Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 195–201

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Preparation and nonlinear optical properties of hybrid sol–gel films doped with triphenylamino-substituted chromophores

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

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

Received 21 March 2006; received in revised form 23 June 2006; accepted 16 August 2006

Abstract

Two similar triphenylamino-substituted chromophores with and without hydroxyl end, named TIOH and TI, respectively, were synthesized and incorporated into hybrid organic–inorganic materials derived from 3-glydoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES). These stilbene-type chromophores were characterized by elemental analysis, ^{1}H NMR, FTIR, UV–vis spectra and thermogravimetric analysis (TGA). The hyperpolarizabilities were characterized through solvatochromic method. Both chromophores possess higher thermal stability and competitive hyperpolarizabilities compared with commercially available nonlinear optical dyes such as C.I. Disperse Red 1 (DR1). Second harmonic generation (SHG) has been observed on poled films. The nonlinear coefficient d_{33} of the samples has been thus estimated about 41.2 pm/V for TIOH doped film and about 24.8 pm/V for TI doped film, with absorption correction.

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

1. Introduction

During the past decade, second-order nonlinear optical (NLO) polymers have been extensively studied as promising candidates for future applications in photonic devices, such as frequency doublers, optical storage devices, electro-optic (EO) switches and modulators, because of their large optical nonlinearity, excellent processability, low dielectric constants, and high laser damage thresholds [1]. Organic molecular materials with high NLO responses have diverse and important technical issues. Attention has been essentially focused on dipolar molecules for several decades in the quest for improving NLO properties [2–5]. Recent progresses include the exploration of ring locked isophorone-bridge chromophores (CLD series), which exhibit high β values and the EO device based on them shows commercial promise [3,4]. But the rigid isophorone-bridge also causes crystallization and solubilization problems [5].

Due to the versatility in organic synthesis, the NLO properties can be custom-tailored depending on the desired application. The research in chromophores' design seems to be shifting to the optimization of the hyperpolarizability of one-dimensional charge of a variety of other parameters, i.e. thermal stability, chemical stability and optical loss [6]. To withstand the poling process and other fabrication steps for high performance photonics devices, the NLO chromophores must be sufficiently thermally robust at high temperatures.

To solve the problems mentioned above, two promising methods were proposed. Firstly, replacing dialkylamino donors with diarylamino functionalities in NLO chromophores could impose a dramatically improved thermal stability [5,7,8]. Additionally, a quinoidal bonding pattern may help to prevent unfavorable organization of the chromophores [1]. Secondly, optimized NLO chromophores were incorporated into inorganic–organic hybrid materials through sol–gel process [9]. This class of hybrid materials is very competitive for photonic application due to its peculiar properties, such as

---

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

doi:10.1016/j.dyepig.2006.08.018

high transparency, low optical propagation losses and easy film processing. Such system containing covalent bond between NLO chromophores and the host matrix network represents an interesting alternative to organic polymers. The rigid silica network provides an inert environment to chemically stabilize the organic molecules [9–11] and theoretically prevents the degradation and alignment relaxation of the noncentrosymmetry NLO chromophore induced by an external electric field.

In particular, we wish to determine the relationship between the hydroxyl functionalization of chromophores bearing diarylamino donor and the solubility, film processing and compatibility. For this purpose, we designed and synthesized two stilbene-type chromophores containing triphenylamino group with hydroxyl end and without hydroxyl end, named 2-(3-(4-((4-(hydroxymethyl)phenyl)(phenyl)amino)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (TIOH) and 2-(3-(4-(diphenylamino)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (TI). Then the NLO chromophores were incorporated into the sol–gel films derived from the precursors 3-glydoxypropyltrimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) by means of a similar method described in literature [11]. The chromophores were characterized by elemental analysis, FTIR, ^{1}H NMR, UV–vis spectra, and thermogravimetric analysis (TGA). The composite magnitude ($\beta_{CT}\mu_g$) of the chromophores 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

Triphenylamine was purchased from ACROS Organics. Isophorone was purchased from Lancaster Synthesis, Inc. 4-(Diphenylamino)benzaldehyde, phosphorus oxychloride ($POCl_3$) and malononitrile were obtained from Shanghai TL Chemical CO., Ltd., Shanghai Tingxin Chemical and Reagent Co., and Sinopharm Chemical reagent Co., Ltd., respectively. Reagent grade solvents were purified when necessary.

