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Syntheses and second-order nonlinear optical properties of a series of new "H"-shape polymers

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ABSTRACT

To develop more "H"-shape nonlinear optical polymers, in this paper, four new polymers embedded with "H"-type chromophore moieties were designed and synthesized through a Suzuki coupling copolymerization reaction. The "H"-type chromophores were easily prepared by the utilization of "Click Chemistry" reactions, and their structures could be conveniently adjusted by changing the diazido groups. All the polymers exhibited good film-forming ability, thermal stability, and large optical nonlinearities. As a typical example, **P4** demonstrated the highest d_{33} value of 94.7 pm/V, and its onset temperature for decay was up to 103 °C, making it promising candidate for practical applications in photonic fields.

1. Introduction

During the past two decades, nonlinear optical (NLO) polymeric materials have been put forth as promising candidates for the future second-order nonlinear optical applications, such as optical information processing, optical sensing, data storage, and telecommunications, due to their high bandwidth, large optical nonlinearity, ease of fabrication, and low cost in comparison with inorganic compounds [1–4]. Generally, polymeric materials can be endowed with NLO functionality easily by attaching various NLO chromophores to the backbone or side chains of the polymer system [5]. Thus, scientists have tried to synthesize new structural chromophores with different shapes to achieve higher optical nonlinearity. Thanks to their great efforts, the $\mu\beta$ values of NLO chromophores have been improved by up to 250-fold. Furthermore, their structure has been developed from linear to various other types, such as L-shape, X-shape, Y-shape, U-shape, octupolar, etc. [6–8]. However, despite the outstanding results achieved, NLO polymers have hardly been accepted into practical applications. One of the major obstacles was that the large $\mu\beta$ values of chromophores could not be efficiently transformed into high macroscopic NLO activities of polymers, due to the strong intermolecular electrostatic dipole–dipole interactions of the high polar chromophore moieties during their poling-induced noncentrosymmetric alignment process, an essential procedure for the generation of macroscopic NLO effects [9,10].

In order to improve the poling efficiency of NLO materials, Dalton et al. suggested that the control of the shape of chromophores by introducing some bulky spacers could inhibit side-by-side aggregation of chromophores, thus suppressing the dipole interactions to enhance the poling efficiency [11,12]. Jen and co-workers has successfully prepared various types of chromophore-containing dendrimers, which demonstrated large NLO values and good temporal stabilities [13]. Other groups also have reported some NLO dendritic macromolecules with good performance [14–16]. Since 2006, we have designed many series of new NLO polymers, in which different isolation groups of different size were introduced into the chromophore moieties. The experimental results obtained demonstrated that the macroscopic nonlinearity of these NLO polymers could be boosted much higher by bonding suitable isolation groups to the NLO chromophore moieties [17–23]. To obtain much better NLO properties using a facile synthetic approach, our group, earlier in 2006, for the first time, designed and synthesized a new type of chromophore, termed an "H"-type chromophore, in which two traditional donor-π-acceptor chromophore moieties were linked together through an isolation group [18]. The synthetic route to this

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type of chromophores was simple and, moreover, their corresponding polyurethanes exhibited much enhanced NLO effects, in comparison with their linear analog polymers [18]. From then on, much work has been conducted in our group to develop "H"-type chromophores, the major effort being devoted to the variation of their chemical structure. For example, indole groups were utilized to construct "H"-type chromophores, which displayed excellent optical transparency [24]. By bonding suitable isolation groups into "H"-type chromophores, a series of dendron-like main-chain polyurethanes, with large NLO effects, were synthesized [25]. In addition, through modifying the linkage mode between two "H"-type chromophores, some new "H"-shape polymers with high performance, in which the linkage mode was shoulder-to-shoulder, were prepared (Fig. 1) [26]. In 2008, Lu et al. prepared some "H"-type chromophores, and investigated their NLO properties in detail. They found that the "H"-structure should be an effective method to solve the nonlinearity-transparency trade-off [27]. Therefore, further to check the advantages of "H"-type chromophores and with the aim to investigate the relationship between the structure and properties in "H"-shape polymers, we synthesized some new shoulder-to-shoulder "H"-shape NLO polymers embedded with "H"-type NLO chromophores, by changing the linked isolation groups and comonomers.

