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Synthesis and properties of an alkoxysilane dye containing three electronic donor groups for nonlinear optical applications

Yuanjing Cui, Lujian Chen, Guodong Qian*, Minquan Wang

Department of Materials Science and Engineering, State Key Lab of Silicon Materials,
Zhejiang University, Hangzhou 310027, PR China

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Abstract

In order to obtain an efficient hybrid inorganic–organic nonlinear optical (NLO) materials, an azo-dye containing three electronic donor groups 2,5-dimethyl-4-(4′-nitrophenylazo)phenol (DMNPAP) was synthesized and reacted with 3-isocyanatopropyl triethoxysilane (ICTES) to give an alkoxysilane dye (ICTES–DMNPAP). Molecular structural characterizations for DMNPAP and ICTES–DMNPAP were investigated by elemental analysis, ^{1}H NMR, FTIR, UV–visible spectra and differential scanning calorimetry (DSC). The alkoxysilane dye could be hydrolyzed and polymerized in the presence of water, and then transparent hybrid films could be fabricated by spin coating on the indium–tin-oxide (ITO) glass substrates. Compared with the dye 4-nitro-4′-hydroxy-azobenzene (NHA) containing only one hydroxyl as donor group, DMNPAP exhibited larger $\beta_{CT}\mu_g$ value measured by solvatochromic method, and second harmonic generation (SHG) measurement of the hybrid films was in agreement with the result.

Keywords: Alkoxysilane dye; Synthesis; Nonlinear optics; Solvatochromic method; Second harmonic generation; Inorganic–organic hybrid

1. Introduction

Second-order nonlinear optical (NLO) polymeric materials have attracted much attention for their potential applications in the fields of optical information processing, optical sensing, and telecommunications [1–3]. Practically, the long-term orientational stability of NLO properties and the high NLO activities are particularly required for developing NLO devices with polymeric materials. However, noncentrosymmetric chromophore-ordering in NLO polymers is thermodynamically unstable, especially at high temperature, it would normally decay to an equilibrium isotropic state due to thermal motion of polymer chains. Various approaches, including incorporation of the chromophore into the polymer backbone, an interpenetration polymer network method, and a cross-linking method, have been used to suppress the relaxation of NLO molecules in the polymeric matrix [4–8].

In short, fundamental requisites for obtaining an efficient polymeric NLO material are: (1) incorporation of highly polarizable chromophores; (2) presence of covalent bond between chromophore and polymeric matrix to increase concentration to avoid phase separation; (3) have a high glass transition temperature (T_g) to prevent chromophore orientational relaxation [9].

Recently, inorganic–organic hybrid NLO materials through sol–gel process have received significant attention for their inherent properties of the silica matrix [10–13]. Traditionally, sol–gel precursors are designed to bear an NLO chromophore in one arm of

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* Corresponding author. Tel.: +86 571 87952334; fax: +86 571 87951234.
E-mail address: gdqian@zju.edu.cn (G. Qian).

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silicon through a flexible spacer. The silicon alkoxides can be hydrolyzed and polymerized in the presence of water and a catalytic amount of acid, and form an amorphous silica network. The resultant structure is similar to that of a side-chain NLO polymer. The rigid silica network provides an inert environment for the organic molecule and theoretically prevents relaxation of the noncentrosymmetry NLO chromophore alignment induced by an electric field. Therefore, the incorporation of an inorganic sol–gel material with an organic NLO molecule is a reasonable approach to enhance long-term stability.

The optimization of molecular hyperpolarizability (β) is also indispensable and actually it represents an important research topic in the engineering design of highly NLO materials. Generally, the NLO molecular feature is a conjugated π-electron moiety, with electron donor and acceptor groups located in a noncentrosymmetric fashion. Theoretical and experimental researchers pointed out that the β value increases with increasing donor and acceptor strength and with increasing separation so long as there is strong electronic coupling through the conjugated bridge [9].