2.2. Instrumentation

Elemental analysis was carried out on an Eager 300 microelemental analyzer. ^{1}H NMR spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded on a Nicolet Avatar 360 in the region of 4000–400 cm^{-1} using KBr pellets. UV–vis absorption spectroscopic study was performed with a Perkin–Elmer Lambda 20 spectrophotometer. The decomposition temperature was studied using a TA Instruments SDT Q600 at a heating rate of 10 °C/min under nitrogen atmosphere. Melting points were recorded on Buchi 535 which was uncorrected. Refractive index (RI) and thickness of the films were measured with Metricon PC 2010 prism coupler at three different wavelengths (633, 1300 and 1549 nm).

2.3. Second harmonic generation (SHG) measurement

The second-order optical nonlinearity of hybrid films was determined by in situ SHG measurement. A closed temperature controlled oven having optical windows and equipped with tungsten needle electrodes was used. The film, which was kept at 45° to the incident beam, was poled inside the oven. The poling condition was as follows: voltage, 4.5 kV; gap distance, 1 cm. The laser source is a Q-switched Nd:YAG pulse laser with a 1064 nm fundamental beam (500 mJ maximum energy, 3–5 ns pulse width, and 10 Hz repeating rate). The generated second harmonic wave was passed through a monochromator and detected by a photomultiplier. The 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.

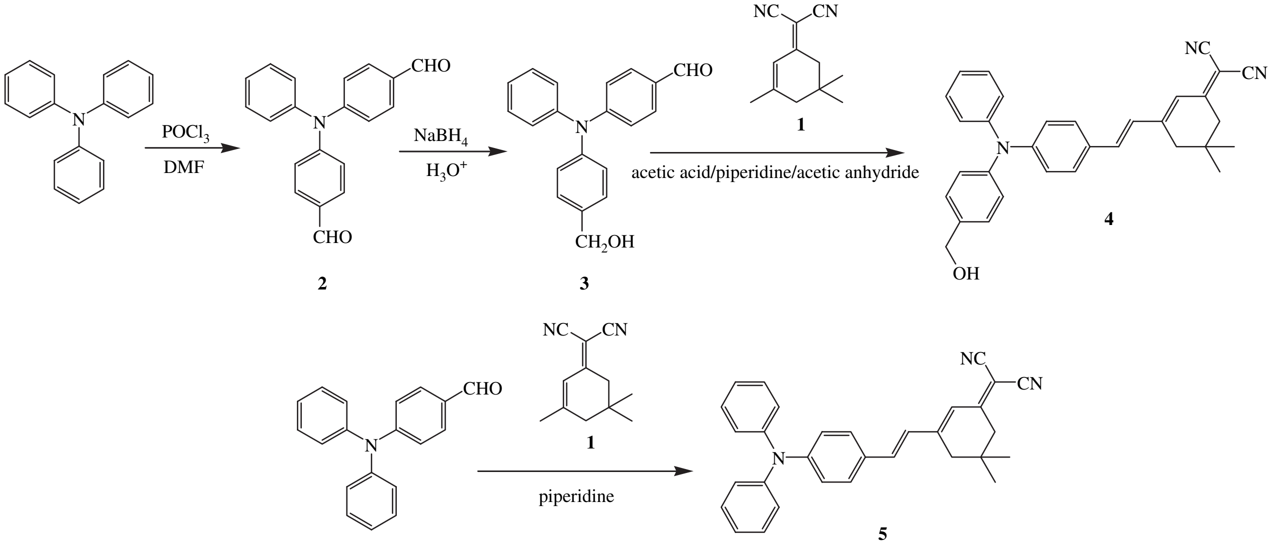
2.4. Synthesis of NLO chromophore TIOH (**4**) and TI (**5**) (Scheme 1)

2.4.1. 2-(3,5,5-Trimethylcyclohex-2-enylidene)malononitrile (**1**) [12]

