

## Design and synthesis of a novel polymer with a large macroscopic second harmonic generation coefficient based on quantum chemical calculations

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### ABSTRACT

The macroscopic second harmonic generation (SHG) coefficient ( $d_{33}$ ) of polymer depends on several factors, including the first hyperpolarizability ( $\beta$ ) and dipole moment ( $\mu$ ) of chromophore, the combination of different donors (D) and acceptors (A), chromophore–chromophore electrostatic interactions, asymmetric structure of chromophore, the effect of main-chain on NLO properties of polymer, hydrogen bond and so on, therefore, several parameters should be comprehensively considered to design desired materials with high  $d_{33}$  value. Based on quantum chemical calculations, a polyimide containing isophorone derivatives as chromophores were designed and synthesized. Experimental results show that the polyimide exhibits a large macroscopic nonlinear optical coefficient ( $d_{33} = 63.9 \text{ pm V}^{-1}$ ), thermal stability ( $T_g = 171 \text{ }^\circ\text{C}$ ;  $T_d = 308 \text{ }^\circ\text{C}$ ) and good optical transparency ( $\lambda_{\text{max}} = 418 \text{ nm}$ ). This paper could suggest a potentially practical way for designing effective NLO polymers.

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### 1. Introduction

Design and synthesis of effective polymeric nonlinear optical (NLO) materials are very important due to their potential applications in the fields of telecommunication, optical data storage and optical information processing. Polymeric NLO materials have exhibited several advantages superior to conventional inorganics, such as large nonlinear optical coefficient, ultrafast response, wide response wave band, high optical damage threshold, and easy combination and modification [1–6]. Generally, in order to acquire an effective polymer, chromophores with high first hyperpolarizabilities ( $\beta$ ) and large dipole moments should be designed and synthesized firstly [7–9]. Then, the designed chromophores are employed to incorporate into main-chain [10–15] or side-chain [16–21] polymers by covalent linkages. However, an effective chromophore would not simply result in acquiring a polymer with a high  $d_{33}$  value. Because the macroscopic second harmonic generation (SHG) coefficient ( $d_{33}$ ) of a polymer depends on several factors, such as the first hyperpolarizability ( $\beta$ ) and dipole moment ( $\mu$ ) of chromophore [22–24], the combination of different donors

(D) and acceptors (A) [2,25–27], chromophore–chromophore electrostatic interactions [28,29], asymmetry structures of chromophores [22,30–35], the effect of main-chain on NLO properties [3], hydrogen bond [2], etc. These factors should be comprehensively considered to design effective NLO polymers [22–35]. Therefore, the design of desired materials with high  $d_{33}$  value is always a challenging topic [2,4,36,37]. Firstly, chromophore number density (chromophore loading) in a polymer would play an important role [28,29]. Because the electrostatic interactions between chromophores with large  $\mu$  and  $\beta$  values would increase with increasing chromophore loading in polymer. The increase of the electrostatic interactions between chromophores would result in decrease of  $d_{33}$  of polymer. According to Zhang's report [28], the  $d_{33}$  value of the polymer containing effective chromophores with high dipole moments ( $\mu > 7.5D$ ) and high hyperpolarizabilities increases with increasing chromophore number density (chromophore loading) at low chromophore loading. Then the maximal  $d_{33}$  value of the polymer would be experimentally observed when the chromophore loading were suitable. At last, the  $d_{33}$  value of the polymer decreases with increasing chromophore number density at high chromophore loading. Therefore, chromophore loading would play an important role in designing desired polymer containing high dipole moments–high hyperpolarizabilities chromophores. Secondly, structure of chromophore plays a critical role [30–35]. If chromophores tended to be arranged to form a noncentrosymmetric structure in poled polymer films, the polymers would exhibit a large  $d_{33}$ . Thirdly, the combination of donors (D) and acceptors (A) should be optimized to avoid the formation

