DOI: 10.1002/cplu.201300252

Introduction of an Isolation Chromophore into an "H"-Shaped NLO Polymer: Enhanced NLO Effect, Optical Transparency, and Stability**

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In this study, a new polymer **P1** embedded with "H"-type chromophore moieties was designed and synthesized through Suzuki coupling copolymerization, in which the isolation chromophore was introduced to further improve its comprehensive performance. This polymer demonstrated good solubility and film-forming ability. In comparison with normal "H"-shaped

Introduction

Over the past two decades, organic/polymeric nonlinear optical (NLO) materials have been put forth as promising candidates for future applications such as optical information processing, optical sensing, data storage, and telecommunications because of their large optical nonlinearity, high bandwidth, ease of fabrication, and low cost.^[1] At present, one of the major problems encountered in optimizing organic NLO materials is how to efficiently translate the large hyperpolarizability (β) values of the organic chromophores into high macroscopic NLO activities of polymers, since the strong intermolecular electrostatic dipole-dipole interactions of the highly polar chromophore moieties make the poling-induced noncentrosymmetric alignment of chromophore moieties (necessary for the materials to exhibit the NLO effect), during the poling process under an electric field, a daunting task.^[2,3] According to experimental results and some theoretical calculations, Dalton et al. suggested that to control the shape of the chromophore some bulky spacers could be introduced to inhibit these strong dipole-dipole interactions, and further improve the poling efficiency of NLO materials.^[2,4] Based on this site-isolation principle, various structures of chromophores have been developed, from linear to various other shapes, such as "U"-, "X"-, "H"-, and star-shaped, to improve their topological struc-

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NLO=nonlinear optical
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201300252.

NLO polymers only containing one type of chromophore, nearly all the performance of **P1** was improved. Its NLO coefficient was as high as 134 pm V^{-1} , and its onset temperature for decay was up to $150 \,^{\circ}$ C. Coupled with its improved optical transparency, all these properties made it a promising candidate for practical applications in photonic fields.

tures.^[5] Among the numerous studies on the control of the shape of the NLO chromophore, "H-type" chromophores are typically a successful example.^[6] Based on the site-isolation principle, as well as our systematic study on the "concept of a suitable isolation group",^[6a,7] in 2006, for the first time, we designed and synthesized this H-type chromophore, in which the two pieces of D- π -A blocks were linked together through an isolation group. As shown in Scheme S1 in the Supporting Information, the order parameter (Φ , which shows the alignment of the chromophore moieties in the polymers) of the polymer embedded with this H-type chromophore was more than twice that of its analogues with a normal rodlike chromophore.^[6a] Then, from 2009 to 2012, a series of new H-shaped NLO polymers PS1-PS6 (Scheme S2), in which the linkage positions of the two H-type chromophores were shoulder-toshoulder and the comonomers bonded into the π bridge of the chromophores act as effective isolation groups, was prepared to further reduce the intermolecular electrostatic interactions between chromophore moieties.^[8] Among them, PS5 demonstrated the best performance with a second-harmonic generation (SHG) coefficient (d_{33} value) of 94.7 pm V⁻¹.

However, according to the site-isolation principle, nearly all the isolation groups used before were nonpolar groups, just to control the shape of the NLO chromophore and decrease the strong interactions between the chromophore moieties. They did not contribute directly to the macroscopic NLO effect, but rather decreased the effective concentration of the NLO chromophore moieties, which was harmful to the macroscopic NLO activities for the diluted chromophore concentrations. In 2012, for the first time, our group used one chromophore with a lower $\mu\beta$ value (μ =dipole moment), not the normal nonpolar spacer, as the isolation group for another chromophore with a higher $\mu\beta$ value, to achieve high poling efficiency (**PS7**–**PS10**, Scheme S3).^[9] The results showed that the isolation group for the main chromophore with a higher $\mu\beta$ value could act as an isolation group for the main chromophore with a higher $\mu\beta$ value to achieve

a high poling efficiency owing to the decreased strong electronic interactions, but would not decrease the effective concentration of the NLO chromophore moieties to a large degree. As a result, the d_{33} value of **PS10** with two different chromophores (the sulfonyl- and nitro-based ones) arranged orderly was increased to a large degree, in comparison with that of **PS7**, which only contains one type of chromophore.