In this work, an NLO azo-dye 2,5-dimethyl-4-(4′-nitrophenylazo)phenol (DMNPAP) containing methyl and hydroxyl as electronic donor groups was synthesized and then reacted with 3-isocyanatopropyl triethoxysilane (ICTES) to give an alkoxysilane dye (ICTES–DMNPAP) through a nucleophilic addition reaction. After hydrolysis and condensation process of the precursor in the presence of water and acid as catalyst, hybrid films with high optical quality were obtained. We reported the details of the synthesis and spectroscopic characterization of the dye and alkoxysilane dye. The composite magnitude ($\beta_{CT}\mu_g$) of the dye was experimentally derived by solvatochromic method and the NLO properties of the films were also studied by second harmonic generation (SHG) measurement.

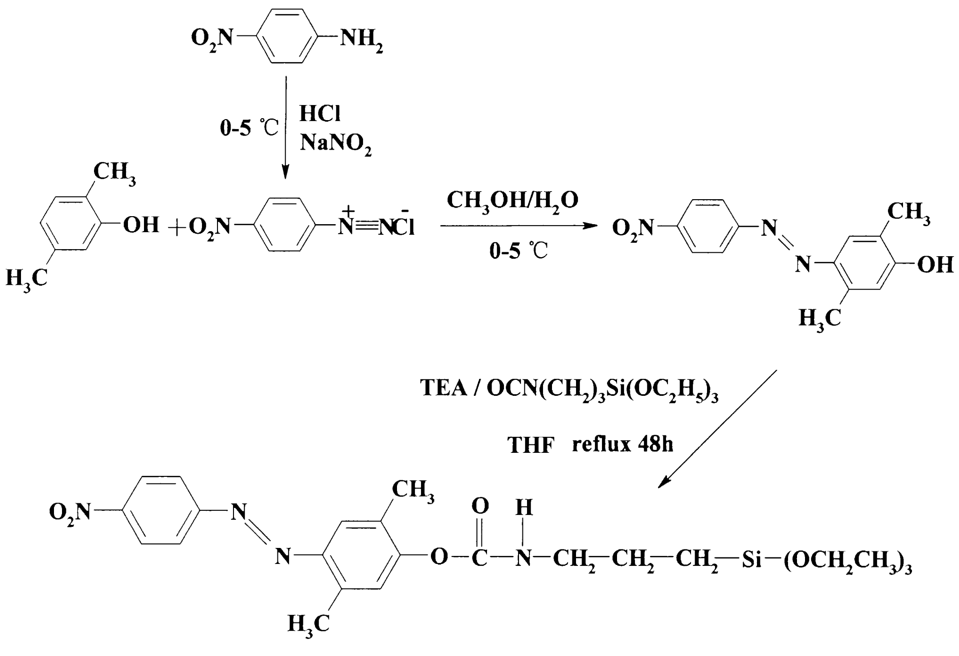
2. Experimental

2.1. Materials

Tetrahydrofuran (THF, purity > 99%) was purified by refluxing and distilling from calcium hydride. 3-Isocyanatopropyl triethoxysilane (ICTES, purity > 95%) was obtained from Tokyo Chemical Industry Co. All other reagents, of analytical-grade quality, were commercial products and used as received.

2.2. Synthesis of NLO dye 2,5-dimethyl-4-(4′-nitrophenylazo)phenol (DMNPAP)

The diazonium coupling reaction was employed to prepare DMNPAP and its reaction scheme is outlined in Scheme 1. A solution of sodium nitrite (1.38 g, 20 mmol) in water was added dropwise, with stirring, to a solution of *p*-nitroaniline (2.76 g, 20 mmol) in 20 cm^3 distilled water and 18 cm^3 concentrated HCl in an ice bath. After 15 min stirring, 2,5-dimethyl phenol (2.44 g, 20 mmol) and NaOH (7 g) dissolved in 50 cm^3 methanol/water (2:1) was added with vigorous stirring for half an hour. The precipitate formed was filtered and washed



Scheme 1. Synthesis of DMNPAP and ICTES–DMNPAP.

repeatedly with water to remove any remaining reactants. The product was recrystallized from ethanol/water (1:3) and dried under vacuum at 40 °C for 6 h. Yield: 65%. Anal. Calcd for $C_{14}H_{13}O_3N_3$ (271.3): C, 61.98; H, 4.83; N, 15.49. Found: C, 61.41; H, 4.84; N, 15.10.