A solution of isophorone (16.5 ml, 110 mmol), malononitrile (6.6 g, 100 mmol), piperidine (1.8 ml, 18.2 mmol), glacial acetic acid (0.40 ml, 7.0 mmol), and acetic anhydride (0.2 g, 2.0 mmol) in *N*,*N*-dimethylformamide (55 ml) was stirred at room temperature for 6 h and then refluxed at 120 °C for 6 h under nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was poured into water. The crude solid was collected and washed with brine, then the residue was purified by column chromatography (silicagel); eluent, petroleum ether/ethylacetate (12/1, v/v). Brown crystals were obtained. Yield: 27%.^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ 1.04 (s, 6H), δ 2.05 (s, 3H), δ 2.20 (s, 2H), δ 2.54 (s, 2H), δ 6.64 (s, 1H). Anal. calcd for $C_{12}H_{14}N_2$ (186.25): C, 77.38; H, 7.58; N, 15.04. Found: C, 77.26; H, 7.80; N, 15.00.

2.4.2. 4,4′-(Phenylazanediyl)dibenzaldehyde (**2**)

4,4′-(Phenylazanediyl)dibenzaldehyde (**2**) was prepared by a literature method [13]. It is prepared from 10 g (40 mmol) of triphenylamine in the presence of Vilsmeier reagent prepared from 17.5 ml (180 mmol) of $POCl_3$ and 13.8 g (180 mmol) of DMF. The product was recrystallized from toluene/petroleum ether three times to give yellow crystal. Yield: 63%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ 7.17–7.19 (m, 6H), δ 7.25–7.28 (t, 1H), δ 7.38–7.41 (t, 2H), δ 7.76–7.78 (d, 4H), δ 9.89 (s 2H, C*H*O). Anal. calcd for $C_{20}H_{15}NO_2$ (301.34): C, 79.72; H, 5.02; N, 4.65; O, 10.62. Found: C, 79.65; H, 5.07; N, 4.75.



Scheme 1. Synthetic route of TIOH and TI.

2.4.3. 4-((4-(Hydroxymethyl)phenyl)(phenyl)amino) benzaldehyde (**3**) [14]

To a solution of 4 g (13.28 mmol) of 4,4′-(phenylazanediyl)dibenzaldehyde (**1**) in 25 ml of dry THF, 128 mg (0.16 mmol) of sodium borohydride in 8 ml of ethanol was added dropwise under stirring. After stirring for 1.5 h at room temperature, the reaction mixture was neutralised with diluted hydrochloric acid, extracted with dichloromethane, the extract was washed with water and dried. After filtration the solvent was evaporated and the residue purified by column chromatography (silicagel); eluent, petroleum ether/ethylacetate (4/1, v/v). Light yellow oil was obtained. Yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ 4.69 (s, 2H, −Ph−C*H*$_2$-OH), δ 7.15−7.18 (t, 5H), δ 7.32−7.35 (t, 4H), δ 7.66−7.68 (d, 2H), δ 9.80 (s, 1H, C*H*O).

2.4.4. Chromophore TIOH (**4**)

To a solution of 2.4 g (7.9 mmol) of 4-((4-(hydroxymethyl)phenyl) (phenyl)amino)benzaldehyde (**3**) and 1.47 g (7.9 mmol) of 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile (**1**) in 10 ml of DMF, 2 ml of acetic acid, 2 ml of piperidine and 1 ml of acetic anhydride were added. The reaction mixture was heated at 80 °C for 8 h under stirring, cooled, and poured into water. After filtration the crude reaction product was purified first by column chromatography on silicagel using dichloromethane/ethylacetate (4/1, v/v) as eluent. After evaporation of the solvent the remaining reaction product was recrystallized from ethanol to obtain pure chromophore **4**. Yield: 42%. Anal. calcd for $C_{32}H_{29}N_3O$ (471.23): C, 81.50; H, 6.20; N, 8.91; O, 3.39. Found: C, 80.91; H, 6.26; N, 8.66.

