9−1.2 (−(CH$_2$)$_4$−), 1.2−1.4 (−CH$_3$), 1.9−2.1 (−C−CH$_2$−), 3.0−3.2 (−SO$_2$CH$_2$−), 3.6−3.8 (−N−CH$_2$−), 3.8−4.0 (−N−CH$_2$−), 4.5−4.7 (−O−CH$_2$−), 6.8−7.0 (ArH), 7.4−7.6 (ArH), 7.7−7.9 (ArH), 8.0 (ArH), 8.1 (ArH). UV−vis (THF, 0.01 mg/mL) λ_{max} (nm): 445.

2.5.3. Compound *P3*

3 (0.67 g, 1.20 mmol), **4** (0.60 g, 1.20 mmol). Red powder (0.76 g, 86.4%). $M_w = 13\,500$, $M_w/M_n = 1.78$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1720 (C=O), 1697 (−CHO). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.6−0.8 (−CH$_3$), 0.8−1.1 (−(CH$_2$)$_4$−), 1.2−1.4 (−CH$_3$), 1.9−2.1 (−C−CH$_2$−), 3.6−3.8 (−N−CH$_2$−), 3.8−4.0 (−N−CH$_2$−), 4.5−4.7 (−O−CH$_2$−), 6.8−7.0 (ArH), 7.4−7.5 (ArH), 7.6−7.9 (ArH), 8.0 (ArH), 8.1 (ArH), 10.0 (−CHO). UV−vis (THF, 0.01 mg/mL) λ_{max} (nm): 453.

2.5.4. Compound *P7*

1 (0.115 g, 0.20 mmol), **5** (0.033 g, 0.20 mmol). Dark red powder (0.065 g, 66.1%). $M_w = 6700$, $M_w/M_n = 1.57$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1721 (C=O), 1518, 1334 (−NO$_2$). ^{1}H NMR (CDCl$_3$) δ (ppm): 1.2−1.4 (−CH$_3$), 3.5−3.7 (−N−CH$_2$−), 3.8−4.0 (−N−CH$_2$−), 4.4−4.6 (−O−CH$_2$−), 6.8−7.0 (ArH), 7.4−7.8 (ArH), 7.9−8.1 (ArH), 8.2 (ArH). UV−vis (THF, 0.01 mg/mL) λ_{max} (nm): 474.

2.5.5. Compound *P8*

2 (0.081 g, 0.13 mmol), **5** (0.022 g, 0.13 mmol). Orange red powder (0.043 g, 55.8%). $M_w = 7400$, $M_w/M_n = 1.47$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1721 (C=O), 1300, 1121 (−SO$_2$). ^{1}H NMR (CDCl$_3$) δ (ppm): 1.2−1.4 (−CH$_3$), 3.0−3.2 (−SO$_2$CH$_2$−), 3.5−3.7 (−N−CH$_2$−), 3.8−4.0 (−N−CH$_2$−), 4.5−4.7 (−O−CH$_2$−), 6.8−7.0 (ArH), 7.4−7.7 (ArH), 7.7−7.9 (ArH), 7.9−8.1 (ArH). UV−vis (THF, 0.01 mg/mL) λ_{max} (nm): 446.

2.6. General procedure for syntheses of polymers *P4–P6*

P3 (1.00 equiv) and H$_2$A (1.30−1.50 equiv) were dissolved in THF (the concentration of **P3** is about 25 mg/mL). Then absolute ethanol (1/2 of the volume of THF) was added to the above solution. The reaction condition was different while H$_2$A was different, and the reaction was followed by IR spectra. The solid precipitate in the reaction mixture was collected and then dissolved in proper THF. The obtained solution was then dropped into methanol. The precipitate was filtered and washed with a lot of methanol and acetone. The resultant polymer was collected and dried under vacuum at 40 °C overnight.

2.6.1. Compound **P4**

P3 (0.073 g), 3-phenyl-5-isoxazolone (0.02 g, 0.13 mmol), and the reaction mixture were stirred at 70 °C for 24 h without any catalyst. **P4** was obtained as dark powder (0.06 g, 68.7%). $M_w = 21\,800$, $M_w/M_n = 1.68$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1754 (C=O), 1720 (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 0.6–1.1 ($-CH_3$ and $-(CH_2)_4-$), 1.2–1.4 ($-CH_3$), 1.8–2.1 ($-C-CH_2-$), 3.5–3.8 ($-N-CH_2-$), 3.8–4.0 ($-N-CH_2-$), 4.5–4.7 ($-O-CH_2-$), 6.8–7.0 (ArH), 7.4–7.5 (ArH), 7.6–7.8 (ArH), 8.0–8.2 (ArH), 8.4 (ArH), 10.0 (−CHO). UV–vis (THF, 0.01 mg/mL) λ_{max} (nm): 513.

2.6.2. Compound **P5**

P3 (0.11 g), 1,3-diethylthiobarbituric acid (0.04 g, 0.20 mmol), and the reaction mixture were stirred at room temperature for 24 h without any catalyst. **P5** was obtained as dark powder (0.08 g, 58.4%). $M_w = 9000$, $M_w/M_n = 1.63$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 1720 (C=O), 1700 (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 0.6–1.1 ($-CH_3$ and $-(CH_2)_4-$), 1.2–1.4 ($-CH_3$), 1.8–2.1 ($-C-CH_2-$), 3.6–3.8 ($-N-CH_2-$), 3.8–4.0 ($-N-CH_2-$), 4.4–4.7 ($-O-CH_2-$ and $-N-CH_2-$), 6.8–7.0 (ArH), 7.4–7.6 (ArH), 7.6–7.9 (ArH), 7.9–8.1 (ArH), 8.2 (ArH), 8.5 (ArH), 10.0 (−CHO).