2.3. Synthesis of alkoxysilane dye (ICTES–DMNPAP)

To a three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and reflux condenser, (2.71 g, 10 mmol) of DMNPAP, (2.96 g, 12 mmol) of ICTES, 60 cm^3 of THF and 10 drops of triethylamine (TEA) as catalyst were introduced. The mixture was stirred and refluxed for 48 h under nitrogen atmosphere. The solution was poured into dried hexane, the resulting red precipitate was collected by suction filtration, and the product was dried under vacuum at 40 °C for 6 h and stored in a desiccator. Yield: 52%. Anal. Cacld for $C_{24}H_{34}O_7N_4Si$ (518.7): C, 55.58; H, 6.60; N, 10.80. Found: C, 55.34; H, 6.57; N, 10.77.

2.4. Preparation and corona poling of hybrid films bearing DMNPAP or NHA

The alkoxysilane dye ICTES–DMNPAP (1.04 g, 2 mmol) or ICTES–NHA synthesized in previous work [14] (0.98 g, 2 mmol) and tetraethyl silicate (TEOS, 2.08 g, 10 mmol) were mixed in 10 cm^3 THF, and hydrolyzed with acidic water (HCl, pH = 1). The H_2O:Si molar ratio was 4:1. The solution was stirred 3 h and aged at room temperature for 7 days. The films with high optical quality could be obtained by spin coating on the indium–tin-oxide (ITO) glass substrates. For second harmonic generation (SHG) experiment, we poled the films using a corona poling technique for 30 min at 140 °C with a high voltage of 5.5 kV on a needle located 1 cm from the samples through the heating process.

2.5. Second harmonic generation (SHG) measurement

The second-order NLO properties of the films were measured by means of the maker fringe method [15]. SHG signal was monitored at incident angle (θ) of -80° to 80°. The laser source is a Q-switched Nd:YAG pulse laser with a 1064 nm P-polarized fundamental beam (300 mJ maximum energy, 3–5 ns pulse width, and 10 Hz repeating rate). The generated second harmonic wave was passed through colored glass filters and a monochromator to eliminate all traces of the fundamental light and was detected by a photomultiplier. The SHG signal was averaged on a Stanford Research Systems (SRS) model SR-250 gated integrator and boxcar averager module and transferred to a microcomputer through a computer interface module SR-254.

2.6. Characterization

Elemental analysis was carried out on an Eager 300 microelemental analyzer. ^{1}H nuclear magnetic resonance (NMR) measurements were done with a Bruker Avance DMX500 apparatus using tetramethysilane (TMS) as an internal standard and dimethyl sulfoxide-d_6 (DMSO-d_6) as solvents. FTIR spectra were recorded on a Nicolet Avatar 360 in the region of 4000–400 cm^{-1} using KBr pellets. UV–visible absorption spectroscopic study was performed with a Perkin–Elmer Lambda 20 spectrophotometer. Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer DSC-7 with a heating rate of 5 °C/min.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the pathways for the synthesis of alkoxysilane dye as the precursor for the preparation of hybrid inorganic–organic materials. The NLO dye DMNPAP was synthesized by the diazonium coupling reaction of *p*-nitroaniline with 2,5-dimethyl phenol in 65% yield. Through a coupling reaction between the ICTES and DMNPAP, the alkoxysilane dye ICTES–DMNPAP was obtained with 52% yield. The elemental analysis values of the compounds are generally in good agreement with the calculated values for the proposed structures. The synthesized products have good solubility in many common organic solvents, such as THF, DMF, DMSO, ethanol, chloroform, etc. They are insoluble in nonpolar solvents such as hexane, heptane, etc. The melting point of DMNPAP and ICTES–DMNPAP were determined to be 227 °C and 124 °C, respectively, by means of DSC at a heating rate of 5 °C/min, as presented in Fig. 1.