Thus, it was very reasonable to consider whether the isolation chromophore could work in the H-shaped NLO polymers to further improve their performance. Therefore, in this paper, the isolation chromophore was introduced into **PS5**, the H-shaped NLO polymer with the highest d_{33} value, to yield a new H-shaped NLO polymer **P1** (Scheme 1). The result was encouraging. The d_{33} value of **P1** was up to 134 pmV⁻¹, nearly 40 pmV⁻¹ higher than that of **PS5**; its onset temperature for decay of d_{33} was up to 150 °C, nearly 50 °C higher than that of



Scheme 1. The original idea of this study: introducing an isolation chromophore into a H-shaped NLO polymer.

PS5 (Table 1). Herein, we report the syntheses, characterization, and properties of this new H-shaped NLO polymer in detail.

Results and Discussion

Synthesis and structural identification

Scheme 2 shows the whole synthetic route to the target polymer. The nitro-based chromophore **C1** contains one alkyne group and one bromine atom, the sulfonyl-based chromophore **C2** contains two azido groups, and bronic ester monomer **M2** was prepared in our previous study. The cycloaddition between azides and alkynes to yield 1,4-triazoles under a copper(I)-catalyzed, namely, Sharpless "click chemistry" reaction,^[10]

Table 1. The contradistinction of P1 and PS5.							
Polymer	Τ _g [°C] ^[a]	λ_{\max} [nm] ^[b]	$d_{_{33}}$ [pm V ⁻¹] ^[c]	$d_{_{33(\infty)}}$ $[pmV^{-1}]^{[d]}$	T_{onset} [°C] ^[e]	N ^[f]	
P1 PS5 ^[h]	150 122	471 491	134 94.7	23 11	150 101	0.621 ^[g] 0.467	
[a] Glass transition temperature of polymers detected by DSC analyses under nitrogen at a heating rate of 10 °C min ⁻¹ . [b] The maximum absorp- tion wavelength of polymers in film. [c] SHG coefficient. [d] The nonreso- nant d_{33} values calculated by using the approximate two-level model. [e] Onset temperature for decay of d_{33} . [f] Loading density of the effective chromophore moieties, which could be calculated from the weight of the chromophores divided by the weight of all the macromolecular systems. [g] This value contains both the main chromophore and the isolation chromophore. [h] Another H-shaped NLO polymer with the best perfor- mance before, its proportion ware toted in our proviour study.							

was very famous for its nearly quantitative yields, mild reaction conditions, broad tolerance toward functional groups, low susceptibility to side reactions, and simple product isolation. By use of this powerful reaction, monomer **M1** could be yielded efficiently (the reaction could be complete in only 3 hours with a yield of 86.2%). And then, under the typical reaction conditions of the Suzuki coupling copolymerization, **M1** could react with bronic ester monomer **M2** to yield the target H-shaped NLO polymer **P1**, embedded with both H-type chromophore and isolation chromophore. Thus, the whole synthetic route was very simple, making its potential practical applications much cheaper.

The obtained H-shaped NLO polymer P1 and its corresponding monomer M1 were characterized by spectroscopic methods, such as FTIR and NMR, and all gave satisfactory data. The structure of monomer M1 was further characterized by MALDI-TOF mass spectrometry (Figure S1), and the result was consistent with the theoretical value. Figure 1 displays the ¹H NMR spectra of P1 and its corresponding monomer M1, which were conducted in the solvent [D]chloroform. The chemical shifts of M1 are consistent with the proposed structure, with its characteristic peaks marked in Figure 1. Furthermore, only the

proton peak of 1,4-triazole, which was marked as peak 13, could be observed in its ¹H NMR spectrum, which confirmed that **M1** was the sole 1,4-isomer. Aside from the resonance peaks of the monomer **M1**, there were still some characteristic peaks assigned to the resonances of protons of the fluorene-based monomer in the ¹H NMR spectra of **P1**, for example, the new peak at δ =7.4–7.6 ppm was attributed to ArH of 9,9-dihexylfluorene; the new peak at δ =0.4–1.0 ppm was attributed to $-CH_2$ - and $-CH_3$ of 9,9-dihexylfluorene, and so forth. Furthermore, in comparison with the ¹H NMR spectrum of **M1**, the peaks in that of **P1** were broad because of the polymerization. A similar phenomenon could be observed also in their ¹³C NMR spectra. As shown in Figure 2, in comparison with monomer **M1**, some new peaks appeared in the spectrum of **P1**

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Scheme 2. The synthesis of H-shaped NLO polymer P1.