2.6.3. Compound **P6**

P3 (0.095 g), TCF (0.034 g, 1.7 mmol), and the reaction mixture were stirred at 70 °C for 3 h with piperidine/acetic acid (0.017 mL/0.051 mL) as catalyst. **P6** was obtained as dark powder (0.09 g, 71.7%). $M_w = 17\,800$, $M_w/M_n = 1.37$ (GPC, polystyrene calibration). IR (thin film) ν (cm^{-1}): 2233 (CN), 1720 (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 0.6–1.1 ($-CH_3$ and $-(CH_2)_4-$), 1.2–1.4 ($-CH_3$), 1.5–1.8 ($-CH_3$), 1.8–2.2 ($-C-CH_2-$ and $-CH_3$), 3.5–3.8 ($-N-CH_2-$), 3.8–4.0 ($-N-CH_2-$), 4.4–4.7 ($-O-CH_2-$), 6.8–7.0 (ArH), 7.4–7.6 (ArH), 7.6–7.9 (ArH), 7.9–8.2 (ArH). UV–vis (THF, 0.01 mg/mL) λ_{max} (nm): 551.

2.7. Synthesis of compound **S10**

The procedure was similar as the synthesis of **S5**–**S7**. **S9** (1.42 g, 5.50 mmol), **S4** (0.80 g, 6.61 mmol). The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (3/1) as an eluent to afford red powder (1.60 g, 74.0%). Mp = 146–147 °C. IR (thin film) ν (cm^{-1}): 1687 (CHO). ^1H NMR ($CDCl_3$) δ (ppm): 3.74 (t, $J = 5.1$ Hz, 4H, $-N-CH_2-$), 3.96 (t, $J = 4.2$ Hz, 4H, $-O-CH_2-$), 6.70 (d, $J = 9.6$ Hz, 1H, ArH), 7.04 (s, 1H, ArH), 7.88 (d, $J = 9.0$ Hz, 1H, ArH), 8.00 (br s, 4H, ArH), 10.07 (s, 1H, CHO).

2.8. Synthesis of compound **6**

S10 (0.39 g, 1.00 mmol) and 3-phenyl-5-isoxazolone (0.18 g, 1.10 mol) were dissolved in absolute ethanol (20 mL), and the reaction mixture was refluxed for 4 h under nitrogen. After being cooled, the solvent was removed on a rotary evaporator. The crude product was purified by chromatography on silica gel using acetate/petroleum ether (10/1) as an eluent to afford dark purple solid (0.33 g, 62.3%). Mp = 189–190 °C. IR (thin film) ν (cm^{-1}): 1749 (C=O). ^1H NMR (acetone-d_6) δ (ppm): 3.74 (t, $J = 5.1$ Hz, 4H, $-N-CH_2-$), 3.85 (t, $J = 5.1$ Hz, 4H, $-O-CH_2-$), 6.95 (dd, $J = 2.4$, 9.6 Hz, 1H, ArH), 7.22 (d, $J = 3.0$ Hz, 1H, ArH), 7.6–7.8 (m, 6H, ArH), 7.91 (s, 1H, CH=C), 7.99 (d, $J = 8.7$ Hz, 2H, ArH), 8.62 (d, $J = 8.7$ Hz, 2H, ArH). ^{13}C NMR (acetone-d_6) δ (ppm): 54.6, 59.8, 112.6, 115.9, 119.1, 123.1, 128.4, 129.6, 129.9, 131.5, 131.8, 134.4, 136.0, 140.3, 152.3, 153.8, 156.5, 168.8. MS (EI), *m/z* [M^+]: 534.3, calcd: 534.1. UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 524 nm; ε_{max}: 4.09×10^4 $mol^{-1}\,L\,cm^{-1}$.

2.9. Synthesis of compound **8**

A mixture of compound **6** (0.20 g, 0.37 mmol), phenylboronic acid (**7**) (0.05 g, 0.41 mmol), sodium carbonate (0.39 g, 3.68 mmol), THF (the concentration of **6** is about 0.03 M)/water (3/1 in volume), and $Pd(PPh_3)_4$ (3 mol%) were carefully degassed and charged with nitrogen. Then the reaction mixture was stirred at 60 °C for 30 h. After cooling to room temperature, the mixture was extracted by $CHCl_3$. The crude product was purified by recrystallization from acetone to afford red solid (0.11 g, 76.4%). Mp = 149–150 °C. IR (thin film) ν (cm^{-1}): 1694 (CHO). ^1H NMR (acetone-d_6) δ (ppm): 3.78 (t, $J = 5.1$ Hz, 4H, $-N-CH_2-$), 3.87 (t, $J = 5.1$ Hz, 4H, $-O-CH_2-$), 6.95 (m, 2H, ArH), 7.44 (m, 3H, ArH), 7.56 (d, $J = 7.2$ Hz, 2H, ArH), 7.81 (d, $J = 8.7$ Hz, 2H, ArH), 8.00 (m, 3H, ArH), 10.06 (s, 1H, CHO). ^{13}C NMR (acetone-d_6) δ (ppm): 54.3, 59.5, 112.0, 112.7, 117.3, 122.9, 127.4, 127.7, 130.6, 131.0, 136.6, 140.2, 140.5, 145.9, 152.2, 157.1, 191.6. MS (EI), *m/z* [M^+]: 389.2, calcd: 389.2. UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 459 nm; ε_{max}: 3.90×10^4 $mol^{-1}\,L\,cm^{-1}$.

2.10. Hydrolysis reaction from **1** to **S5**

Compound **1** (16.0 mg) and sodium carbonate (30 mg) were dissolved in THF/H_2O (3 mL/1.5 mL) and the mixture was stirred at 60 °C for 24 h under nitrogen. After being cooled, the mixture was extracted with $CHCl_3$. The crude product was purified by chromatography on silica gel using acetate/petroleum ether (1/2) as an eluent to afford red solid **S5** (10.0 mg, 91.0%). Mp = 140–141 °C. ^1H NMR ($CDCl_3$) δ (ppm): 1.25 (t, $J = 7.5$ Hz, 3H, $-CH_2CH_3$), 3.50–3.61 (m, 4H, $-N-CH_2-$), 3.90 (t, $J = 5.7$ Hz, 2H, $-O-CH_2-$), 6.69 (dd, $J = 2.4$, 9.3 Hz, 1H, ArH), 7.04 (d, $J = 2.1$ Hz, 1H, ArH), 7.78 (d, $J = 8.7$ Hz, 1H, ArH), 7.96 (d, $J = 8.7$ Hz, 2H, ArH), 8.30 (d, $J = 8.7$ Hz, 2H, ArH). MS (EI), *m/z* [M^+]: 392.5, calcd: 392.1.