On the other hand, recently, our group have prepared some NLO dendrimers, dendronized polymers and hyperbranched polymers conveniently by the usage of Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between azides and alkynes [28–32], which was also termed as Sharpless "Click Chemistry" [33], a versatile synthetic tool to construct a diverse range of macromolecules [34]. Thus partially based on our previous work [28–32], to explore more convenient synthetic routes to "H"-type chromophores, the click reaction has been applied to the preparation of "H"-type chromophores.

2. Experimental section

2.1. Materials

Tetrahydrofuran (Sinopharm Chemical Reagent Beijing Co., Ltd.) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Chromophore **1** and compound **6** were prepared according to our previous work [26]. 1,4-Diazidobutane (**2**) and 1,4-bis(azidomethyl)benzene (**3**) were synthesized following the literature methods [35,36]. 9,9-Dihexylfluorene-2,7-bis(trimethylene borate) (**7**) was purchased from Aldrich (China). All other reagents were used as received.

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 or a Bruker ARX 400 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer-2 spectrometer in the region of 3000-400 cm^{-1} on NaCl pellets. UV–visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode. Elemental analysis was carried out on a Carlo Erba-1106 micro-elemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. Dimethylformamide (DMF, TEDIA) was used as eluent, and the flow rate was 1.0 mL/min. 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 mL/min for thermogravimetric analysis and the thermal transitions of the polymers. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

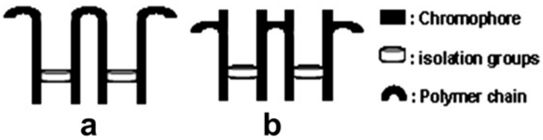


Fig. 1. Different linkage mode between two "H"-type chromophores: a) head-to-head; b) shoulder-to-shoulder.

2.3. General procedure for syntheses of "H"-type chromophores **4** and **5**

Chromophore **1** (2.25 equiv), azide **2** or **3** (1.0 equiv), $CuSO_4 \cdot 5H_2O$ (5 mol %), $NaHCO_3$ (10 mol %), ascorbic acid (10 mol %) was dissolved in THF/H_2O (3:1 in volume) under an atmosphere of nitrogen in a Schlenk flask. The mixture was stirred overnight at room temperature for 5–10 h, then stopped, extracted with chloroform, and washed, in turn, with 1N HCl, 1N NH_4OH and water. The organic layer was collected and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel using ethyl acetate as eluent.

"H"-type chromophore **4**: **1** (284 mg, 0.62 mmol), **2** (39 mg, 0.28 mmol). **4** was obtained as deeply red powder (170 mg, 57.3%). IR (thin film), υ (cm^{-1}): 1514, 1336 (-NO_2). ^{1}H NMR (300 MHz, $CDCl_3$, 298K) δ (ppm): 1.23 (t, J = 6.6 Hz, 12H, -CH_3), 1.83 (br, s, 4H, -CH_2CH_2-), 2.32 (m, 4H, -CH_2-), 2.99 (t, J = 6.6 Hz, 4H, -CH_2C-), 3.46 (q, J = 7.2 Hz, 8H, -NCH_2-), 4.27 (t, 8H, -OCH_2- and -NCH_2-), 6.62 (dd, J = 2.4, 9.6 Hz, 2H, ArH), 6.96 (s, 2H, C=CH), 7.28 (s, 2H, ArH), 7.74–7.90 (m, 8H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 12.65, 22.05, 27.09, 28.45, 44.99, 49.15, 68.85, 109.32, 110.91, 114.45, 116.71, 118.06, 119.42, 121.15, 131.76, 140.18, 147.00, 147.13, 148.26, 151.53, 155.22. MALDI-TOF MS: calcd for ($C_{46}H_{54}Br_2N_{14}O_6$): m/z [M+1]: 1059.18; found: m/z 1058.27. $C_{46}H_{54}Br_2N_{14}O_6$ (EA) (%, found/calcd): C, 52.33/52.18; H, 5.33/5.14; N, 18.38/18.52. UV–Vis (THF, 0.01 mg/mL): $\lambda_{max} = 482$ nm; $\varepsilon_{max} = 3.17 \times 10^4$ mol^{-1} L cm^{-1}.

