Significant Effect of Bromo Substituents on Nonlinear Optical Properties of Polymer and Chromophores

Chao-Zhi Zhang,[*,†,‡] **Chuang-Yu Wang,**[§] **Chan Im,**[†] **Guo-Yuan Lu,**[‡,||] **and Chang-Shun Wang**[§,⊥]

Department of Chemistry, Konkuk University, Seoul 143-701, Korea, Department of Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China, and Department of Physics, Shanghai Jiaotong University, Shanghai 200240, People's Republic of China

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Four chromophores containing bromo substituents, a ployimide with bromo-containing chromophores, four reference functional polyimides, and fourteen reference chromophores were synthesized for studying effect of bromo substituents on nonlinear optical (NLO) properties of materials and chromophores. The results of hyper-Rayleigh scattering and UV−vis spectra show that static first molecular hyperpolarizability (β_0) values of bromo-containing chromophores are 1.24−5.75 times as β_0 of the corresponding chloro-containing chromophores (Hammett constants σ of chloro and bromo groups are same) without causing a visible shift of the absorption band to longer wavelength. UV−vis spectra and the results of Maker Fringe method show that the polyimide with chromophores containing bromo substituents exhibits a good optical transparency and a much higher macroscopic nonlinear optical coefficient (d_{33} = 20.1 pm/V) than the reference polyimides containing nitro (d_{33} = 9.6 pm/V) and cyano (d_{33} = 8.9 pm/V) groups in spite of nitro and cyano groups being strong electron acceptors. d_{33} of polyimide with chloro-containing chromophores is very small. Therefore, this paper suggests an effective strategy for improving the NLO properties of polymeric materials and chromophores without reducing optical transparency in designing NLO polymers and chromophores. On the basis of quantum chemistry calculations, the reasons of effect of bromo substituents on NLO properties of chromophores and materials were discussed.

1. Introduction

Organic and polymeric nonlinear optical (NLO) materials have continuously drawn great interest due to their 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] Generally, desired NLO materials should exhibit a high NLO property, good optical transparency, and thermal stability.[2] Designs and syntheses of effective chromophores are very important for acquiring desired NLO materials. Two-state model is usually employed to estimate first hyperpolarizability (β) of chromophore in designing effective organic chromophores. The equation shows as following:[3,4]

$$\beta^{\text{two−state}} = \frac{3\mu_{\text{eg}}^2 \Delta\mu_{\text{eg}}}{E_{\text{eg}}^2} \times \underbrace{\frac{\omega_{\text{eg}}^2}{(1 - 4\omega^2/\omega_{\text{eg}}^2)(\omega_{\text{eg}}^2 - \omega^2)}}_{\text{Dispersion factor}}$$

$$\underbrace{\phantom{\frac{3\mu_{\text{eg}}^2 \Delta\mu_{\text{eg}}}{E_{\text{eg}}^2}}}_{\text{Static factor}}$$

(1)

where μ_{eg} is the transition dipole moment between the ground state |g> and the charge-transfer excited state |e>, $\Delta\mu_{\text{eg}}$ is the difference in dipole moment, and E_{eg} is the transition energy.

Many methods, such as employing special conjugated bridge[5] or using different types of conjugation bridge combinations[6] and optimizing the combination of different donors (D) and

acceptors (A),[1d,7] have been adopted to develop effective chromophores for further acquiring desired NLO materials. Especially, employing effective substituents to improve NLO properties still plays an important role in designing effective chromophores.[2] For traditional chromophore with D−π−A structure, β of a chromophore usually increases with increasing strength of the donor and/or acceptor.[1d,2] However, the increase of β-value is always accompanied by a bathochromic shift due to stronger donor and acceptor ability.[1d] Therefore, it would be very interesting that designed and synthesized organic chromophores and functional polymers containing weak D and A have high NLO properties. Recently, we have designed and synthesized chromophores containing bromo-substituted groups, which exhibit larger hyperpolarizabilities than corresponding chromophores containing chloro-substituted groups. To comprehensively study effect of bromo substituents on NLO properties of the chromophores, chromophores containing nitro, cyano, trifluoromethyl, and chloro substituents have also been synthesized.[8] The β-values of chromophores were determined by hyper-Rayleigh scattering (HRS).[9] The results of HRS and UV−vis spectra show that static first hyperpolarizability (β_0) values of bromo-containing chromophores are 1.24−5.75 times as β_0 of the corresponding chloro-containing chromophores (Hammett constants σ of chluroro and bromo groups are the same[7c]), without causing a visible shift of the absorption band to longer wavelength.