The structures of the dye and alkoxysilane dye were confirmed by FTIR, ^{1}H NMR spectroscopy and UV–visible absorption spectra. Fig. 2 shows FTIR spectra of DMNPAP and ICTES–DMNPAP. Compared with the spectrum of DMNPAP, it is noted for the spectrum of ICTES–DMNPAP that the peaks of the characteristic hydroxyl absorption was at 3201 cm^{-1} disappeared, together with obvious bands at 3296, 1708 and 1537 cm^{-1} due to the carbamate group and the 1078 cm^{-1} due to the Si–O–C_2H_5 group. In addition, the bands of benzene and nitro group do not exhibit much change on going from chromophore to alkoxysilane dye. In Fig. 3, ^{1}H NMR spectra of DMNPAP and ICTES–DMNPAP are shown, in which, the peak assigned to the hydroxyl group of DMNPAP vanished

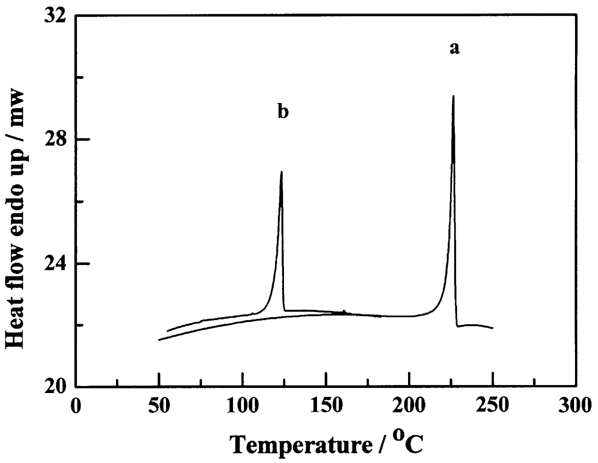


Fig. 1. DSC curves of DMNPAP (a) and ICTES–DMNPAP (b).

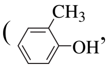
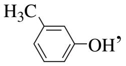
and several new peaks emerged on going from DMNPAP to ICTES–DMNPAP. The line 7.91 ppm is assigned to the carbamate (–N*H*COO, 1H). The lines assigned to the methylene and methyl are as follows: 3.74–3.78 ppm (–O–CH_2–CH_3, 6H), 3.05–3.09 ppm (–NH–CH_2–CH_2, 2H), 1.54–1.57 ppm (–CH_2–CH_2–CH_2, 2H), 0.58–0.62 ppm (–CH_2–CH_2–Si, 2H), 1.15–1.17 ppm (–O–CH_2–CH_3, 9H), 2.17 ppm (, 3H) and 2.67 ppm (, 3H). These assignments clearly support the proposed structures.

Fig. 4 compares the UV–visible spectra of the DMNPAP and ICTES–DMNPAP in ethanol. The absorption maxima for the π–π* electronic transitions of the dye and alkoxysilane dye were at 403 nm and 360 nm, respectively. This means that the introduction of the NLO chromophore into the silicon oxide causes a 43 nm blue shift in its intrinsic absorption. The phenomena may be due to a decrease of electron-release behavior caused by the structure change of the donor. In summary, these analytical results clearly show the formation of alkoxysilane dye by the incorporation of NLO chromophore with the silicon alkoxide after the coupling reaction.

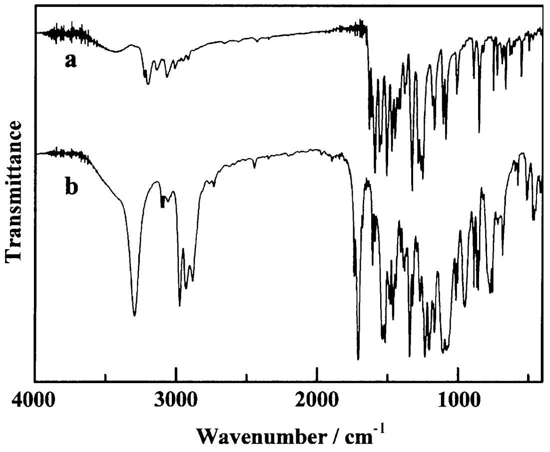


Fig. 2. FTIR spectra of DMNPAP (a) and ICTES–DMNPAP (b).