Figure 1. ¹H NMR spectra of polymer P1 and its corresponding monomer M1 in [D]chloroform.

after polymerization: δ =55.1 ppm, which is the characteristic peak of C-9' of 9,9-dihexylfluorene; six new peaks at δ =14.1, 22.1, 24.1, 28.7, 31.7, and 40.1 ppm, attributable to the peaks of the sp³-C atom of the hexyl group in 9,9-dihexylfluorene and some ArC of 9,9-dihexylfluorene. In addition, the peak at δ =83.4 ppm, a typical signal of the boronic ester group, could not be observed at all in the ¹³C NMR spectrum of **P1**.

Characterization

The weight-average molecular weight of P1, determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene standards as calibration standards, was tested to be 14850, with a polydispersity index (PDI) of 1.10. The low PDI might be due to the special topological structure. As shown in Figure 3, P1 was very stable, with a 5% weight loss temperature (T_d) as high as 283 °C. Also, its glass transition temperatures (T_q) were tested by using differential scanning calorimetry (DSC). To our surprise, as shown in Figure 3 and Table 1, its T_{q} value was found to be 150 °C, which is 28 °C higher than that of PS5 (122°C), which should be ascribed to the presence of iso-

lation chromophore moieties. The high T_g value could lead to the high stability of the ordered dipole alignment of NLO chromophores, and is surely a benefit to their potential practical applications.

The H-shaped NLO polymer **P1** was easily soluble in common organic solvents, such as $CHCI_3$, THF, DMF, and DMSO. Thus, its UV-visible absorption spectra in different solvents could be tested easily. As shown in Figure 4, an interest-



Figure 2. ¹³C NMR spectra of polymer P1 and its corresponding monomer M1 in [D]chloroform.



Figure 3. TGA and DSC (insert) thermograms of P1, measured in nitrogen at a heating rate of 10° C min⁻¹.



Figure 4. UV/Vis spectra of P1 in different solvents (0.02 mg mL⁻¹).

ing phenomenon was observed. As **P1** consisted of two types of chromophores, and the maximum absorption wavelengths (λ_{max}) for their $\pi - \pi^*$ transition was not the same, there was a broad absorption in its UV-visible spectrum, which actually possessed two absorptions: one was from the nitro-based chromophore and the other from the sulfonyl-based one. Generally, the NLO chromophore displayed different absorption peaks in different solvents, because of solvatochromic effects,

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and the different environment around the NLO chromophore could lead to different solvatochromic effects. In P1, there were two triazole units and two nitro-based chromophore moieties surrounding the sulfonylbased chromophore, whereas a fluorine, a triazole, and two different chromophores surrounded the nitro-based chromophore, which could result in different solvatochromic effects in P1. Thus, the peak shapes of P1 were also a little different in different solvents, especially in CH_2CI_2 and $CHCI_3$. However, λ_{max}

of **P1** in films was 471 nm, which was blueshifted 20 nm relative to that of **PS5** (491 nm), thereby resulting in the better transparency.

The NLO effect should be the most important parameter for NLO materials, and it could be characterized by the SHG coefficient, the d_{33} value. The test procedure was similar to that reported previously,^[7-9] and from the experimental data, its d_{33} value was found to be 134 pm V⁻¹, at the 1064 nm fundamental wavelength. This was an exciting result, since the d_{33} values of all the H-shaped NLO polymers only containing one type of chromophore were not higher than 94.7 pmV^{-1} . This is a large improvement, and indicates that the isolation chromophore could also work in these H-shaped NLO polymers, thereby confirming our previous idea about isolation chromophores: when two types of chromophore are arranged orderly with a regular AB structure, the chromophore with the lower $\mu\beta$ value can act as an isolation group to decrease the strong electronic interactions between the chromophore moieties with higher $\mu\beta$ values, and would not decrease the effective concentration of the NLO chromophore moieties anymore. Usually, when the effective concentration of the NLO chromophore moieties was higher than 30%, accompanied by an increase in the concentration of the NLO chromophore moieties in polymers, the intermolecular dipole-dipole interactions among chromophore moieties would become stronger and stronger, which would lead to a much decreased NLO coefficient (Figure S2).^[11] However, from PS5 to P1, owing to the introduction of an isolation chromophore, the concentration of NLO chromophores improved from 0.467 to 0.621, and the NLO coefficient also improved from 93.4 to 134 pm V⁻¹, which indicated that the intermolecular dipole-dipole interactions could be overcome in P1 to some degree, thanks to the presence of the isolation chromophore moieties. Also, the special H-shaped topological structure could contribute greatly to such high d_{33} value. As shown in Chart S3, we have synthesized another normal NLO polymer PS10, also containing two types of chromophore moieties with a regular AB structure, in our previous study. Its d_{33} value was 116.8 pm V⁻¹, which is also higher than PS7 with only one type of chromophore, but lower than that of P1, thereby confirming the advantage of the H shape again. As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of these polymers should be smaller, which was calculated by using the approximate twolevel model. Here, owing to the outstanding optical transparency of P1, which has been already discussed before, the $d_{33(\infty)}$ value of P1 was still excellent, up to 23.3 pmV⁻¹, more than twice that of **PS5** (11.0 pmV^{-1}), thereby confirming the advantages of the isolation chromophore once again. However, although the d_{33} value of 134 pm V⁻¹ was not a high value, in comparison with those of the dendric systems also containing an isolation chromophore,^[7-9] this result still showed that the concept of an isolation chromophore could be applied also to this H-type chromophore, and not only limited to the normal rod one. Thus, if a dendritic NLO system could be constructed by using this H-type chromophore containing an isolation chromophore, an even higher NLO coefficient should be achieved. This research is in progress in our laboratory.