"H"-type chromophore **5**: **1** (284 mg, 0.62 mmol), **3** (53 mg, 0.28 mmol). **5** was obtained as deeply red powder (140 mg, 44.3%). IR (thin film), υ (cm^{-1}): 1514, 1336 (-NO_2). ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 1.24 (t, J = 6.8 Hz, 12H, -CH_3), 2.30 (m, 4H, -CH_2-), 2.99 (t, J = 6.8 Hz, 4H, -CH_2C-), 3.45 (q, J = 7.2 Hz, 8H, -NCH_2-), 4.27 (t, J = 6.4 Hz, 4H, -OCH_2-), 5.42 (s, 4H, -CH_2Ph-), 6.62 (dd, J = 2.8, 9.2 Hz, 2H, ArH), 6.96 (s, 2H, C=CH), 7.14 (s, 4H, ArH), 7.25 (s, 2H, ArH), 7.74–7.90 (m, 8H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 12.65, 22.01, 28.05, 44.99, 53.43, 63.72, 109.27, 110.90, 114.44, 116.68, 118.03, 119.41, 121.26, 128.44, 131.77, 135.41, 140.17, 146.97, 147.40, 148.22, 151.53, 155.20. MALDI-TOF MS: calcd for ($C_{50}H_{54}Br_2N_{14}O_6$): m/z [M+1]: 1107.26; found: m/z 1106.27. $C_{50}H_{54}Br_2N_{16}O_6$ (EA) (%, found/calcd): C, 54.14/54.26; H, 5.07/4.92; N, 17.55/17.72. UV–Vis (THF, 0.01 mg/mL): $\lambda_{max} = 484$ nm; $\varepsilon_{max} = 2.93 \times 10^4$ mol^{-1} L cm^{-1}.

2.4. General synthetic procedure of "H"-shape polymers **P1**–**P4**

A mixture of **4** or **5** (1.00 equiv), **6** or **7** (1.00 equiv), sodium carbonate (10.0 equiv), THF (monomer concentration was about 0.01 M)/water (12/1 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 4 days. After the solution was cooled to ambient temperature, it was dropped into methanol to

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[e] (°C)	l_s[f] (μm)	d_{33}[g] (pm/V)	$d_{33(\infty)}$[h] (pm/V)
P1	56.7	6800	1.11	488 (482)	80	240	72	0.41	75.1	9.4
P2	67.2	8200	1.10	490 (482)	87	240	75	0.55	64.4	8.2
P3	54.3	6500	1.30	486 (484)	100	231	95	0.51	64.8	8.5
P4	64.0	20000	1.43	491 (484)	122	287	135	0.31	94.7	11.0

[a] Determined by GPC in DMF on the basis of a 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 are given in the parentheses.

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

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

[e] The best poling temperature.

[f] Film thickness.

[g] Second harmonic generation (SHG) coefficient.

[h] The nonresonant d_{33} values calculated by using the approximate two-level model.

remove monomers. The obtained solid was dissolved in THF, the insoluble solid was filtered out. The filtrate was concentrated and further precipitated by the addition into methanol. The resultant polymer was collected and then dried under vaccum at 40 °C overnight.

P1: **4** (64 mg, 0.060 mmol), **6** (32 mg, 0.060 mol). **P1** was obtained as deeply red powder (40 mg, 56.7%). $M_w = 6800$, $M_w/M_n = 1.11$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1518, 1336 (-NO_2). ^1H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 0.9–1.1 (-CH_3), 1.1–1.3 $(-CH_2)_2$- and -CH_3), 1.3–1.45 (-CH_2-), 1.7–1.9 (-CH_2-), 2.2–2.3 (-CH_2-), 2.9–3.0 (-CH_2C-), 3.3–3.5 (-NCH_2-), 4.1–4.3 (-OCH_2-), 6.5–6.7 (ArH), 6.9 (C═CH), 7.2–7.3 (ArH), 7.7–7.9 (ArH). UV–Vis (THF, 0.01 mg/mL): λ_{max} (nm): 488.

P2: **4** (64 mg, 0.060 mmol), **7** (31 mg, 0.060 mol). **P2** was obtained as deeply red powder (50 mg, 67.2%). $M_w = 8200$, $M_w/M_n = 1.10$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1514, 1336 (-NO_2). ^1H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 0.5–0.7 (-CH_3), 0.9–1.1 (-CH_2-), 1.1–1.3 (-CH_2- and -CH_3), 1.7–2.0 (-C-CH_2-), 2.1–2.3 (-CH_2-), 2.8–3.0 (-CH_2C-), 3.3–3.5 (-NCH_2-), 4.1–4.3 (-OCH_2-), 6.6–6.8 (ArH), 7.2–7.4 (ArH), 7.4–7.5 (ArH), 7.6–7.9 (ArH). UV–Vis (THF, 0.01 mg/mL): λ_{max} (nm): 490.