Generally, chromophores with large β-values are usually employed to acquire effective NLO polymeric materials. However, effective chromophores would not simply result in acquiring a polymer with a large macroscopic second harmonic generation (SHG) coefficient (d_{33}), because the d_{33} value of polymer depends on β of chromophore and arrangement of

* To whom correspondence should be addressed. E-mail: chzhzhang@sohu.com. Fax: +82-2-34365382.
† Konkuk University.
‡ Nanjing University.
§ Shanghai Jiaotong University.
|| E-mail: lugyuan@nju.edu.cn. Fax: +86-025-83317761.
⊥ E-mail: cswang@sjtu.edu.cn.

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chromophores in poled polymeric film.[10] In general, if chromophores tend to be arranged in a parallel fashion in poled polymeric films, the polymers would exhibit a large d_{33}. However, the electrostatic interactions between chromophores with large dipole moment (μ) at ground state would result in two adjacent chromophores tending to be arranged in an antiparallel fashion in poled polymer thin film.[10,11] Therefore, a chromophore with a small μ at ground state and a large β would be a desired chromophore for acquiring a polymer with a large d_{33}. According to two-state model, chromophore with large μ_{eg} and $\Delta\mu_{eg}$ values would exhibit a large β-values. Therefore, a chromophore that has a small μ-value at ground state and a large μ-value at excited state would be a desired one for being grafted on polymeric main-chain to synthesize functional polymers with large d_{33}. Because bromo substituted group is a weak electron-withdrawing group, the chromophore containing bromo group would exhibit a small dipole moment at ground state. Moreover, the chromophore containing bromo substituent exhibits a larger hyperpolarizability than a corresponding chromophore containing chloro substituent. Therefore, chromophores containing bromo substituents could be a desired one for acquiring effective materials. In this paper, a fluoro-containing polyimide was employed as a main chain of functional polyimide due to its high thermal stability, small optical losses, and good solubility in organic solvent.[12] Bromo-containing chromophores were grafted on the polyimide main chain to synthesize NLO polyimide materials. To comprehensively study the effect of bromo substituents on NLO properties of materials, other chromophores were also grafted on polyimide main-chain to synthesize functional polyimides. The functional polyimides were further made into polyimide thin films by a spinning coater. Their second harmonic coefficients (SHG, d_{33}) were determined via Maker Fringe method.[13] UV–vis spectra and the results of Maker Fringe method show that the polyimide with chromophores containing bromo substituents exhibits a good optical transparency and a much larger macroscopic nonlinear optical coefficient ($d_{33} = 20.1$ pm/V) than reference polyimides containing nitro ($d_{33} = 9.6$ pm/V) and cyano ($d_{33} = 8.9$ pm/V) groups in spite of nitro and cyano groups being strong electron acceptors. d_{33} of polyimide with chloro-containing chromophores is very small. Therefore, this paper suggests an effective strategy for improving the NLO properties of polymeric materials and chromophores without reducing optical transparency in designing NLO polymers and chromophores. On the basis of density functional theory (DFT)[14] calculations of β values of chromophores at the B3LYP/6-31G(d)[15] level, the reasons of the effect of bromo substituent on optical properties of NLO materials were discussed.

2. Experimental Methods

Melting points were determined on a Yanaco micromelting point apparatus (uncorrected). ^{1}H NMR were recorded on Bruker AM 300 (Germany), and δ 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–visible 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 mL/min, at 25.5 °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 solvents were purified by standard procedures. All other chemicals were purchased from Sigma or Aldrich.

Five azo chromophores (**1a**−**5a**), eight H-typed azo chromophores (**1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b**, and **4c**), five Λ-typed azo chromophores (**1d**−**5d**) and five chromophores (**1e**−**5e**) were synthesized according to the literature.[7c,8] All NLO chromophores were obtained as yellow or red powders. The analytical data of the chromophores (^{1}H NMR, ^{13}C NMR, IR, and MS) are in accord with the assigned structures, respectively. Their structures are shown as Scheme 1.

Polyimide **PI** was synthesized is similar to that in the literature.[16] The fluoro-containing polyimides (**1P** -**5P**) were synthesized by an etherification of NLO chromophores **1e** - **5e**[17] with **PI** in alkaline solution (Yield: 86.0% − 89.0%). Reactive routes are shown as Scheme 2.

3. Results and Discussion

3.1. First Hyperpolarizabilities (β) of Chromophores. Determination of first hyperpolarizabilities (β) of chromophores was performed using HRS method. The HRS experimental setup was similar to that in the literature.[9] An external reference method (EFM) was utilized in these HRS experiments by choosing *para*-nitroaniline (*p*NA) as standard.[9]

Figure 1 shows profile of HRS intensity versus molar concentration of **1a** and **2a**. Because the HRS signals have a good linear relationship with the concentrations of the solute, any concentration dependent effect, such as aggregation and hydrogen bonds, could be ignored. An effect of solvent on local fields could also be ignored, because the structures of two chromophores are similar, and the refractive index change of the solutions of two chromophores is neglectable.