2.11. Synthesis of compound **10**

A mixture of compound **1** (46.0 mg, 0.08 mmol), phenylboronic acid (**7**) (22.0 mg, 0.18 mmol), sodium carbonate (84.8 mg, 0.80 mmol), THF (the concentration of **1** is about

Table 1
Polymerization results and characterization data

No.	Yield (%)	M_w[a]	M_w/M_n[a]	λ_{max}[b] (nm)	T_g[c] (°C)	T_d[d] (°C)	T[e] (°C)	l_s[f] (μm)	d_{33}[g] (pm/V)	Φ[h]
P1	78.3	18 200	1.65	477 (465)	144	319	140	0.53	42.1	0.24
P2	74.7	15 500	1.56	445 (442)	126	292	120	0.62	32.1	0.10
P3	86.4	13 500	1.78	453 (448)	125	322				
P4	68.7	21 800	1.68	513	156	249	150	0.59	32.8	0.11
P5	58.4	9000	1.63		160	242	150	0.44	36.6	
P6	71.7	17 800	1.37	551	163	331	140	0.40	47.9	0.13
P7	66.1	6700	1.57	474 (465)	118	249	[i]	[i]	[i]	[i]
P8	55.8	7400	1.47	446 (442)	148	266	150	0.24	48.0	0.15

[a] Determined by GPC in THF on the basis of polystyrene calibration.

[b] The maximum absorption wavelength of polymer solutions in THF, while the maximum absorption wavelength of the corresponding small chromophore molecules in diluted THF solutions is given in the parentheses.

[c] Glass transition temperature (T_g) of polymers detected by DSC analyses under argon at a heating rate of 10 °C/min.

[d] The 5% weight loss temperature of polymers detected by TGA analyses under nitrogen at a heating rate of 10 °C/min.

[e] The best poling temperature.

[f] Film thickness.

[g] Second harmonic generation (SHG) coefficient.

[h] Order parameter $\Phi = 1 - A_1/A_0$, where A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively.

[i] Not obtained.

0.06 M)/water (2/1 in volume), and $Pd(PPh_3)_4$ (3 mol%) was carefully degassed and charged with nitrogen. Then the reaction mixture was stirred at 60 °C for 25 h. After being cooled, the mixture was extracted by $CHCl_3$. The crude product was purified by chromatography on silica gel using acetate/petroleum ether (1/1) as an eluent to afford red solid (40.0 mg, 87.1%). Mp = 57–59 °C. IR (thin film) ν (cm^{-1}): 1720 (C=O), 1517, 1339 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.28 (m, 3H, $-CH_2CH_3$), 3.64 (q, $J = 6.6$ Hz, 2H, $-N-CH_2-$), 3.90 (t, $J = 6.0$ Hz, 2H, $-N-CH_2-$), 4.60 (t, $J = 6.0$ Hz, 2H, $-O-CH_2-$), 6.90 (m, 2H, ArH), 7.4–7.6 (m, 8H, ArH), 7.61 (m, 4H, ArH), 7.76 (d, $J = 8.7$ Hz, 2H, ArH), 7.99 (d, $J = 9.3$ Hz, 1H, ArH), 8.06 (d, $J = 8.1$ Hz, 2H, ArH), 8.26 (d, $J = 8.7$ Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.7, 45.9, 49.2, 62.4, 111.8, 112.8, 118.0, 123.2, 124.9, 127.4, 127.5, 127.8, 128.5, 129.2, 130.4, 131.1, 139.8, 140.0, 141.1, 146.2, 146.5, 147.5, 151.5, 157.1, 166.7. MS (EI), m/z [M^+]: 569.7, calcd: 570.3. UV–vis (THF, 2.5×10^{-5} mol/L) λ_{max}: 474 nm; ε_{max}: 2.72×10^4 mol^{-1} L cm^{-1}.

2.12. Preparation of polymer thin films

The polymers were dissolved in THF (concentration ~4 wt%) and the solutions were filtered through syringe filters. Polymer films were spin coated onto indium tin oxide (ITO)-coated glass substrates, which were cleaned by *N,N*-dimethylformide, acetone, distilled water and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

2.13. NLO measurement of poled films

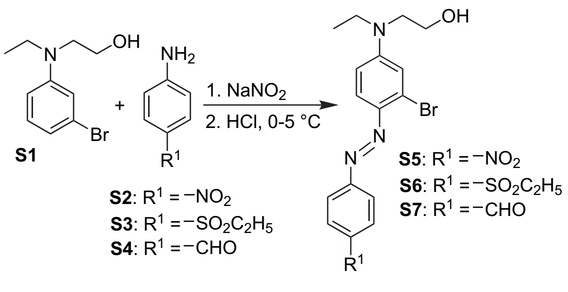
The second-order optical nonlinearity of the polymers was determined by in situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows. Temperature: different for each polymer (Table 1); voltage: 7.0 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with an Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

3. Results and discussion

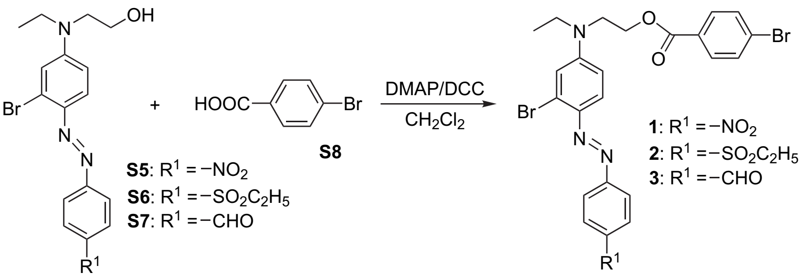
3.1. Synthesis

Co-monomers **1–3** were prepared from the esterification reactions between *p*-bromobenzoic acid and **S5** or **S6** or **S7**, which were obtained through the normal azo coupling reactions from the same starting material, 3-bromo-*N*-ethyl-*N*-hydroxyethyl-aniline (Schemes 4 and 5) [12]. As shown in Scheme 1, these three co-monomers **1–3** underwent the Suzuki polymerization process with DHFBTMB to yield the corresponding polymers **P1–P3** [13]. Then, through the Knoevenagel condensation reactions, different acceptors could be introduced to the polymeric backbone, forming the new push–pull structure to produce polymers **P4–P6** (Scheme 2) easily.