3.2. Nonlinear optical properties

Second-order NLO properties of the dyes were measured by solvatochromic method, which is based on the solvent dependence of the UV–visible absorption spectrum of a molecule. As previously described in literature [16,17], the values of $\beta_{\mathrm{CT}}\mu_{\mathrm{g}}$ can be found:

$$\beta_{\mathrm{CT}}\mu_g = 4.612 \times 10^{-5} \times \frac{f(\lambda) \times \varepsilon \times \Delta\nu_{1/2} \times \Delta\nu \times a^3}{\Delta f(D)}$$

$$f(\lambda) = \frac{\lambda^3 \lambda_0^4}{(\lambda_0^2 - 4\lambda^2)(\lambda_0^2 - \lambda^2)}$$

$$f(D) = \frac{2(D-1)}{2D+1}$$

where λ is the maximum absorption wavelength of molecule in exited state, and here, it is assumed to be the maximum absorption wavelength of molecule in dipolar solvent; ε, $\Delta\nu_{1/2}$, $\Delta\nu$ and λ_0 are maximum of absorption coefficient in dipolar solvent, the difference of the width of peaks at the middle, shift of the maximum absorption in different solvents and wavelength of base frequency, respectively. CGS unit system is adopted, the unit of ε is $\mathrm{mol^{-1}\,L\,cm^{-1}}$ and unit of D is Debye.

The experimental values of DMNPAP and NHA are listed in Table 1. It can be found that the $\beta_{\mathrm{CT}}\mu_{\mathrm{g}}$ value of DMNPAP is 340.6×10^{-30} esu D, higher than that of NHA. This may be attributed to the strong electron-donating ability of DMNPAP.

To confirm this result, SHG measurement for the films containing NHA and DMNPAP was carried out. Fig. 5 describes the relationship between SHG signal intensity and the incident angle of an exciting beam for a poled film. The SHG signal of the film bearing DMNPAP exhibits a higher second-order NLO coefficient d_{33} than NHA. In the theoretical expression, d_{33} can be written as [18]:

$$d_{33} = \frac{N_{\mathrm{d}} f_\omega f_{2\omega} \beta \mu_{\mathrm{g}} E_{\mathrm{p}}}{10KT}$$

where N_{d} is the number density of noncentrosymmetric NLO molecules, β is the hyperpolarizability of the NLO molecules, f_ω and $f_{2\omega}$ are Lorentz–Lorenz field factor, μ_{g} is the dipole moment of the chromophore at the ground state, E_{p} is the poling electric field, K is Boltzman's constant, and T is the poling temperature. In this study, N_{d}, f_ω, $f_{2\omega}$, T and E_{p} values are almost

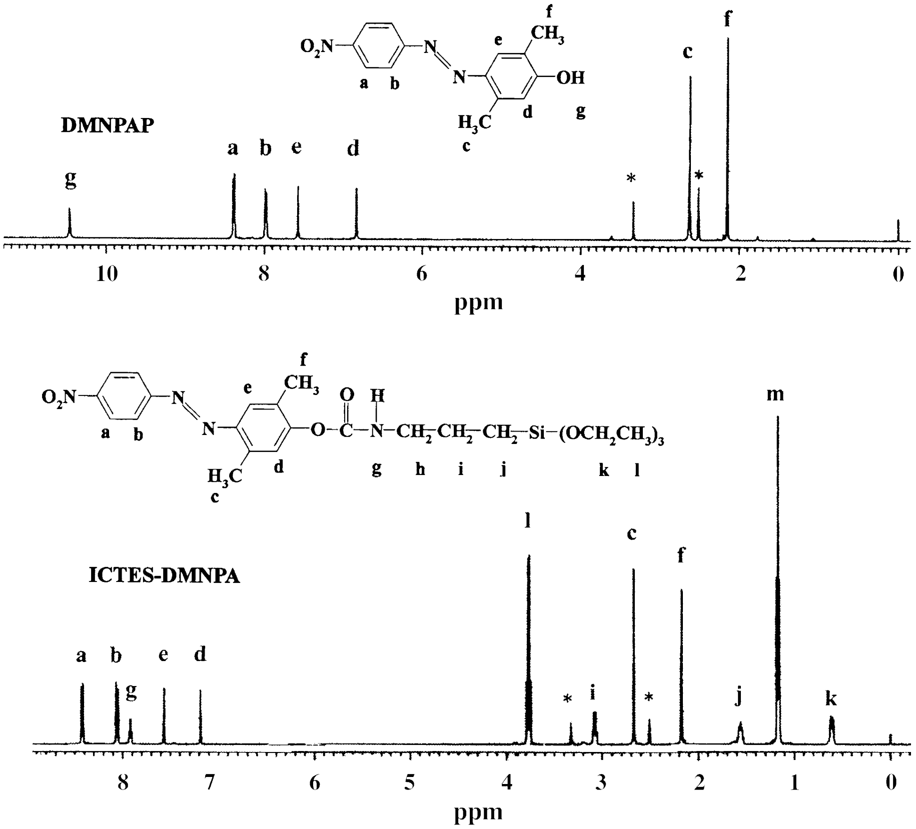


Fig. 3. ^{1}H NMR spectra (500 MHz) of DMNPAP and ICTES–DMNPAP in DMSO-d_6 (the signal marked with * is caused by the solvents) and the assignment of peaks.