A popular two-level model could be used to estimate their static first hyperpolarizabilities (β_0) which reflect the intrinsic polarizations of the molecules at zero frequency. The two-level model could be expressed as eq 2[18]

$$\beta(\omega) = \frac{\lambda^4}{[(\lambda^2 - \lambda_{gn}^2)(\lambda^2 - 4\lambda_{gn}^2)]}\beta_0 \qquad (2)$$
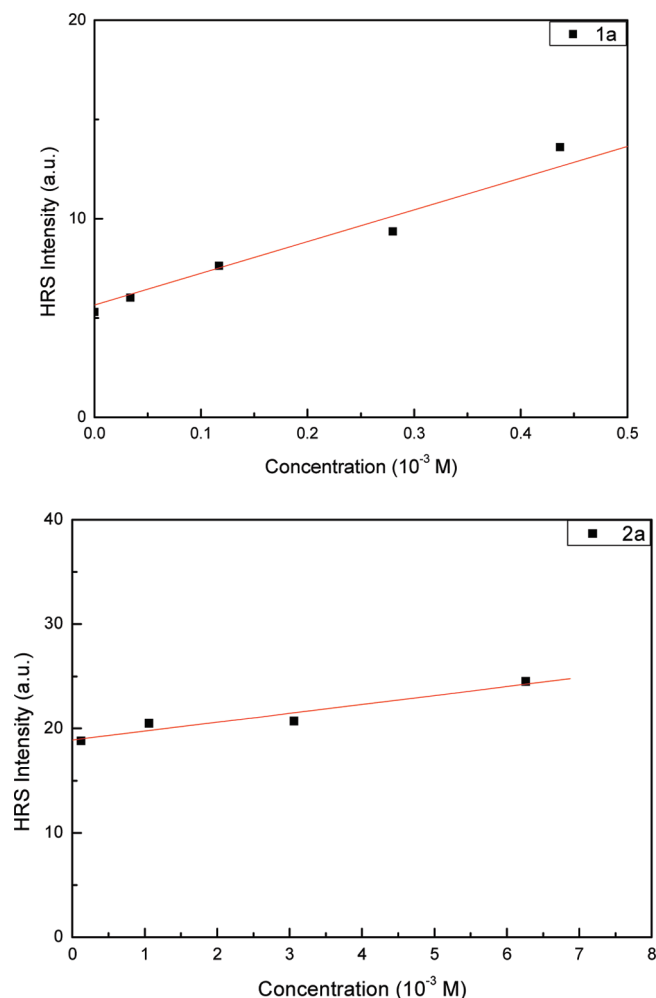
where λ_{gn} is the wavelength corresponding to the transition between the ground and the first excited state, which can be estimated as the peak wavelength λ_{max} in the UV–visible absorption spectra; λ is the wavelength of incident light. β and β_0 values of chromophores are shown in Table 1.

Generally, β_0 of chromophores would increase with increasing the strength of electron acceptors and electron donors, that is, the difference between the Hammett constants (σ)[19] of the electron withdrawing and electron pushing groups in the D−π−A units. Hammett constants of para-substituted groups in benzene rings, bromo, chloro, trifluoromethyl, cyano, nitro, and hydroxyl are 0.23, 0.23, 0.54, 0.66, 0.78, and −0.37, respectively. According to the reports of Verbiest et al.,[20] chromophores containing bromo groups and the corresponding reference chromophores containing chloro groups could exhibit similar β_0 values due to Hammett constants σ of chloro and bromo groups being same. Table 1 shows that in a whole, the β_0 of chromophores containing bromo substituents are close to that of chromophores containing trifluoromethyl or cyano substituents and smaller than that of chromophores containing nitro substituents. However, both β and β_0 values of bromo-containing chromophores **1a**−**1e** are larger than that of the corresponding chloro-containing chromophores **2a**−**2e**. The β_0 of **1a**−**1e** are 1.24−5.75 times as that of the corresponding