2.4.5. Chromophore TI (**5**) [15]

A 30 ml acetonitrile solution containing 2.73 g (10 mmol) 4-(diphenylamino)benzaldehyde and 1.86 g (10 mmol) of 2-(3,5,5-trimethylcyclohex-2-enylidene) malononitrile (**1**) as well as 3 drops of piperidine was refluxed for 10 h and a precipitate was formed upon cooling the solution to room temperature. The precipitate filtered from the solution was very pure as indicated by thin-layer chromatography. Yield 85%. Anal. calcd for $C_{31}H_{27}N_3$ (447.48): C, 84.32; H, 6.61; N, 9.52. Found: C, 84.03; H, 6.23; N, 9.50.

2.5. Film processing

For preparing the solution to fabricate the thin film, 3 mmol TEOS and 7 mmol GPTMS were co-hydrolyzed with 16.5 mmol acidic water (HCl, pH = 1) in 10 ml THF for 2 h under reflux. Then 10 ml THF containing 1.9 mmol chromophore (TIOH or TI) and 4.5 mmol APTES was added. After 6 h stirring, the sol was aged at room temperature for 1 day. The final molar ratio of chromophore:Si was 1:7.6. The solution was filtered with a 0.2 mm Teflon filter before spin coating. For second-order NLO study, films were spun onto glass substrates, which had been previously coated with indium tin oxide (ITO) transparent electrodes. Films were spun onto glass substrates for RI measurement. After deposition the films were dried overnight in a vacuum oven at 60 °C before SHG experiment.

3. Results and discussion

3.1. Synthesis and characterization of NLO chromophore TIOH (**4**) and TI (**5**)

Scheme 1 shows the pathways for the synthesis of TIOH and TI. The elemental analysis values of the compounds are generally in good agreement with the calculated values for the proposed structures. As shown in Fig. 1, the main differences between TIOH and TI in ^{1}H NMR spectra lie in the additional line 5.16−5.19 ppm assigned to the hydroxy group and the line 4.47−4.48 ppm assigned to the methylene nearby in TIOH. Other unassigned peaks in ^{1}H NMR spectra are related to H-atom on the vinyl-bridge and triphenylamino-substituted group. Some extent of chemical shifts was

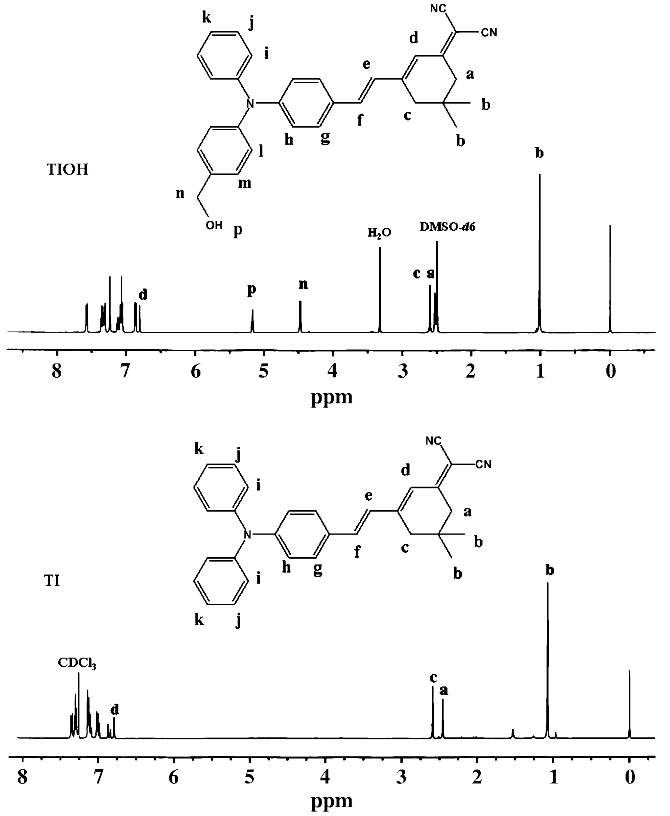


Fig. 1. ^{1}H NMR spectra (500 MHz) and the assignment of peaks of TIOH and TI.