To further study the alignment behavior of the chromophore moieties in **P1**, the order parameter (Φ) of the polymer was also measured from the change of the UV-visible spectra of their films before and after poling. As shown in Figure 5, after



Figure 5. Absorption spectra of the film of P1 before and after poling.

poling, the absorbance of P1 decreased and the Φ value of P1 was calculated as 0.24, which indicated that the chromophore moieties in P1 were noncentrosymmetric. In addition, the shape of the absorption peak after poling was different from that before poling, owing to the different behavior of the two types of chromophore moieties. As we know, λ_{max} of the nitrobased chromophore should be redshifted relative to that of the sulfonyl-based one. Thus, the blueshifted λ_{max} after poling indicated that the Φ value of the nitro-based chromophore of P1 should be higher than that of the sulfonyl-based one. This could also confirm our idea: the chromophore moieties with a higher $\mu\beta$ value act as the main chromophore, which contribute most to the macroscopic NLO effect; while those with a lower $\mu\beta$ value are used as the isolation chromophore, an isolation group between two main chromophore moieties to decrease the dipole-dipole interactions among the main chromophore moieties and could be also beneficial to the macroscopic NLO effect.

In the depoling experiment, the real-time decays of their SHG signals were monitored as the poled film of **P1** was heated from room temperature to 180° C in air at a rate of 4° C min⁻¹. As shown in Figure 6, the NLO stability of **P1** was much better than that of **PS5**, and its onset temperature for decay of the d_{33} value was up to 150° C, which is 50° C higher than that of **PS5**, as a result of its higher T_{α} value.



Figure 6. Decay curves of the SHG coefficients of polymers as a function of temperature.

Conclusion

In summary, an H-shaped NLO polymer was prepared successfully by means of Suzuki coupling copolymerization. To further research whether the advantage of an isolation chromophore could work in this H-shaped topological structure, a sulfonylbased chromophore was introduced into P1 to act as the isolation chromophore. In comparison with PS5, which has the highest d_{33} value and the best NLO stability in the H-shaped NLO polymers reported previously, almost all the performance, including the NLO coefficient, optical transparency, and NLO stability, of P1 was improved to a large degree. Its d_{33} value was up to 134 pm V^{-1} , which is about 40 pm V^{-1} higher than that of **PS5**; its λ_{max} in films was 471 nm, which is 20 nm blueshifted relative to that of PS5; its onset temperature for the decay of its d_{33} value was up to 150 °C, which is 50 °C higher than that of PS5. Thus, owing to such good comprehensive performance and its simple synthetic route, P1 might be a good candidate for practical applications.

Experimental Section

Materials and instrumentation

THF was dried over and distilled from a K–Na alloy under an atmosphere of dry nitrogen. The boronic ester $M2^{[12]}$ and chromophores C1^[5h,8a] and C2^[9c] have been prepared already in our previous study. All other reagents were used as received. ¹H and ¹³C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The FTIR spectra were recorded on a PerkineElmer-2 spectrometer in the region of 4000–400 cm⁻¹. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. GPC was used to deter-

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mine 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. THF was used as an eluent and the flow rate was 1.0 mL min⁻¹. 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. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10°C min⁻¹ in nitrogen at a flow rate of 50 cm³ min⁻¹ for thermogravimetric analysis (TGA). The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of monomer M1