P3: **5** (50 mg, 0.045 mmol), **6** (24 mg, 0.045 mol). **P3** was obtained as deeply red powder (30 mg, 54.3%). $M_w = 6500$, $M_w/M_n = 1.30$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1518, 13399 (-NO_2). ^1H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 0.7–1.1 (-CH_3), 1.1–1.4 (-CH_2- and -CH_3), 2.1–2.3 (-CH_2-), 2.8–3.0 (-CH_2C-), 3.2–3.5 (-NCH_2-), 4.1–4.2 (-OCH_2-), 5.3–5.4 (-CH_2Ph), 6.5–6.7 (ArH), 6.9 (C═CH), 7.0–7.2 (ArH), 7.6–7.9 (ArH). UV–Vis (THF, 0.01 mg/mL): λ_{max} (nm): 486.

P4: **5** (44 mg, 0.040 mmol), **7** (21 mg, 0.040 mol). **P2** was obtained as deeply red powder (33 mg, 64.0%). $M_w = 20{,}000$, $M_w/M_n = 1.43$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1518, 1336 (-NO_2). ^1H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 0.5–0.7 (-CH_3), 0.9–1.1 (-CH_2-), 1.1–1.3 (-CH_2- and -CH_3), 1.7–1.9 (-C-CH_2-), 2.1–2.3 (-CH_2-), 2.9–3.0 (-CH_2C-), 3.3–3.5 (-NCH_2-), 4.1–4.2 (-OCH_2-), 5.2–5.4 (-CH_2Ph), 6.6–6.8 (ArH), 7.0–7.2 (ArH), 7.2–7.4 (ArH), 7.4–7.5 (ArH), 7.5–7.8 (ArH), 7.8–7.9 (ArH). UV–Vis (THF, 0.01 mg/mL): λ_{max} (nm): 491.

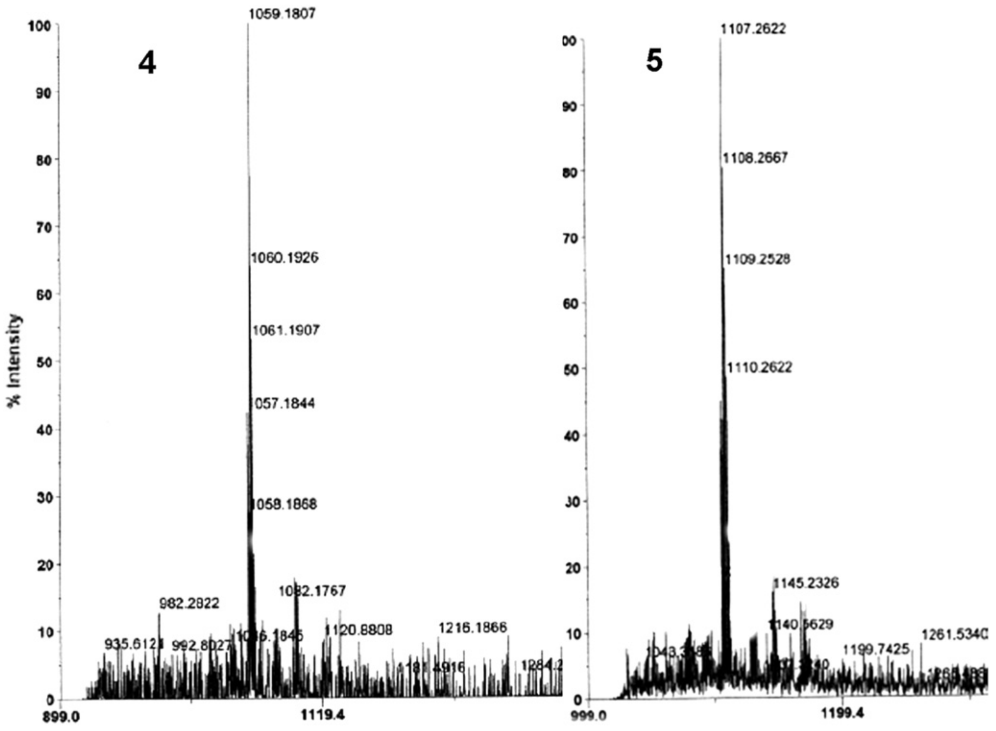


Fig. 2. MALDI-TOF mass spectrum of "H"-type chromophores **4** and **5**.