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of hydrogen bonds between the chromophores [2,25–27,38]. Lastly, optical transparency and thermal stability of polymer should also be taken into account. Based on quantum chemical calculations, a side-chain functional polymer was designed and synthesized. A fluoro-containing polyimide was employed as a main-chain of functional polymer due to its high thermal stability, small optical losses and good solubility in organic solvent [39]. 3-Dicyanomethylene-5,5-dimethyl-1-[2-(4-(2-bromoethyl)hydroxyphenyl)-ethenyl]-cyclohexene was employed as a chromophore owing to the asymmetrical structure, a suitable  $\mu$  and  $\beta$ , the suitable combination of donors (D) and acceptors (A), etc. Experimental results show that the polyimide containing isophorone derivatives exhibits a large second harmonic coefficient ( $d_{33} = 63.9 \text{ pm V}^{-1}$ ), high glass transition temperature ( $T_g = 171 \text{ }^\circ\text{C}$ ) and decomposition temperature ( $T_d = 308 \text{ }^\circ\text{C}$ , 5% mass lost), and little absorption in working wavelength ( $\lambda_{\text{max}} = 418 \text{ nm}$ ). In order to compare the  $d_{33}$  of designed polymer with that of popular polymer, a polyimide with azo chromophores containing nitro substituents was synthesized and its NLO property was also determined.

## 2. Experimental

### 2.1. Materials and instrumentations

Melting points were determined on a Yanaco micro-melting point apparatus (uncorrected).  $^1\text{H}$  NMR were recorded on Bruker AM 300 (Germany), and  $\delta$  were given in ppm (relative to TMS) and coupling constants ( $J$ ) in Hz. Mass spectra were recorded by a GCMS-QP2010 gas chromatogram mass spectrometer under GC/MS mode. UV–vis spectra were recorded on a Lambda 25 Perkin-Elmer spectrophotometer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer, in which samples were embedded in KBr thin films. Precoated silica gel plates (GF254) were used for analytical TLC. The gel permeation chromatographic (GPC) analysis was carried out with a WATERS SEC-244 instrument with tetrahydrofuran as the eluent (flow rate:  $1 \text{ mL min}^{-1}$ , at  $25.5 \text{ }^\circ\text{C}$ ) and polystyrene as the standard. Thermal analyses were performed by using the SETARAM DSC-131 and TGA-DTA system from TA instruments under nitrogen atmosphere.

All the solvents were purified by standard procedures. All other chemicals were purchased from Sigma or Aldrich. Compound 4-(4-nitrophenylazo)phenol (**2a**) was synthesized according to literatures [3,6]. All NLO chromophores were obtained as yellow or red powders. The analytical data of the chromophores ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, MS) are in accord with the assigned structures, respectively. Their structures are shown in Fig. 1.

### 2.2. Synthesis of polymers

Polymer **PI** was synthesized according to literature [40]. The fluoro-containing polyimides (**1P–2P**) were synthesized by an etherification of NLO chromophores

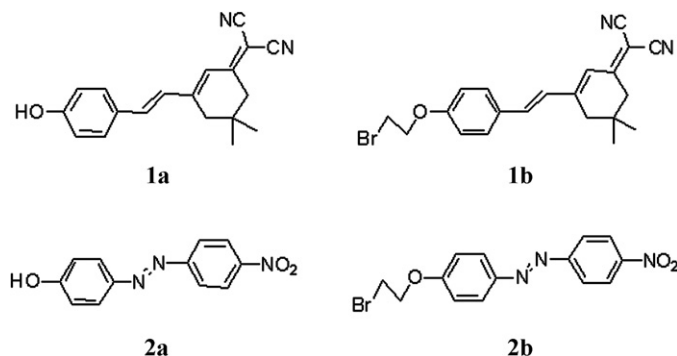


Fig. 1. The chromophores **1a–2a** and **1b–2b**.

**1b–2b** [6,41] with **PI** in alkaline solution (yield: 86.0–86.7%). Reactive routes are shown in Fig. 2.

#### 2.2.1. Synthesis of polyimide **PI**

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (0.888 g, 2 mmol) and hexafluoro-isopropylidenebis(3-hydroxy-4-aminobenzene) (0.732 g, 2 mmol) were added to *N,N*-dimethylformamide (10 mL) at  $0 \text{ }^\circ\text{C}$ . The mixture was then stirred for 30 h under  $\text{N}_2$  atmosphere at room temperature. Dry xylene was added to the flask, and the poly(amic acid) was thermally cyclized at  $160 \text{ }^\circ\text{C}$  for 3 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. After the reaction solution was cooled down to room temperature. The resulting solution was added dropwise into an agitated solution of methanol and 2 N HCl (50 mL,  $v/v = 1:1$ ) to obtain the brown polyimide. The polymer was redissolved in THF (10 mL) and further purified by reprecipitating into a solution of methanol and 2N HCl (50 mL,  $v/v = 1:1$ ) from its THF solution for acquiring a deposition. The mixture was filtrated and the solid was dried for 48 h under vacuum at  $80 \text{ }^\circ\text{C}$  to give **PI**. Yield: 1.36 g, 87.9%.