SCHEME 1: Five Azo Chromophores Containing Bromo Substituents (1a−1e) and Their Reference Chromophores (2a−2e, 3a−3e, 4a−4e, 5a, 5d, and 5e)
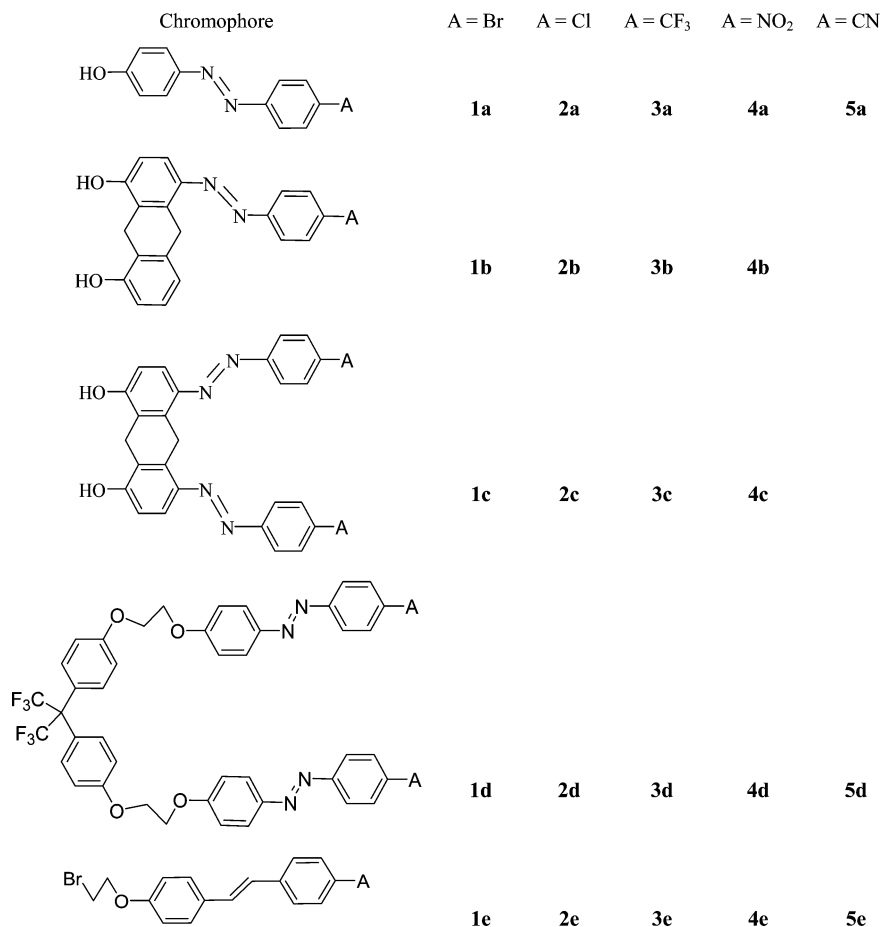
SCHEME 2: Synthetic Routes of Fluoro-Containing Polyimides
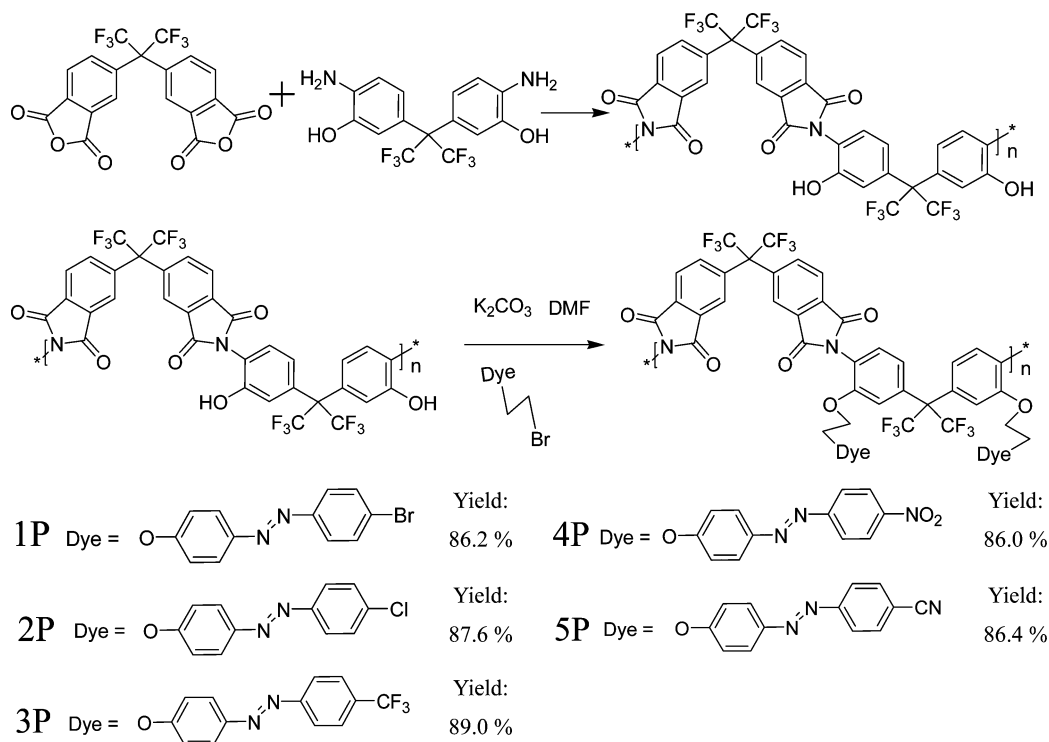
reference chromophores **2a−2e**. Therefore, bromo-substituted group could exhibit a special property to improve the first hyperpolarizability.

On the basis of theoretical calculation, the reasons of effect of bromo substituents on NLO properties of chromophores and materials were discussed. All geometries of chromophores **1f−5f**

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Figure 1. HRS intensity versus molar concentration of **1a** and **2a** in THF. Solid line is linear fitting of the experimental data.