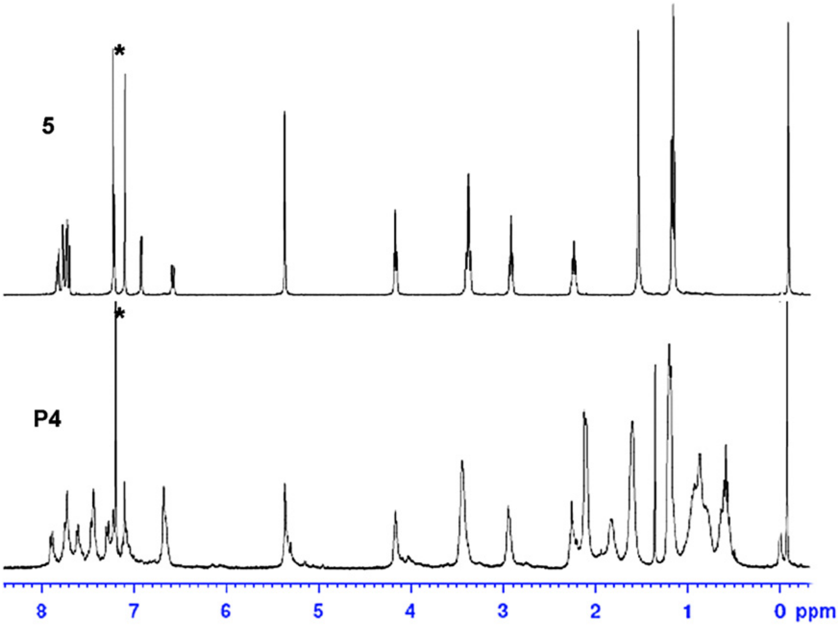


Fig. 3. The ^{1}H NMR spectra of “H”-type chromophore **5** and polymer **P4**, conducted in chloroform-*d*.

2.5. *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 with DMF, acetone, distilled water and THF sequentially in ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

2.6. *NLO measurement of poled films*

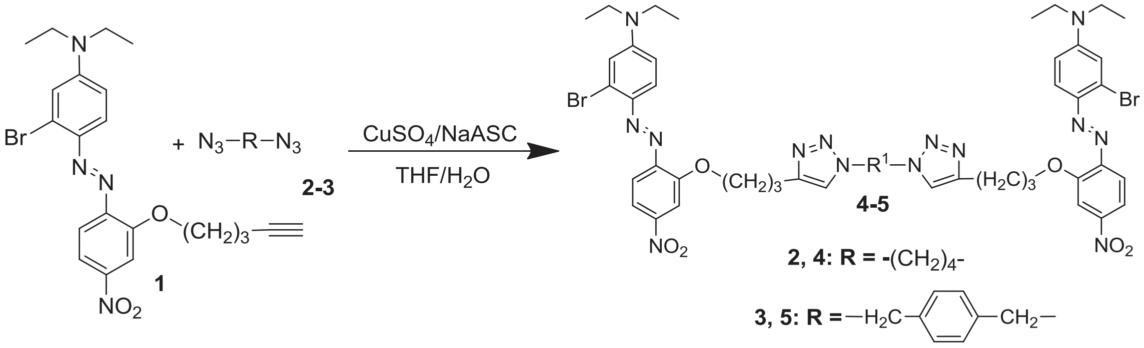
The second-order optical nonlinearity of the polymers was determined by *in-situ* second harmonic generation (SHG) measurement using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, different for each polymer (Table 1); voltage, 7.2–7.5 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with a 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