#### 2.2.2. Synthesis of polyimide **1P**

Potassium carbonate (0.2 g), **PI** (77 mg) and **1b** (87 mg, 0.22 mmol) were added to *N,N*-dimethylformamide (5 mL), and the mixture was stirred for 48 h under  $\text{N}_2$  atmosphere at  $100 \text{ }^\circ\text{C}$ . After the reaction solution was cooled down to room temperature, the mixture was filtrated and solid was washed by DMF ( $3 \times 2 \text{ mL}$ ). The solution was dried to obtain an orange solid. The orange solid was dissolved in tetrahydrofuran (4 mL) to give a solution. The solution was further added into another solution of methanol and water (10 mL,  $v/v = 1:1$ ) to acquire a deposition. The mixture was filtrated and the solid was dried to give an orange powder polyimide **1P**. Yield: 122 mg, 86.7%,  $T_g = 171 \text{ }^\circ\text{C}$ .

$^1\text{H}$  NMR (DMSO):  $\delta = 7.94$  (s, 2 H, ArH), 7.85–6.20 (m, 24 H, C=C–H and ArH), 3.91 (s, 4 H,  $\text{CH}_2$ ), 3.67 (s, 4 H,  $\text{CH}_2$ ), 2.88 (s, 4 H,  $\text{CH}_2$ ), 2.72 (s, 4 H,  $\text{CH}_2$ ), 1.18 (s, 12 H,  $\text{CH}_3$ ). Anal. Calcd. for  $\text{C}_{76}\text{H}_{54}\text{F}_{12}\text{N}_6\text{O}_8$  (1406.4): C, 64.86; H, 3.87; N, 5.97. Found:

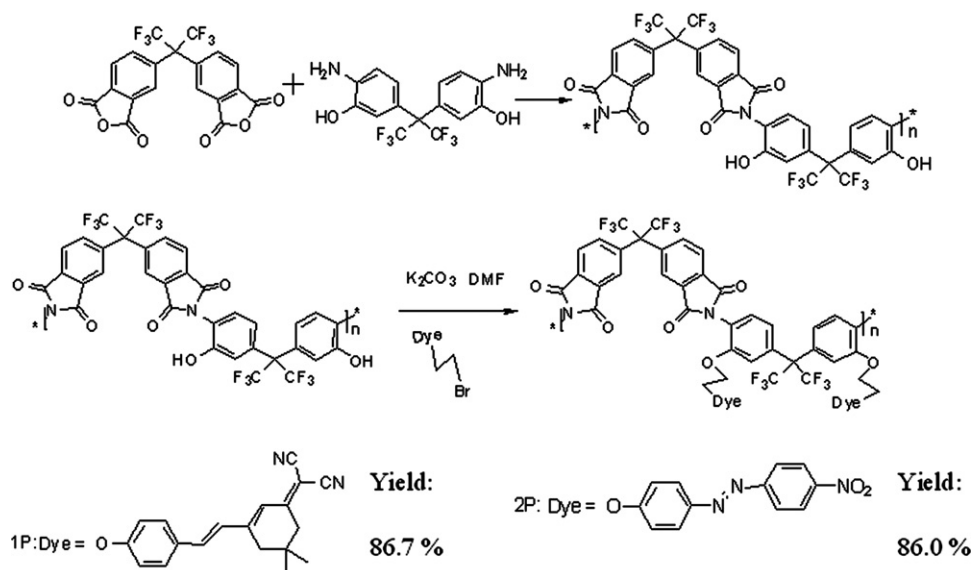


Fig. 2. Synthetic routes of polyimides **1P–2P**.

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