TABLE 1: Melt Points, Static First Hyperpolarizabilities (β_0) and λ_{max} of Chromophore in Tetrahydrofuran

no.	$\lambda_{max}{}^a$ (nm)	red shift[b] (nm)	β^c (10^{-30} esu)	$\beta_0{}^d$ (10^{-30} esu)	enhancement[e] (%)	melt point (°C)
1a	357		84	42	(75)	155
2a	355	−2	50	24	−43	160
3a	357	0	108	52	24	127
4a	381	24	70	28	−33	210
5a	372	15				203
1b	375		162	72	(24)	>300
2b	370	−5	127	58	−19	>300
3b	370	−5	207	92	28	>300
4b	402	27	208	77	7	>300
1c	365		211	97	(47)	>300
2c	366	1	142	66	−32	>300
3c	367	2	252	117	21	>300
4c	398	33	277	105	8	>300
1d	353		49	25	(32)	184
2d	352	−1	39	19	−24	210
3d	353	0	47	23	−8	105
4d	372	19	102	46	84	178
5d	364	11	62	30	20	142
1e	352		46	23	(475)	136
2e	351	−1	8	4	−83	138
3e	351	−1	70	35	52	98
4e	361	9	85	41	78	156
5e	372	20				161
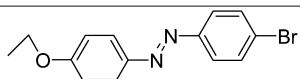
^{a} The maximal absorption wavelength (λ_{max}) data in THF. ^{b} Red shift of λ_{max} was variation of λ_{max} in THF between reference chromophores and the corresponding chromophores containing bromo groups. The values of red shfit were the differences between λ_{max} of reference chromophores and λ_{max} of the corresponding chromophores containing bromo groups. ^{c} Data of hyperploarizabilities (β) were determined with concentration 10^{-4} to 10^{-3} mol L^{-1} of compounds at a wavelength of 1064 nm in tetrahydrofuran medium by hyper-Rayleigh scatter (HRS). ^{d} Static first hyperpolariabilities (β_0). ^{e} The value of static first hyperpolariabilities (β_0) enhancement were calculated according to following methods. (β_0 of of reference chromophores − β_0 of the corresponding chromophores containing bromo groups)/β_0 of the corresponding chromophores containing bromo groups × 100%. Values in brackets were the value of static first hyperpolariabilities (β_0) enhancement of chromophores containing bromo groups comparing the corresponding reference chromophores containing chloro groups according to following methods. (β_0 of chromophores containing bromo groups − β_0 of the corresponding reference chromophores containing chloro groups)/β_0 of the corresponding reference chromophores containing chloro groups × 100%.
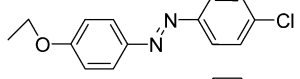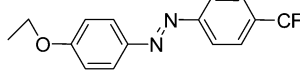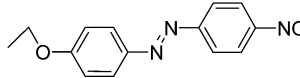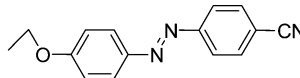
were optimized by the density functional theory (DFT)[14] calculations using Gaussian03 software at the B3LYP/6-31G(d) level.[15] Then, time-dependent density functional theory (TD-DFT)[3] was used to calculate their first hyperpolarizabilities. The first hyperpolarizabilities are estimated by a two-state model (eq 1).

Table 2 shows clearly that the dipole moments of **1f** at ground state is smaller than that of **3f**, **4f**, and **5f**. However, both transition dipole moment (μ_{eg}) from ground to excited state and the difference in dipole moments ($\Delta\mu_{eg}$) of **1f** are the largest among five chromophores (**1f**–**5f**). According to eq 1, increase of the μ_{eg} and $\Delta\mu_{eg}$ values would result in increase of β_0. It implies that bromo substituent would improve NLO of chromophore. μ_{eg} And $\Delta\mu_{eg}$ values of **5f** are similar as that of **1f**, however, E_{eg} of **5f** (3.29 ev) is lower than that of **1f** (3.40 ev). According to eq 1, decrease of the E_{eg} value would result in increase of β_0, therefore, the β_0 value of **5f** is the largest. Similarly, E_{eg} of **4f** (3.13 ev) is the lowest, therefore, **4f** also exhibit a large β_0 in spite of μ_{eg} and $\Delta\mu_{eg}$ values of **4f** being lower than that of **1f**.

3.2. Maximal UV−vis Absorption Wavelength (λ_{max}) of the Chromophores. UV−vis absorption spectra of all chromophores in THF were determined by using a lambda 25 Perkin-Elmer spectrophotometer and the maximal absorption wavelength (λ_{max}) data are summarized in Table 1. Table 1 shows that maximal UV−vis absorption wavelength (λ_{max}) of the chromophores **1a**−**1e** is close to that of corresponding chro-

mophores **2a**−**2e** or **3a**−**3e** and shorter than that of corresponding chromophores **4a**−**4e** (9−33 nm) or **5a**−**5e** (11−20 nm).