observed after the incorporation of methanol group. These assignments clearly support the proposed structures. Fig. 2 shows the FTIR spectra of TIOH and TI. For both of them, the C–H stretching vibration of CH_2 and CH=CH was observed around 2870, 2930, 2960 and 3040 cm^{-1}. In the spectrum of TIOH, the absorption corresponding to hydroxyl absorption was observed at 3460 and 3580 cm^{-1}. Both FTIR spectra reveal the sharp absorption peak corresponding to CN stretching at 2220 cm^{-1}. These results indicate that TIOH and TI were successfully synthesized. The melting points of TIOH and TI were determined to be 183–185 °C and 170–172 °C, respectively. Enhancement of the melting point after functionalization of methanol group may lie in the formation of intramolecular H-bond. The decomposition temperatures (T_d) of TIOH, TI and DR1 (for comparison, obtained from Aldrich) are defined by the onset of the TGA curves as shown in Fig. 3, being 291.7 °C (TIOH), 322.9 °C (TI) and 252.1 °C. It revealed that TI has the best thermal stability. The T_d of TIOH is about 30 °C lower than its analogue TI without methanol group. Both of the analogues show increased thermal stability compared to DR1.

Fig. 4 presents the UV–vis spectra of the TIOH and TI in THF and in hybrid film. The absorption maxima for the intercharge transfer (ICT) of the dyes in THF were located at 492 nm (TIOH) and 487 nm (TI). This means that the introduction of methanol group causes a 5 nm red shift in its intrinsic absorption, due to an increase of electron-release behavior caused by the structural change of the donor. When these two chromophores were doped in hybrid sol–gel films, a same absorption maximum at 500 nm was found. The shift of absorbance was caused by the changed polarity of the environment around doped molecules, as usually found in NLO chromophore doped hybrid films [11].

3.2. Determination of molecular hyperpolarizabilities

The $\beta_{CT}\mu_g$ values of chromophores were evaluated by solvatochromic method, based on the solvent dependence of the UV–vis absorption spectrum of a molecule. As previously described in literature [16,17], the values of $\beta_{CT}\mu_g$ can be found as follows:

$$\begin{aligned}\beta_{CT}\mu_g &= 4.612\times10^{-5}\times\frac{f(\lambda)\varepsilon\Delta\nu_{1/2}\Delta\nu a^3}{\Delta f(D)}\\ f(\lambda) &= \frac{\lambda^3\lambda_0^4}{(\lambda_0^2-4\lambda^2)(\lambda_0^2-\lambda^2)} \qquad (1)\\ f(D) &= \frac{2(D-1)}{2D+1}\end{aligned}$$

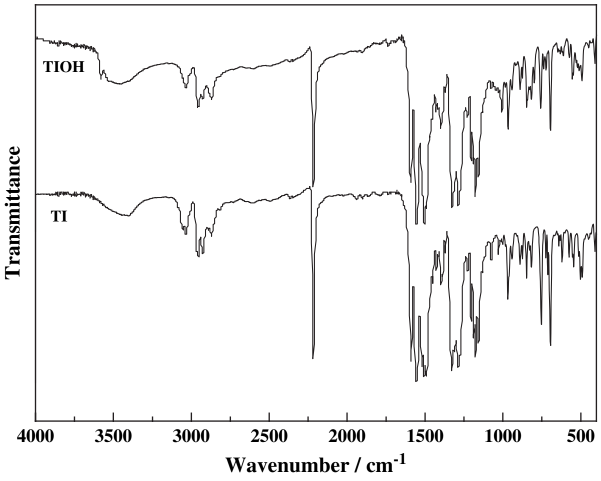


Fig. 2. FTIR spectra of TIOH and TI.

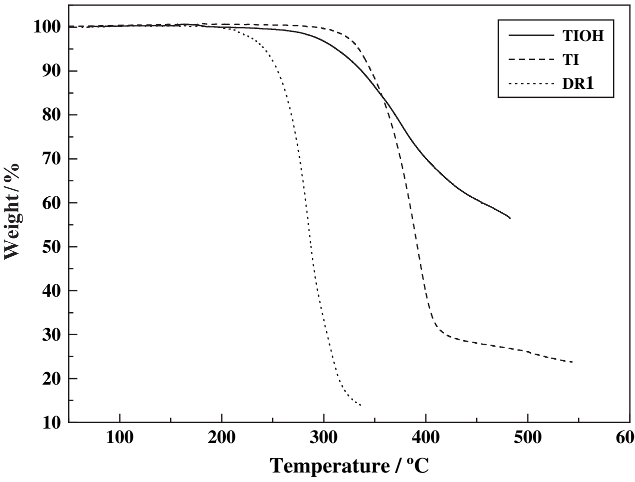


Fig. 3. TGA trace for TIOH, TI and DR1.