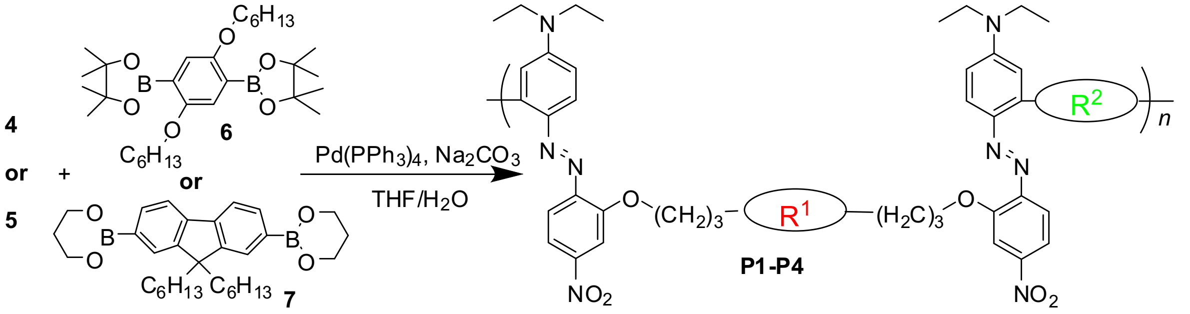
3.1. *Synthesis*

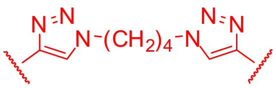
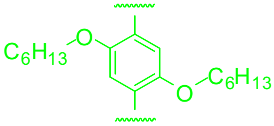
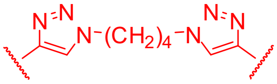
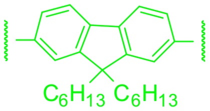
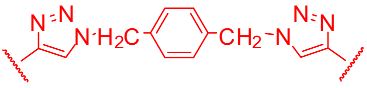
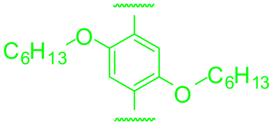
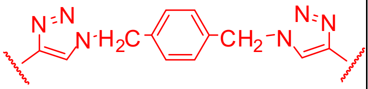
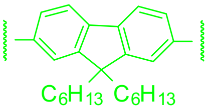
By the usage of Sharpless “Click” reaction, “H”-type chromophores **4** and **5** could be easily prepared. The reaction was complete in 5–10 h, much faster than the Sonogashira coupling reaction in our previous work [25,26]. However, the yields were not high enough, although monitored by TLC, there were no by-products apparent. The main reason might be that the “H”-type chromophores **4** and **5** were poorly adsorbed by the silica column during the purification process.

Under the typical reaction conditions of the Suzuki coupling copolymerization, “H”-type chromophores **4** and **5** could react with different borates (**6** or **7**) to yield the corresponding “H”-shape polymers **P1**–**P4**. Because of the low solubility of chromophores **4** and **5** in THF, the reaction solution had to be diluted to lower concentrations compared to our previous work [26], in which the monomer concentration was controlled at about 0.05 M. Even though the concentration of chromophores **4** or **5** was adjusted to 0.01 M, they were not completely soluble. However, fortunately, during with the copolymerization, the reaction solution gradually



Scheme 1. The synthetic route to Chromophores 4 and 5.



	R^1	R^2
P1		
P2		
P3		
P4		

Scheme 2. The synthetic route to polymers.

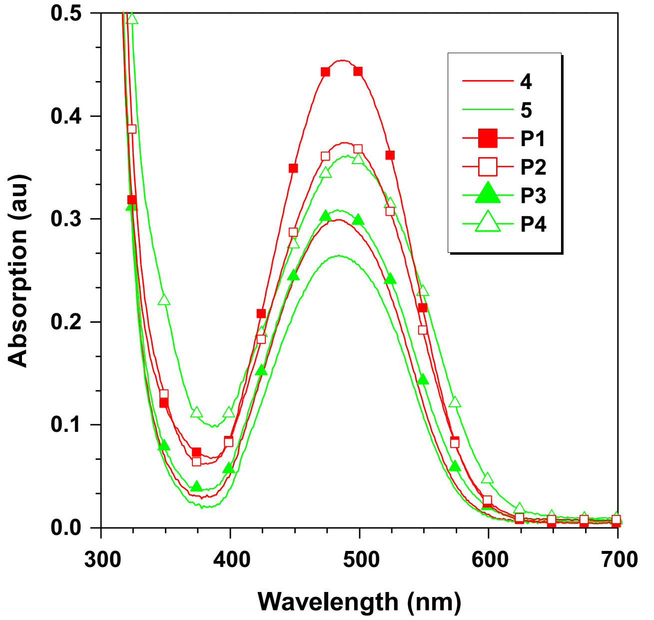


Fig. 4. UV–Vis spectra of “H”-type chromophores 4–5 and their corresponding polymers **P1**–**P4** in THF solutions. Concentration: 0.01 mg/mL.