Figure 2 shows clearly that the chromophores containing bromo, chloro, and trifluoromethyl groups (**1a**, **2a**, and **3a**) have nearly same maximal absorption wavelengths (λ_{max}) and are shorter than that of corresponding chromophores containing nitro groups (**4a**) or cyano groups (**5a**), because **4a** and **5a** are stronger electron-withdrawing substituted groups than **1a**, **2a**, and **3a**. For a chromophore containing a D−π−A unit, a chromophore with a strong electron-withdrawing substituted group would exhibit a longer UV−vis absorption wavelength than a chromophore with a weak electron-withdrawing substituted group.[1d] Therefore, chromophore with a bromo substituent at a benzene ring would exhibit a shorter UV−vis maximal absorption wavelength than that of chromophores containing stronger electronic acceptors. Therefore, bromo-containing chromophores could have a good optical transparency. In a word, bromo substituent could improve β and β_0 values of chromophore and

TABLE 2: Static First Hyperpolarizabilities of Supposed Chromophores 1f−5f Being Given from Quantum Chemistry Calculations

No.	Structure	β_0 $(10^{-30}$ esu)	μ_{eg} (D)	$\Delta\mu_{eg}$ (D)	μ_g (D)	μ_e (D)	E_{eg} (ev)
1f		77.0	9.17	9.08	4.21	13.29	3.41
2f		67.1	8.78	8.61	4.17	12.74	3.40
3f		60.2	8.48	8.36	5.39	13.70	3.42
4f		78.3	8.85	8.84	8.42	17.26	3.13
5f		81.9	9.14	9.06	7.79	16.82	3.29
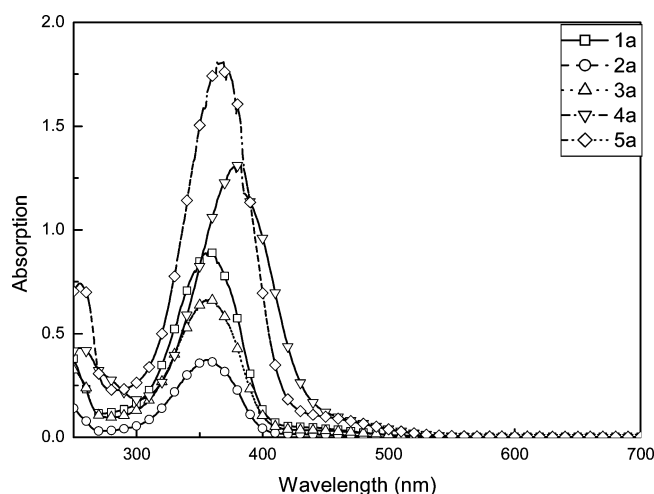
Figure 2. UV−vis spectra of chromophores (**1a−5a**).

the bromo-containing chromophore would have a good optical transparency.

3.3. The Macroscopic Second Harmonic Coefficients (d_{33}) of the Polyimides (1P−5P). The macroscopic second harmonic coefficients (d_{33}) of the polyimides were determined by Marker Fringe method. The experimental setup was similar to that in the literature.[13] The ployimides were dissolved in THF to acquire a mass percent 12% solution. Then the polyimides were coated on a clear glass by a spinning coater to give polymer thin films. The thicknesses of thin films were measured by the conventional *m*-line method to be from 1.3 to 2.4 μm, respectively. The films was poled by applying a 4 kV DC voltage at the approaching their glass transition temperatures between the grid electrode and the conductive glass. Then the second-order nonlinear coefficient d_{33} can be evaluated utilizing eqs 3 and 4[13]

$$d_{33} = d^{(2)}_{zzz(\text{quartz})}[R]^{1/2}\frac{l_c^{\text{quartz}}}{l}F \qquad (3)$$

where R is the relatively intensity of SHG, l_c^{quartz} is the relatively length of quartz, l is the thickness of the thin film. The F of thin film can be obtained as the following equation[13]

TABLE 3: Macroscopic Nonlinear Optical Coefficients (d_{33}) and the Maximal Absorption Wavelengths (λ_{max}) in THF of Polyimides (1P−5P)

polyimide	λ_{max} (nm, in THF)	ε^a	red shift (nm)	d_{33} (pm/V)	enhancement $(\%)^b$
1P	355	28095		20.1	
2P	352	30896	−3	weak	
3P	354	54822	−1	weak	
4P	375	35993	20	9.6	−52
5P	365	28420	10	8.9	−56

^{a} The absorption coefficient of molar polymeric units at the maximal absorption wavelengths (ëmax) in THF. ^{b} The value of macroscopic nonlinear optical coefficients (d_{33}) enhancement were calculated according to following methods. (d_{33} of of reference polyimide − d_{33} of the chromophores containing bromo groups)/d_{33} of the chromophores containing bromo groups × 100%.