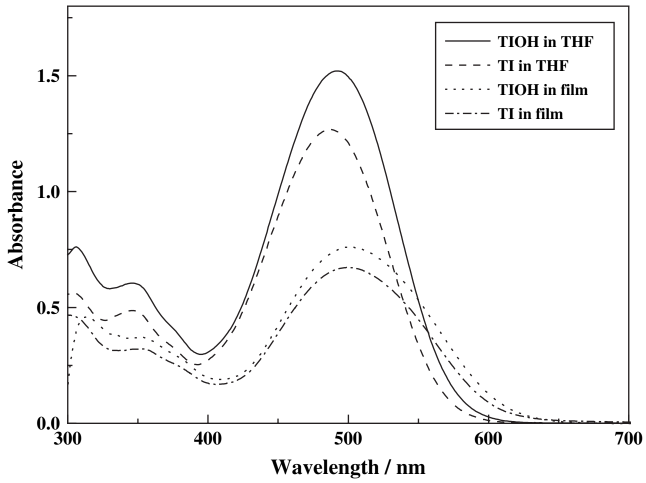


Fig. 4. UV–vis absorption spectra of TIOH and TI in THF and films.

where λ is the maximum absorption wavelength of the molecule in the excited state, and here, it is assumed to be the maximum absorption wavelength of the molecule in dipolar solvent; ε, $\Delta\nu_{1/2}$, $\Delta\nu$ and λ_0 are the 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 $\beta_{CT}\mu_g$ values for chromophores TIOH and TI at the wavelength of 1064 nm are listed in Table 1. It can be found that the $\beta_{CT}\mu_g$ values of TIOH and TI are 4353×10^{-30} esu D and 4002×10^{-30} esu D, respectively, very close to the value of DR1. Comparing with the triphenylamino-substituted molecules using nitrobenzene group as electron-acceptor [18], the newly synthesized molecules showed increased hyperpolarizabilities, which can be attributed to lengthened conjugated isophorone-bridge and the strong electron-withdrawing ability of the cyano group. The incorporation of methanol group also results in the enhancement of $\beta_{CT}\mu_g$ value.

3.3. Preparation and refractive index (RI) of hybrid films

The use of organically modified alkoxides containing amine functionalities in sol–gel synthesis of hybrids has a strong effect on the final properties of the material [10,11]. Transparent and homogeneous films doped with TIOH thicker than 2 μm could be formed without any crack and aggregation, but spin-coated thick films doped with TI show a less smooth surface. Sols doped with different chromophores also lead to different gelation times. The gelation of TIOH doped sol occurred in 2 days, but the TI doped sol is stable in a time range of more than 3 days. In particular, it was considered that APTES plays a double role during the sol–gel synthesis of hybrids [10]. It acts as strong bases that promote the inorganic polymerization and simultaneously catalyze the opening of the epoxy ring in GPTMS. APTES also has the effect of modifying the network, because the organic group that terminates the amine functionalities will directly bind to the silica backbone and will react by a coupling reaction with the epoxy rings of GPTMS.

The refractive index (RI) for the transverse electric field (TE) mode is measured using the prism coupling method at wavelengths of 633, 1300 and 1547 nm. The wavelength dispersion of RI, $n(\lambda)$, can be fitted to a one oscillator Sellmeier-dispersion formula [19],

$$n^2(\lambda) - 1 = \frac{q}{1/\lambda_0^2 - 1/\lambda^2} + A \qquad (2)$$

where λ_0 is the absorption wavelength of the dominant oscillator, q is a measure for the oscillator strength, and A is a constant containing the sum of all the other oscillators. Fig. 5 shows the curves of RI using Eq. (2) with $\lambda_0 = 500$ nm. RI values at 532 and 1064 nm obtained from the plot are listed in Table 2. It was found that the films doped with TIOH have a higher RI value than the film doped with TI. The phenomenon may be caused by distinct sol–gel behaviors implied by different gelation times, which were influenced by various species of doped chromophores.