identical, so the d_{33} value is only relative to the $\beta_{CT}\mu_g$ parameter. Therefore, such a difference between the NHA-contained film and DMNPAP-contained film in the magnitude of the SHG signal is attributed to the difference in the microscopic optical nonlinearity of the chromophore involved. It means DMNPAP has a higher $\beta_{CT}\mu_g$ value than NHA, which is in good agreement with the calculated value in the solvatochromic method. This result can be explained by considering the molecular structure. There are two methyl and one hydroxyl as electronic donor group in DMNPAP, whose electronic donor strength is higher than that of the dye NHA containing only one hydroxyl as donor. This molecular structure allows a strong charge-transfer interaction between donor and acceptor groups and strongly influences the optical nonlinearity.

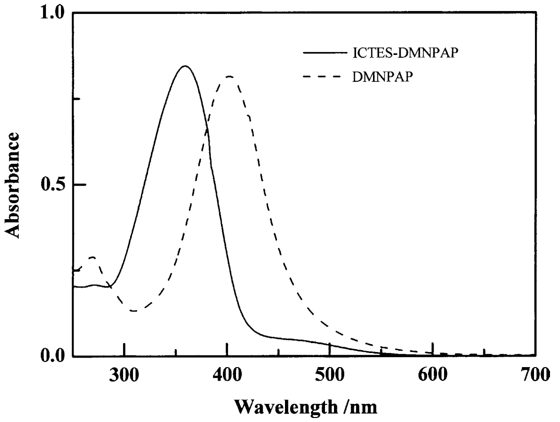


Fig. 4. UV–visible absorption spectra of DMNPAP and ICTES–DMNPAP in ethanol.

4. Conclusions

A silicon alkoxide containing second-order NLO active choromophore was synthesized by the nucleophilic addition reaction between the dye DMNPAP and 3-isocyanatopropyl triethoxysilane (ICTES). The obtained alkoxysilane dye exhibited good solubility in

Table 1
Experimental optical properties of studied molecules

Chromophore	λ_{max}[a] (nm)	ε (10^4 mol^{-1} L cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	λ_{max}[b] (nm)	$\Delta\nu$ (cm^{-1})	$\beta_{CT}\mu_g$ (10^{-30} esu D)
NHA	387	2.35	5261	381	407	141.9
DMNPAP	407	2.61	5380	396	683	340.6

[a] Measured in DMF.
[b] Measured in CHCl$_3$.

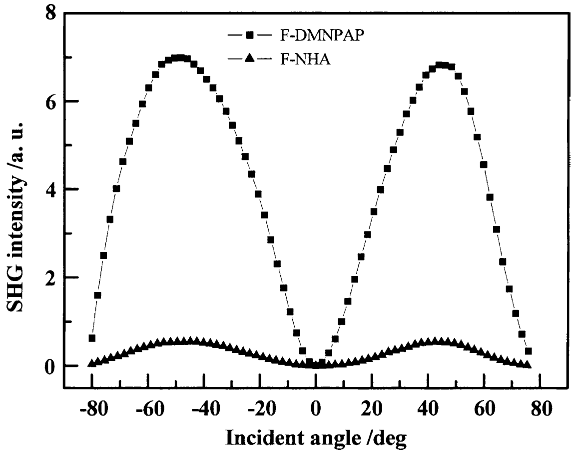


Fig. 5. Relationship between SHG intensity and the incident angle of an exciting beam.

common organic solvents and could provided optical-quality films by spin coating after a hydrolysis and condensation process. The nonlinear optical properties were measured by solvatochromic method and Maker fringe technique. Both of them confirmed that the dye DMNPAP has a larger $\beta_{CT}\mu_g$ value due to its strong electron-donating ability.

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