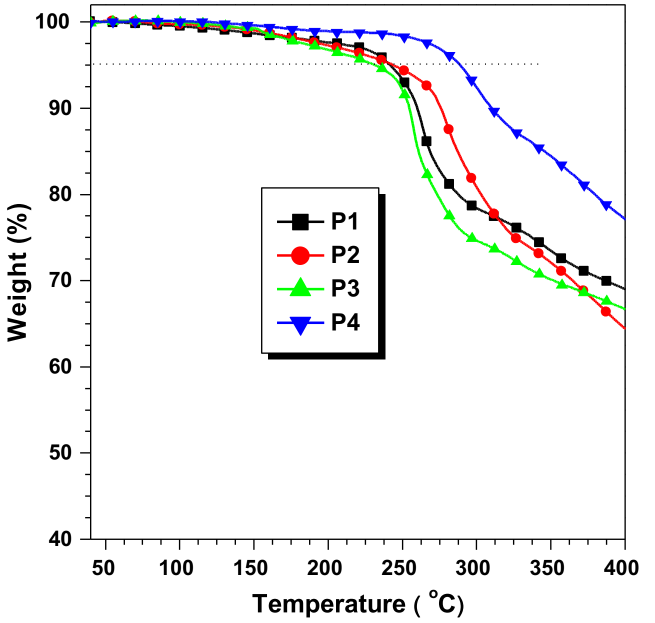


Fig. 5. TGA thermograms of **P1**–**P4**, measured in nitrogen at a heating rate of 10 °C/min.

became clear. By changing the diazides and borates, the size of isolation groups could be adjusted from small to larger, according to the concept of "suitable isolation group". Thus, we could investigate the relationship between the structure and properties of these polymers easily.

3.2. Structural characterization

"H"-type chromophores **4** and **5** are new compounds, and their structure was further characterized by elemental analysis, and MALDI-TOF (Fig. 2 and Experimental Section). The polymers were also well characterized by different spectroscopic methods, and all gave satisfactory spectral data (Table 1). In the IR spectra of **P1**–**P4**, it was easily seen that the absorption bands associated with the nitro groups were at about 1336 and 1518 cm^{-1}. The structure of all the polymers was confirmed by ^1H NMR spectra. As an example, Fig. 3 showed the ^1H NMR spectra of "H"-type chromophore **5** and its corresponding polymer **P4**. All the peaks could be readily assigned to the resonances of appropriate protons as demonstrated in Schemes 1 and 2, with no unexpected resonance peaks observed. In comparison with chromophore **5**, some new peaks were apparent in the spectrum of **P4** upon polymerization: for example, a new peak at 7.4 ppm was attributed to H-1′ and H-8′ of 9,9-dihexylfluorene.

All the polymers were easily soluble in common organic solvents, such as $CHCl_3$, THF, DMF, and DMSO. The UV–Vis absorption spectra of **P1**–**P4** and their corresponding chromophores are shown in Fig. 4. The maximum absorption wavelengths for the π-π^* transition of the azo moieties in them are listed in the experimental section and Table 1. In comparison with their corresponding monomers **4** and **5**, the λ_{max} values of **P1**-**P4** were a little red-shifted, possibly due to the prolonged conjugated bridge in the polymers [23,26]. The molecular weights of polymers were determined by gel permeation chromatography (GPC) with DMF as an eluent and polystyrene as calibration standard. The relatively high molecular weight of **P4** was possibly due to minimal steric hindrance effects during the polymerization process. The temperature for the 5 wt % loss has often been used as a degradation temperature (T_d) to estimate the thermal stability of a synthetic polymer. Here, as shown in Fig. 5, the T_d values for **P1**–**P4** were all higher than 230 °C, indicating that the polymers are thermally stable. The glass transition temperature (T_g) of the polymers were also investigated, by using a differential scanning calorimeter (Table 1). The much better thermal stability of **P4** than other polymers should be ascribed to its higher molecular weights.