Actually, at the very beginning, we would like to prepare **P4–P6** from the copolymerization of their corresponding



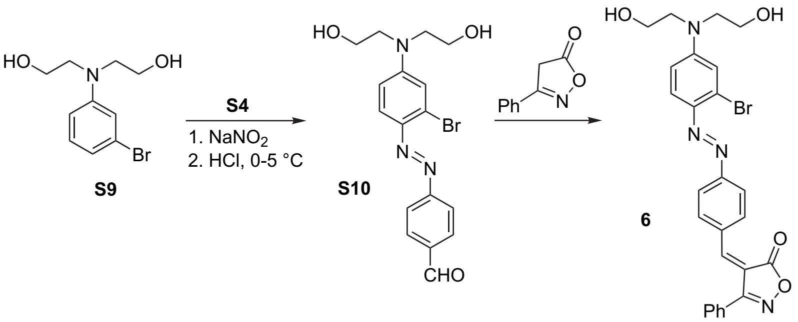
Scheme 4.



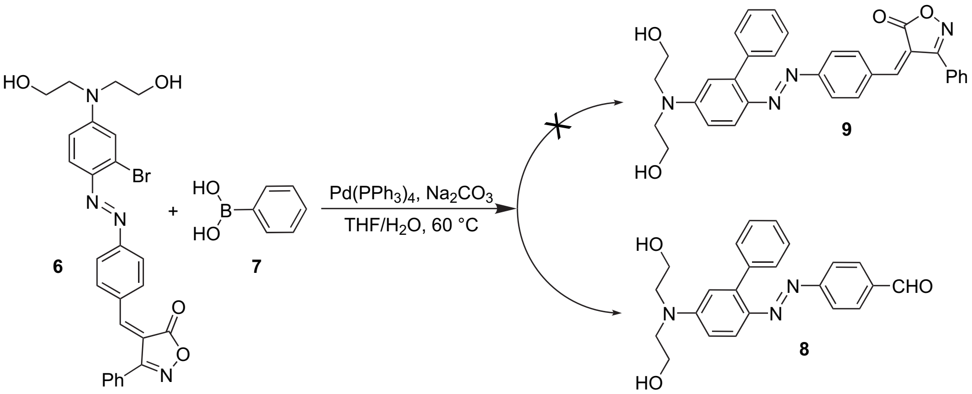
Scheme 5.

chromophore monomers and co-monomer DHFBTMB, since it might be a difficult task for the aldehyde groups in **P3** to react with different acceptors completely. However, the failure for the preparation of another chromophore **9** dissuaded us, and this stuff could be considered as a control experiment (Scheme 7). The synthesis of chromophore **6** is described in Section 2 (Scheme 6). The characterization analysis of the product (shown in Section 2) confirmed that chromophore **8** was yielded instead of chromophore **9**. This indicated that the converse reaction of Knoevenagel condensation took place completely under the normal Suzuki reaction conditions. Thus, the reactive polymer intermediate, **P3**, was designed. The aldehyde moieties were relatively stable during the Suzuki reaction, and they were easily handled to undergo the followed Knoevenagel condensation reactions with different acceptors at mild reaction conditions, according to our previous successful cases [14].

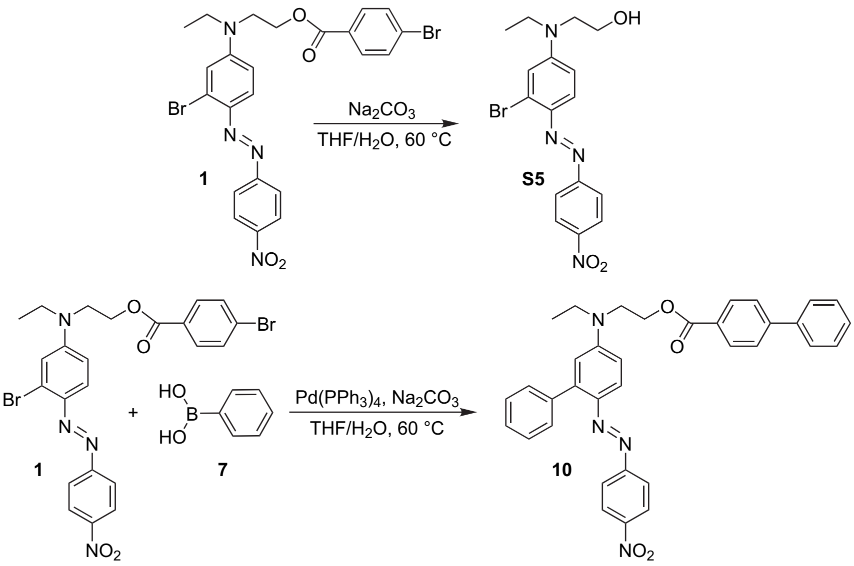
On other hand, since the acceptor group in chromophore **6** escaped under the Suzuki reaction conditions, we worried if the esters would undergo hydrolysis procedure in the same environment. If it were the case, the structure of polymers **P1**−**P3** would be more complicated, and not as demonstrated in Scheme 1. Therefore, we conducted another control experiment (Scheme 8) in which we used chromophore **1** as a model; under the similar Suzuki reaction condition, this compound was stirred for 1 day at 60 °C. The result disappointed us: chromophore **1** was converted to **S5** in a very high yield (91%), similar as our previous case [15]. This fact also confused us: the polymers should not be obtained if the reaction rate of the hydrolysis process was so fast. But we really got polymers **P1**−**P3** with good molecular weights. To make sure of the fact, we conducted another control experiment (Scheme 8): chromophore **1** was used again, however, this time, phenylboronic acid (**7**) and catalyst were added to



Scheme 6.