Chromophore C1 (505.3 mg, 1.10 mmol), chromophore C2 (213.7 mg, 0.50 mmol), CuSO₄·5 H₂O (10 mol %), NaHCO₃ (20 mol %), and ascorbic acid (20 mol%) were dissolved in THF (5 mL)/H₂O (1 mL) under nitrogen in a Schlenk flask. The mixture was stirred at room temperature for 3 h, then extracted with chloroform, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using ethyl acetate/chloroform (1:1) as eluent to afford red solid M1 (580.1 mg, 86.2%). ¹³C NMR (75 MHz, CDCl₃, 298 K): δ = 7.30, 12.48, 21.72, 28.29, 44.80, 47.04, 50.54, 51.00, 68.47, 109.12, 110.76, 111.53, 114.25, 116.43, 117.77, 119.20, 122.21, 122.76, 125.79, 129.03, 131.61, 138.24, 139.90, 144.42, 146.72, 147.01, 147.93, 149.19, 151.39, 155.00 ppm; IR (KBr): $\tilde{\nu} = 1514$, 1338 (-NO₂), 1139 cm⁻¹ (–SO₂–); ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 1.23 (brs, 6H; -CH₃), 1.31 (brs, 2H; -CH₃), 2.25 (brs, 4H; -CH₂-), 2.96 (brs, 4H; --CH2C--), 3.15 (brs, 2H; --SCH2--), 3.43 (brs, 8H; --NCH2--), 3.71 (brs, 4H; -NCH₂-), 4.14 (brs, 4H; -NCH₂-), 4.37 (brs, 4H; -OCH₂-), 6.5-6.7 (m, 4H; ArH), 6.96 (s, 2H; ArH), 7.21 (s, 2H; -C=CH), 7.7-8.0 ppm (m, 14H; ArH); MALDI-TOF MS: m/z calcd for C₆₀H₆₇Br₂N₁₇O₈S: [*M*+Na]⁺: 1369.1; found: 1367.9; elemental analysis calcd (%) for $C_{60}H_{67}Br_2N_{17}O_8S$: C 53.53, H 5.03, N 17.69; found: C 52.99, H 5.23, N 17.75.

Synthesis of H-shaped NLO polymer P1

A mixture of monomer M1 (67.3 mg, 0.05 mmol), monomer M2 (29.3 mg, 0.05 mmol), potassium carbonate (138 mg, 1.0 mmol), THF (3 mL)/water (1 mL), and a catalytic amount of [Pd(PPh₃)₄] was carefully degassed and charged with argon. Then the reaction mixture was stirred at 60°C for 4 days. After polymerization, a lot of methanol was poured into the mixture, and then filtered. The obtained solid was dissolved in THF, and the insoluble solid was removed by filtration. After the removal of all the solvent, the residue was further purified by several precipitations from THF into acetone, and the obtained solid was then washed with a lot of acetone and dried under vacuum at 40°C to a constant weight. The resultant polymer P1 was obtained as a red powder (67.2 mg, 88.5%). $M_r = 14850$; $M_w/M_n = 1.10$ (GPC, polystyrene calibration); ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta = 0.4-1.4$ (–CH₃ and –CH₂–), 1.6-2.0 (-CH2-), 2.0-2.3 (-CH2-), 2.8-3.2 (-CH2C- and -SCH2-), 3.2-3.9 (-NCH₂-), 4.0-4.4 (-NCH₂- and -OCH₂-), 6.4-6.9 (ArH), 7.0-8.0 ppm (-C=CH and ArH); ¹³C NMR (75 MHz, CDCl₃, 298 K): $\delta = 1.2, 7.6, 13.0, 14.1, 22.1, 22.8, 24.1, 24.4, 28.7, 30.2, 31.8, 40.1,$ 45.1, 47.4, 50.9, 51.4, 55.1, 68.9, 109.5, 111.5, 111.9, 112.4, 116.9, 117.5, 118.5, 119.2, 122.6, 123.1, 126.2, 129.5, 129.7, 139.1, 140.1, 141.7, 144.9, 147.0, 147.4, 147.8, 150.7, 151.1, 155.3, 156.1 ppm; IR (KBr): $\tilde{\nu} = 1514$, 1338 (–NO₂), 1139 cm⁻¹ (–SO₂–).

Preparation of polymer thin films

Polymer **P1** was dissolved in THF (concentration $\approx 4 \text{ wt \%}$), and the solution was filtered through a syringe filter. Polymer films were spin-coated onto indium-tin oxide (ITO)-coated glass substrates, which were cleaned by DMF, 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.

NLO measurement of poled films

The second-order optical nonlinearity of **P1** was determined by an in situ 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, 175 °C; voltage, 7.8 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.

Acknowledgements

We are grateful to the National Science Foundation of China (no. 21034006) for financial support.

Keywords: chromophores · cross-coupling · nonlinear optics · polymers · synthesis design

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Received: July 7, 2013 Published online on September 12, 2013