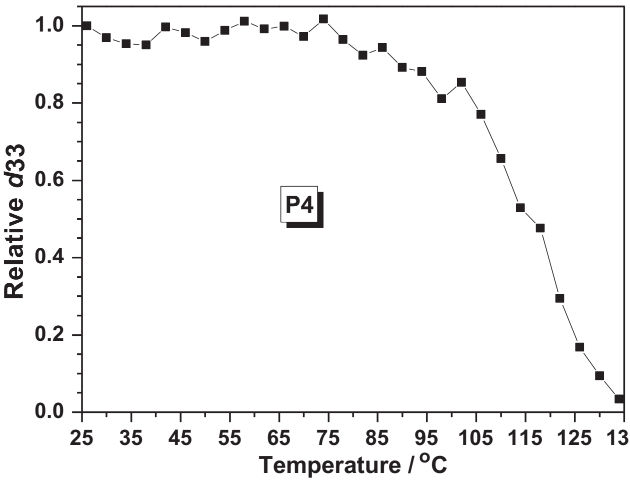


Fig. 6. Decay of SHG coefficient of **P4** as a function of temperature.

3.3. NLO properties

P1–**P4** exhibited good film-forming abilities, and they could be easily spin-coated to provide thin solid films. A convenient technique to study the second-order NLO activity is to investigate the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. Calculation of the SHG coefficients (d_{33}) for the poled films and the poling conditions of these polymers were similar to those used previously [18–23]. From the experimental data, the d_{33} values of polymers were calculated at fundamental wavelength of 1064 nm (Table 1). It was noted that the best poling temperature of **P4** was higher than its glass transition temperature (T_g), while those of others were lower than the corresponding T_g. This was reasonable. Generally, the best poling temperature for one NLO polymer should be around its T_g, possibly lower or higher, as determined by different polymers, due to their different structure, the bulk of the chromophore moieties, molecular weight and some other parameters. The higher best poling temperature of **P4** might be related to its higher molecular weight, which could make the movement of the polymer chain more difficult.

The resultant "H"-Shape polymers demonstrated very good optical nonlinearities, further confirming that "H"-type chromophores might be a better architectural design than the linear ones. This was reasonable, since the linkage spacers (two formed triazole rings) between the two D-π-A moieties could act as effective isolation groups to minimize the strong dipole–dipole interactions, thus enhancing the macroscopic optical nonlinearities, according to the site-isolation principle [11]. In addition, since the linkage mode of "H"-type chromophore moieties in **P1**–**P4** was shoulder-to-shoulder, the co-monomers (phenyl rings or fluorene rings) could also act as isolation groups, further decreasing the strong electronic interactions [23,26]. On the other hand, our previous work has demonstrated that the macroscopic nonlinearity of NLO polymers could be boosted much higher by introducing suitable isolation groups into the NLO chromophore moieties [18–23]. Here, as expected, by introducing isolation groups of different size, the architecture of "H"-shape polymers could be simply modified. **P4** exhibited the highest d_{33} value (94.7 pm/V), indicating that the isolation groups introduced in **P4** were effective in suppressing the strong dipole-dipole interactions to enhance poling efficiency. As there might be some resonance enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of polymers should be smaller as shown in Table 1 ($d_{33}(\infty)$). These were calculated using the approximate two-level model. However, the obtained $d_{33}(\infty)$ values were still good, and **P4** also exhibited the largest value (11.0 pm/V).

The dynamic thermal stability of the NLO activity of **P4** was investigated by the depoling experiment, in which the real time decay of their SHG signals was monitored as the poled film was heated from 25 to 135 °C in air at a rate of 4 °C/min. As shown in Fig. 6, the long-term temporal stability of **P4** was relatively good, the onset temperature for decay was found to be as high as 103 °C. Thus, the relatively good thermal stability, coupled with its large macroscopic nonlinearity, made **P4** a good candidate for practical photonic applications.

4. Conclusion

In this work, four new "H"-shape NLO polymers (**P1**-**P4**) were easily prepared, through the combination of "Click Chemistry" and Suzuki coupling reactions. According to the concept of the "suitable isolation group", the molecular architecture could be adjusted by changing the linkage spacers (diazides groups) between two D-π-A moieties and co-monomers (borates). As a result, the poling efficiency could be enhanced much efficiently. **P1**–**P4** demonstrated good film-forming ability, high thermal stability, and large NLO effects, with a highest d_{33} value of 94.7 pm/V achieved in **P4**. Thus, the obtained results confirmed the advantage of the architecture of the "H"-shaped chromophores and polymers, providing new ideas for the design of NLO polymeric materials.

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