Scheme 7.



Scheme 8.

proceed a real Suzuki reaction. After 25 h, the same time as that of the copolymerization process for **P1**–**P3**, the reaction was terminated. The resultant product was purified by column chromatography to yield chromophore **10** with the yield of 87.1%, in which the ester bonds remained. The results indicated that chromophores **1**–**3** would undergo the polymerization process through Suzuki reaction to give the corresponding polymers, but not the hydrolysis route to other small chromophores. Thus, with and without the presence of phenylboronic acid and catalyst, the results were totally different, indicating the different roles of the base in the two control experiments. In the Suzuki reaction, the base was involved in the catalytic cycle [13], and the hydrolysis route was suppressed. Thus, the product was chromophore **10**, but not **S5**. In the literature, the ester could be used as reagent in the Suzuki reaction to prepare small molecules [16]. So, our examples demonstrated the successful utilization of esters as co-monomers to construct polymers through Suzuki reactions. Then, from the reactive aldehyde groups of **P3**, we could prepare polymers **P4**–**P6** by using different acceptors through the Knoevenagel condensation reaction. The reaction conditions were different for each acceptor according to the reported methods in the literature for the synthesis of small chromophore molecules with similar structures [11,17].

Under the similar polymerization conditions, **P7** and **P8** were prepared smoothly, in which the isolation groups were phenyl ring, but not fluorene moieties as **P1**–**P6**. Thus, we could use these two polymers as references for other polymers while discussing their NLO properties.

3.2. Structural characterization

The chromophores and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data (see Section 2 and Table 1 for detailed analysis data). The NLO chromophores **1**–**3** were new compounds, and all the polymers **P1**–**P8** were not reported yet. Fig. 1 shows the

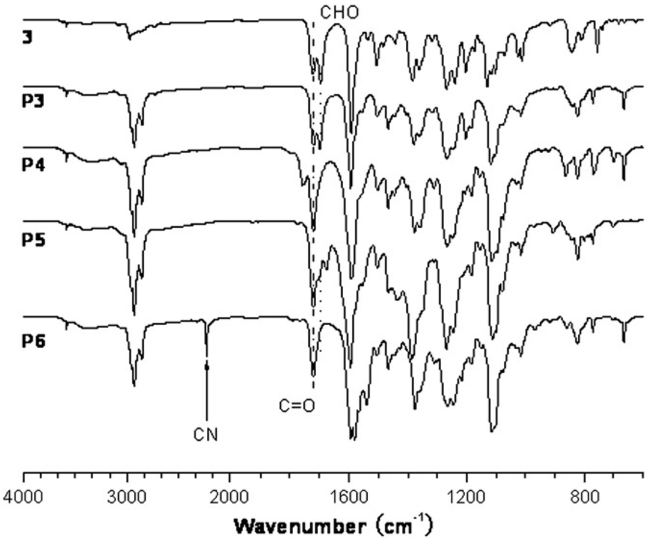


Fig. 1. IR spectra of monomer **3** and polymers **P3**–**P7**.

IR spectra of chromophore **3**, and **P3**–**P6**, in which the absorption band associated with the carbonyl groups was at about 1720 cm^{-1}, and that of aldehyde moieties in **3** and **P3** at about 1696 cm^{-1}. It was seen that there was still a weak absorption peak centered at 1695 cm^{-1} in the IR spectrum of **P5**, indicating that, perhaps, some aldehyde groups remained without reaction during the post-Knoevenagel condensation process. Also, there was another possibility: this weak peak was the absorption signal of the carbonyl groups in the 1,3-diethylthiobarbituric moieties. Thus, we measured the IR spectrum of 1,3-diethylthiobarbituric acid. Really, there was a strong absorption peak centered at about 1706 cm^{-1}. So, we could not know if there were some aldehyde groups remained in **P5** from its IR spectrum (we would discuss this point in the next part). In the IR spectra of monomers **1**–**2**, and polymers **P1**–**P2** and **P7**–**P8**, the typical absorption bands of nitro and sulfonyl groups were easily observed. In the IR spectra of **S10**, **6** and

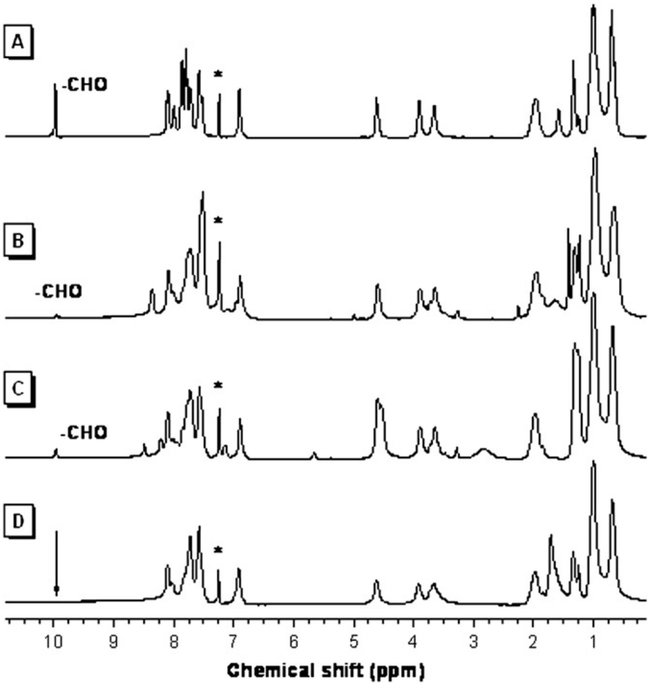


Fig. 2. ^{1}H NMR spectra of **P3** (A), **P4** (B), **P5** (C) and **P6** (D) in chloroform-*d*. The solvent peaks are marked with asterisks (*).