TABLE 4: Atomic Charges and Hammett Constants of Substituted Groups in Chromophores 1f−5f

no.	$\delta_A{}^a$	e_O (AU)^b	e_A (AU)^c
1f	0.23	−0.513	−0.127
2f	0.23	−0.530	−0.011
3f	0.54	−0.513	−0.271^d
4f	0.66	−0.510	−0.397^e
5f	0.78	−0.512	−0.478^f

^{a} Hammett constants of electron-withdrawing groups in benzene rings. ^{b} Atomic charges (unit: atomic unit) of O atoms in ethoxy substituted groups. ^{c} Atomic charges (unit: atomic unit) of electron-withdrawing groups in benzene rings. ^{d} Atomic charges (unit: atomic unit) of F atom in CF$_3$ group. ^{e} Atomic charges (unit: atomic unit) of O atom in NO$_2$ group. ^{f} Atomic charges (unit: atomic unit) of N atom in CN group.

$$F^2 \approx \left(0.28\frac{l_c^2}{l^2}\right)\left[1 - \cos\frac{\pi l}{l_c}\right] \qquad (4)$$

The l_c is the coherent length of polymer film. When $l < l_c$, function F is approximated to be a constant ($F = 1.2$).

The values of d_{33} are shown as Table 3.

Table 3 shows that macroscopic nonlinear optical coefficient (d_{33}) of **1P** ($d_{33} = 20.1$ pm/V) is more than two times as that of **4P** ($d_{33} = 9.6$ pm/V) and **5P** ($d_{33} = 8.9$ pm/V) in spite of electron-withdrawing strengths of nitro and cyano groups being much stronger than that of bromo group. d_{33} of **2P** containing
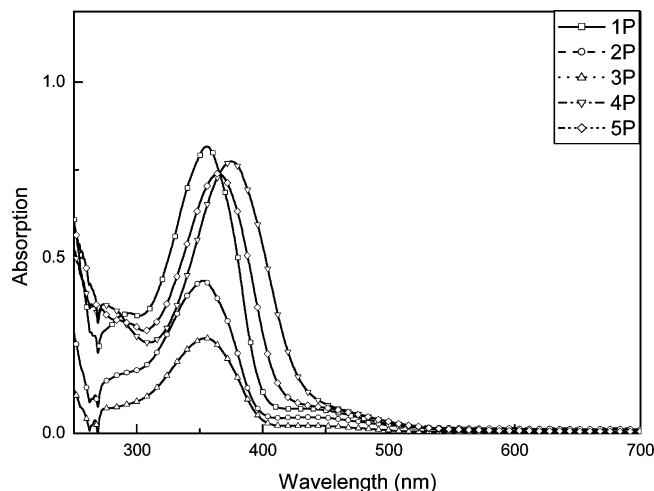
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Figure 3. UV−vis spectra of polyimides (**1P**−**5P**).

Figure 4. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) of **1P** and **2P**.

TABLE 5: Molecular Weights of Five Polyimides (1P−5P) and Their Thermal Properties

polyimide	$\bar{M}_w{}^a$ (10^4g/mol)	$\bar{M}_n{}^b$ (10^4g/mol)	D^c	Tg^d (°C)	Td^e (°C)
1P	2.22	1.01	2.2	201	248
2P	2.21	0.97	2.3	197	272
3P	0.26	0.15	1.7	184	198
4P	0.87	0.49	1.8	171	236
5P	0.29	0.16	1.8	163	195

[a] Weight-average molecular weight (M_w). [b] Number-average molecular weight (M_n). [c] Molecular weight distribution (D). [d] Glass transition temperature (Tg). [e] Decomposition temperature (Td).

chloro substituents, which the Hammett constants is same as that of bromo substituent, is very small. d_{33} of **3P** containing trifluoromethyl substituents, which the Hammett constants is bigger than that of bromo substituent, is also very small.

The dipole−dipole interactions tend to form centrosymmetric structures so that dipoles may oppose one another or at the least bring the dipoles out of the required net alignment required for efficient SHG.[10] Minimized dipole−dipole interaction often leads to required noncentrosymmetric structure. Therefore, the bromo group can greatly increase the probability of forming a noncentrosymmetric structure, while strong electron withdrawing substituents, such as NO_2, CN, and so forth, easily lead to centrosymmetric structures. Another reason would be hydrogen bond (Table 4).