8, after the Suzuki reaction, the absorption peak of aldehyde groups appeared to prove the converse reaction of Knoevenagel condensation.

In all the ^{1}H NMR spectra of the polymers **P1–P8**, the chemical shifts were consistent with the proposed polymer structure as demonstrated in Schemes 2 and 3. For example, Fig. 2 shows the spectra of **P3** and its derivatives **P4–P6**. It was obvious that there were absorption peaks assigned to the signal of aldehyde groups present in the downfields (about 10 ppm) in the spectrum of **P3**. Also, this peak could be easily observed in that of **P5**, confirming the presence of aldehyde moieties (not determined by its IR spectrum). Surprisingly, this signal could also be found in the spectrum of **P4**, though no obvious absorption band of aldehyde groups could be seen in its IR spectrum. From their ^{1}H NMR spectra, we could easily calculate the molar ratio of the reacted and unreacted aldehyde groups in **P4** and **P5**, by comparing the integration of the signals of the aldehyde moieties and the methylene groups linked to oxygen atoms at 4.6 ppm in **P4** or nitrogen atoms at 3.9 ppm in **P5**. Their structures should be as shown in Chart 1. The absence of this peak in the spectrum of **P6** indicated that all of the aldehyde groups reacted with TCF completely. Also, it should be pointed out that since there were nearly no different reactivities between the two bromine atoms in the chromophores **1–3**, it was expected that the polymeric architectures cannot be so perfect (alternating polymers as shown in schemes and Chart 1), and there might be other architectures, such as fluorene groups connected with two benzenes in the donors or in the bridges in **P1–P6**. Similar phenomena in other main-chain NLO polymers have been reported previously, and this random structure might benefit the alignment of chromophore moieties upon poling to improve the thermal stability of NLO effects of the resultant polymers [18].

All the polymers were soluble in common polar organic solvents such as chloroform, THF, DMF, and DMSO. The UV–vis absorption spectra of the chromophores and polymers are shown in Figs. 3 and 4, the maximum absorption wavelength for the π–π* transition of the azo moieties in them is given in Section 2 and Table 1. After the linkage of different acceptors, the maximum absorption wavelengths of **P4–P6** were red-shifted, in comparison with those of **P3**, due to the enhanced intramolecular charge-transferring degree. This phenomenon was very apparent in the case of **P6**: the original absorption peak at 453 nm disappeared, and a new strong signal appeared at 551 nm. However, in **P4** and **P5**, there were still some aldehyde groups remained, thus their curves were very broad, and we nearly could not find the newly formed maximum absorption peak in the spectrum of **P5**. As shown in Fig. 4, the maximum absorption wavelengths of **P1–P2** and **P7–P8** were a little red-shifted, in comparison with their corresponding monomers **1** and **2**. This might be due to the prolonged conjugation bridge in the polymers.

Most of the polymers possessed similar molecular weights (Table 1), which would perhaps facilitate the comparison of their properties on the same level. In comparison with those of **P4** and **P6**, the molecular weights of **P5** were much smaller, the possible reason might be its relatively bad solubility after the linkage of the barbituric moieties, and during the

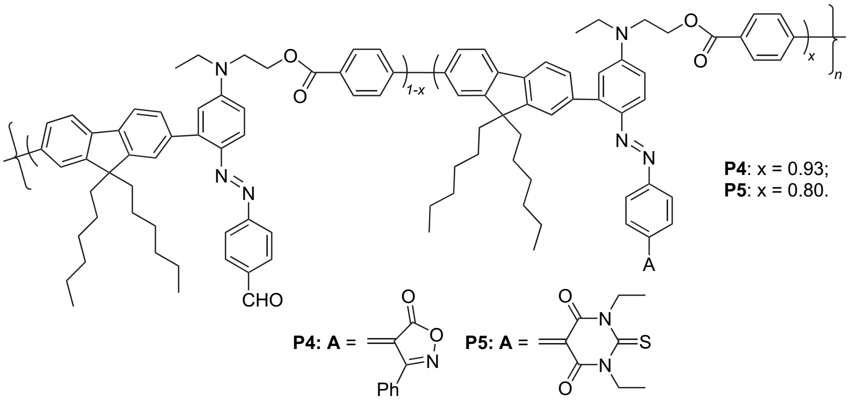


Chart 1.

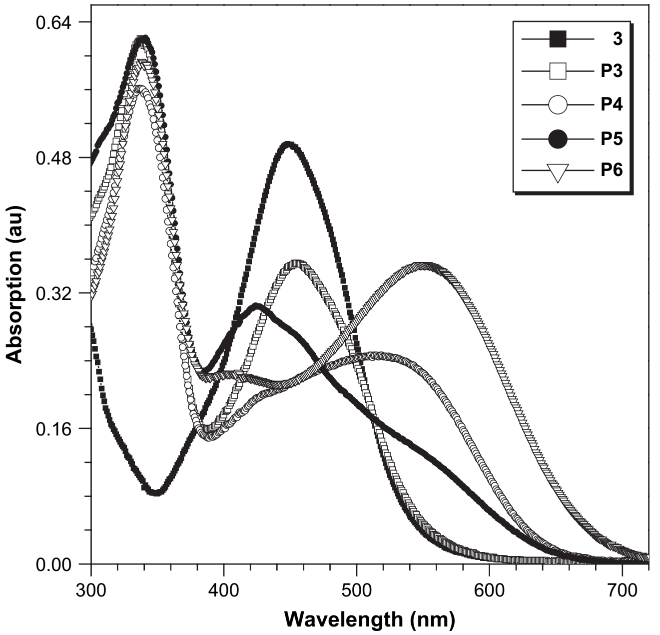


Fig. 3. UV–vis spectra of THF solutions of monomer **3**, and polymers **P3**–**P6**. Concentration: 2.5×10^{-5} mol/L for **3**; 0.01 mg/mL for polymers.

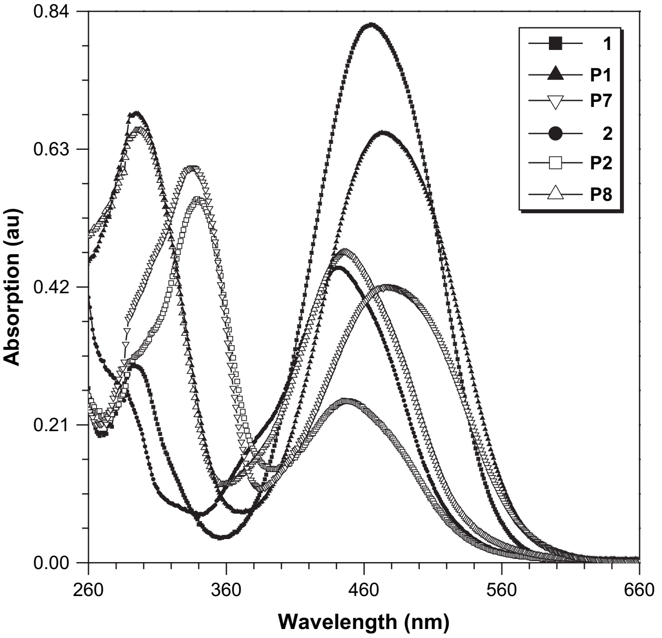


Fig. 4. UV–vis spectra of THF solutions of monomers **1** and **2**, and polymers **P1**, **P2**, **P7** and **P8**. Concentration: 2.5×10^{-5} mol/L for small molecules; 0.01 mg/mL for polymers.

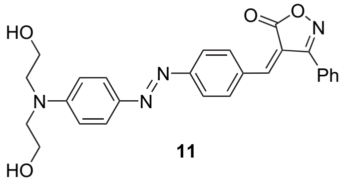


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Chart 2.

purification process of the polymer, those with high molecular weights were insoluble (the lower yield of **P5** partially supporting this point). The molecular weights of **P7**–**P8** were relatively low, possibly due to the usage of boronic acid but not borate. The polymers were thermally stable and the 5% weight loss temperature of polymers is listed in Table 1. Unlike **P6**, **P4** and **P5** exhibited lower thermal stability, although they were derived from the same mother precursor (**P3**). This might be due to the low stability of the formed chromophore moieties, as proved by the thermal behavior of controlled chromophore **11** (Chart 2), whose 5% weight loss temperature was only 181 °C. That is to say, the stability of the chromophore moieties was improved in **P4**. Compared with that of **P1** and **P2**, the bad thermal stability of **P7** and **P8** should be ascribed to their relatively low molecular weights. The glass transition temperature (T_g) of the polymers was investigated using a differential scanning calorimeter (Table 1), and the polymers generally have moderate T_g of about 140 °C.

3.3. NLO properties

Their poled thin films were prepared to evaluate the NLO activity of **P1**–**P8**, which was studied by investigating the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. The method for testing of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers [8]. From the experimental data, their d_{33} values were calculated at 1064 nm fundamental wavelength (Table 1).

As expected, although **P1**–**P6** contained the same isolation moieties (fluorene groups), they demonstrated different d_{33} values (Table 1) due to the different electronic acceptors. Generally, the sulfonyl groups are weaker acceptors than nitro groups, thus with the similar polymeric structure, it was reasonable that the d_{33} value of **P1** was higher than that of **P2**. However, the d_{33} values of **P4** and **P5** were smaller than those of **P1**, although 3-phenyl-5-isoxazolone and 1,3-diethylthiobarbituric acid are considered as stronger acceptors than nitro groups. As to **P6**, TCF is one of the strongest known acceptors, but the tested NLO effect was only a little better than that of **P1**.

In our previous cases [8], we have linked different isolation groups to one fixed chromophore moiety in polymers to modify the subtle structure of the chromophore group. The obtained results of the chromophore-containing polymers demonstrated that for a given chromophore moiety and linkage position, there should be a suitable isolation group present to boost its microscopic β value to possibly higher macroscopic NLO property efficiently, or in other words, the NLO properties and the poling efficiency of the corresponding polymers do not always increase accompanying with the enlargement of the isolation groups linked to the chromophore moieties.

Here, in **P1**–**P6**, on the contrary, the isolation groups were the same, but the chromophore moieties were different as different acceptors used. Based on our previous examples, we could consider that the fluorene groups used in **P1**–**P6** should not always be the suitable isolation spacers for all the chromophore moieties. It might be good isolation group for nitro and sulfonyl moieties, but not for 3-phenyl-5-isoxazolone, 1,3-diethylthiobarbituric acid and TCF. As shown in Chart 3 [8b], the best isolation group for this type of polymers (**PS1**–**PS4**) was carbazolyl group, while that for **PS5**–**PS8** was phenyl group. Thus, we could expect that the fluorene group in **P1**–**P6** should be almost the best isolation spacer in **P1** with nitro group as acceptor, since the size of the fluorene group was similar to that of carbazolyl moieties and the linkage position of isolation spacers in **P1** was the same as in **PS1**–**PS4**. However, the fluorene group might be a little larger in **P2**, as phenyl one was the best for **PS5**–**PS8** with sulfonyl group as the acceptor. Therefore, if a smaller isolation spacer is used instead of the fluorene one in **P2**, perhaps, the NLO effect of the resultant polymer might be higher. To check this point, we further designed two polymers, **P7** and **P8**, in which benzene group was the isolation spacer (Scheme 3). It was a pity that we could not obtain good thin films of **P7** for the NLO test, while those of **P8** could be prepared easily. As shown in Table 1, the d_{33} value of **P8** was 48 pm/V, about 1.5 times that of **P2** (32.1 pm/V), proving that our thought was reasonable. And phenyl group was much better isolation spacer than the fluorene one in the cases of **P2** and **P8**, with sulfonyl group as the acceptor. The reason for this phenomenon should be that the sulfonyl group was weaker acceptor than nitro one. The benzene group was a good choice to balance the good effect (minimizing the interaction of the chromophores to improve the d_{33} value) and bad effect (restraining the orderly alignment of the chromophores to decrease the d_{33} value), caused by the introduced isolation groups in the polymers. Then, according to the above obtained results and previous ones, the fluorene group might be a little smaller as isolation spacer in **P4**–**P6**, since 3-phenyl-5-isoxazolone, 1,3-diethylthiobarbituric acid and TCF are much stronger acceptors than nitro group. Thus, to boost the high microscopic β values of chromophores with TCF as acceptors to possibly higher macroscopic NLO effect, larger isolation group should be introduced if the linkage position was near the donor side, or in other words, in **P4**–**P6**, the fluorene group could not balance the good effect and bad effect well, leading to the relatively low d_{33} value, although the acceptor moieties were stronger than the nitro group.