Table 4 shows clearly that hydrogen bonds are easily formed between two chromophores containing CF_3, NO_2, and CN groups. The O atom in **2f** has the largest electron charges so that hydrogen bonds are easily formed between two chromophores **2f** compared with **1f**. The hydrogen bonds in poled polymeric films of **3p**, **4p**, and **5p** would result in the dipoles out of the required net alignment required for efficient SHG and further result in decreasing macroscopic nonlinear optical coefficient (d_{33}). However, the chromophores containing bromo groups would tend to form a side-to-side arrangement structure in poled thin film due to hydrogen bonds not being easily formed between two chromphores **1f**. The bromo-containing polyimide would therefore exhibit a higher macroscopic nonlinear optical coefficient (d_{33} = 20.1 pm/V) than other reference polyimides.

3.4. Optical Transparency of Polyimides. The UV−vis spectra of the polyimides of **1 P**−**5 P** were measured and the maximal absorption wavelengths (λ_{max}) were 355, 352, 354, 375, and 365 nm. Figure 3 shows that λ_{max} of **1P** is shorter than that of **4P** and **5p**, and close to that of **2p** and **3p**. It suggests that the polyimide with chromophores containing bromo substituents could have good optical transparency.

3.5. Thermal Properties of the Polyimides. Thermal properties of the polyimides were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC).

Figure 4 shows that polyimides **1P** and **2P** have high decomposition temperature Td (5% mass lost). The Td of **1P** (248 °C) is close to that of **2P** (272 °C). It indicates that they have higher thermal stability. The glass transition temperature Tg and decomposition temperature Td of **1P**, **2P**, **3P**, **4P**, and **5P** are 201, 197, 184, 171, and 163 °C and about 248, 272, 198, 236, and 195 °C (Table 5), respectively. From the DSC of
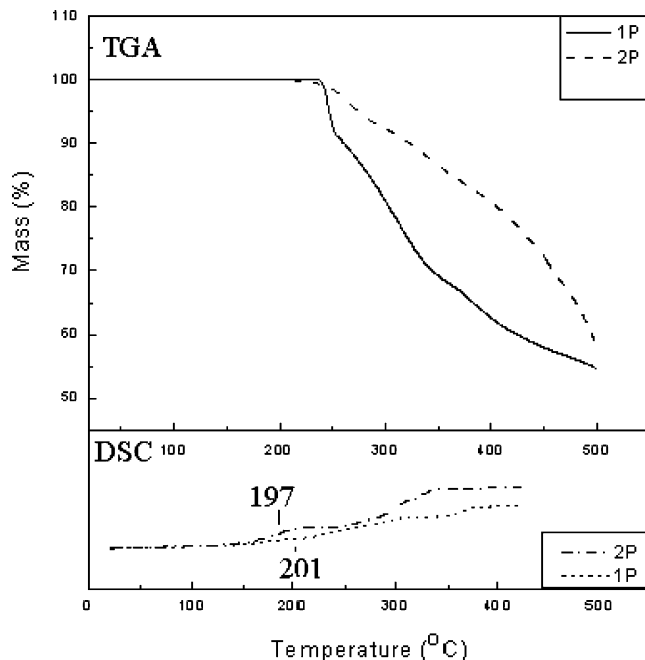
1P and **2P**, Tg of **1P** is slightly higher than that of **2P**. It suggests that a polymer containing bromo-substituted groups could exhibit a higher Tg than a corresponding polymer containing chloro-substituted groups.

3.6. The Molecular Weights of the Polyimides. The molecular weights of the polyimides were estimated by gel permeation chromatography (GPC). **1P**, **2P**, **3P**, **4P**, and **5P** have a weight-average molecular weight $\bar{M}_w$ of 2.22, 2.21, 0.26, 0.87, and 0.29 (× 10^4 g/mol) as well as a number-average molecular weight $\bar{M}_n$ of 1.01, 0.97, 0.15, 0.49, and 0.16 (× 10^4g/mol) with a polydispersity index of 2.2, 2.3, 1.7, 1.8, and 1.8 based on polystyrene standards (Table 5), respectively. **1P**, **2P**, **3P**, **4P**, and **5P** are soluble in organic solvents such as THF, DMF, and DMSO because they have lower average molecular weight and the flexible CF_3 groups are incorporated in the polyimides. Therefore, their poling films can be easily prepared for the measurement of macroscopic nonlinear optical coefficient.

4. Conclusion

In this paper, the effect of bromo substituent on NLO properties of polyimide and chromophores is investigated. The results of HRS and Marker Fringe method show that the bromo substituents used as acceptors in chromophores would remarkably improve first hyperpolarizabilities of chromophores and the macroscopic nonlinear optical coefficients of poled thin films. UV−vis spectra show that chromophores and polyimide

containing bromo substituents have a good optical transparency. Therefore, this paper suggests an effective strategy for improving the NLO properties of polyimide materials and chromophores without reducing optical transparency in designing NLO polymers and chromophores. On the basis of quantum chemistry calculations, the reasons of effect of bromo substituents on NLO properties of chromophores and materials were discussed. It could give an alternative way of design of effective NLO materials and chromophores with large NLO properties and a good optical transparency.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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