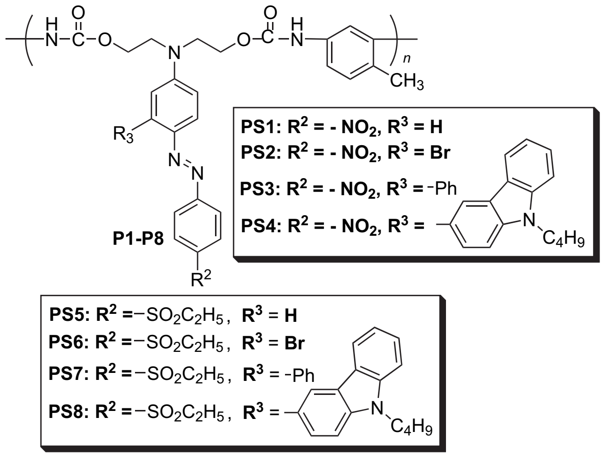

Chart 3.

To further study the alignment behavior of the chromophore moieties in the polymers, the order parameter (Φ) of the polymers (Table 1) was also measured and calculated from the change of the UV–vis spectra of their films before and after corona poling under electric field, according to the equation described in Table 1 (footnote h). The tested Φ values were different when different acceptors were used. **P1** exhibited the highest data, indicating that the fluorene moieties were really good isolation spacer for the nitro group. The relatively low values of **P2**, **P4** and **P6** reported the unsuitableness of fluorene group as the isolation spacer in these polymers. When the isolation spacer in **P2** was changed to phenyl ring in **P8**, the tested Φ value of the latter polymer increased to 0.15, indicating the good alignment of the chromophore moieties in the poled film, in accordance with their d_{33} values. The results further confirmed that the phenyl ring was better isolation spacer for the sulfonyl group as discussed above.

It also should be pointed out that in this case, the results were obtained in the polymers with the special structure as shown in Schemes 1–3. If the topology structures of the polymers are different, the behavior of the resultant NLO properties might be totally different. However, it could be claimed that it would not work well to use the same isolation spacer for similar chromophore moieties with different acceptors, or even for different chromophore ones. The results were similar as we obtained before, but more powerful.

The dynamic thermal stabilities of the NLO activities of the polymers were investigated by the depoling experiments, in which the real time decays of their SHG signals were monitored as the poled films were heated from room temperature to 150 °C in air at a rate of 4 °C/min. As shown in Fig. 5, the long-term temporal stability of most of the polymers was good, making them good candidates for the practical applications. This property might be ascribed to the structure of the random arrangement of the chromophore moieties in the polymer backbone as discussed in the above synthetic part. Among

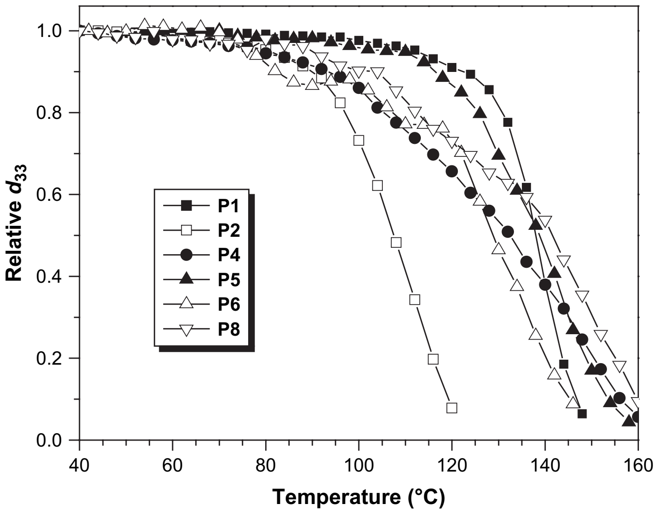

Fig. 5. Decays of SHG coefficient of **P1**, **P2**, **P4**–**P6**, and **P8** as a function of temperature.

them, **P1** showed the best thermal stability with the onset temperature for decays in the d_{33} values around 127 °C, possibly due to the presence of the large fluorene group. The relatively bad stability of **P2** might be caused by its low glass transition temperature or the low best poling temperature.

4. Conclusion

Totally, eight polymers were successfully prepared under the optimized synthetic conditions according to the control experiments. Our results demonstrated the following points.

1. The same isolation group would result in different influence when the chromophore moieties used were different. And for a given chromophore moiety, there should be a suitable isolation group present to boost its microscopic β value to possibly higher macroscopic NLO effect efficiently.
2. The esters could be used as monomers to construct polymers under the normal Suzuki reaction conditions conveniently.
3. Most of the polymers exhibited good processability, thermal stability, and relatively good NLO effects. And they could be promising candidates for practical applications in photonic fields.

Thus, our study may provide some useful information on the preparation of new functional polymers inaccessible from their corresponding monomers directly, and be helpful to obtain even higher NLO effects by using the present chromophores.

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