3.4. Second harmonic generation (SHG) of hybrid films

The second harmonic intensity was measured using p (parallel-polarized) excitation and p detection, using a Y-cut quartz crystal as reference. Calculation of the second harmonic coefficients (d_{33}) for the poled films was based on the following equation [20,21]:

$$\frac{d_{33,\mathrm{s}}}{d_{11,\mathrm{q}}} = \sqrt{\frac{I_\mathrm{s}}{I_\mathrm{q}}\frac{L_\mathrm{qc}}{L_\mathrm{s}}}F \qquad (3)$$

where the $d_{11,\mathrm{q}}$ is d_{11} of the quartz crystal which is 0.5 pm/V. I_s and I_q are the SHG intensities of the sample and the quartz, respectively. L_qc is the coherent length of the quartz, which

Table 1
Experimental properties of studied molecules

Compound	λ_{max}[a] (nm)	ε (10^4 $\mathrm{mol^{-1}\,l\,cm^{-1}}$)	$\Delta\nu_{1/2}$ ($\mathrm{cm^{-1}}$)	λ_{max}[b] (nm)	$\Delta\nu$ ($\mathrm{cm^{-1}}$)	a (nm)	$\beta_{CT}\mu_g$ (10^{-30} esu D)
TIOH	494	3.41	4748	486	333	0.9	4353
TI	494	3.07	4986	483	461	0.8	4002
DR1	503	2.87	3819	477	1083	0.62	4340

[a] Measured in DMF.
[b] Measured in 1,4-dioxane.

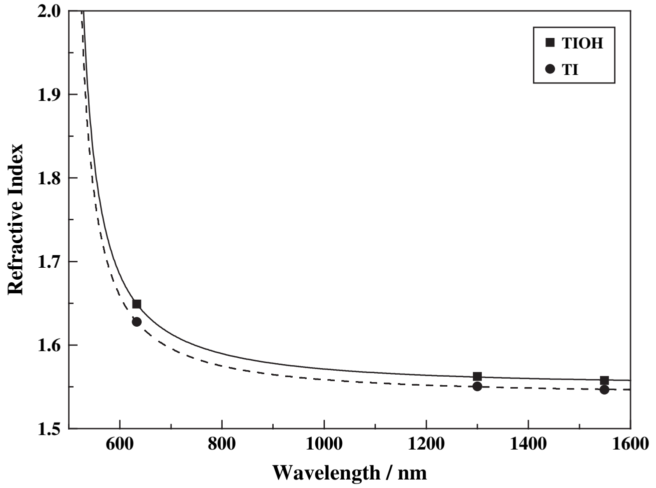


Fig. 5. Dispersion of the refractive index of hybrid films doped with TIOH and TI.

is 20.6 μm, L_s is the thickness of the films, and F is the correction factors of the apparatus and equals 1.2 when $L_{qc} \gg L_s$. The d_{33} values of TIOH and TI doped films without absorption correction were obtained to be 18.4 pm/V and 8.1 pm/V, respectively.

The absorption effect due to the chromophore at the second harmonic wavelength of the poled film was considered as follows [22]:

$$d_{33} = d_{33,\mathrm{O}} \exp(\alpha L/4)(\alpha L/4)/\sin h(\alpha L/4) \tag{4}$$

where $d_{33,0}$ is a second harmonic value without the absorption correction and α is the absorption coefficient of the film, and $\sin h(x) = (\mathrm{e}^x - \mathrm{e}^{-x}/2)$. From Eq. (4), we can obtain the d_{33} value without the absorption effects and is found to be 41.2 pm/V and 24.8 pm/V for TIOH and TI doped films, respectively. Obviously, the film containing TIOH exhibits a higher second-order NLO coefficient d_{33} than that doped with TI.

In the theoretical expression, d_{33} can be written as [23] follows:

$$d_{33} = \frac{N_d f_\omega f_{2\omega} \beta \mu_g E_p}{10\,KT} \tag{5}$$

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 identical, so the d_{33} value is only relative to the $\beta_{CT}\mu_g$ parameter.

Table 2
Refractive indices of films at the wavelength of 633, 1300, 1549, 532 and 1064 nm

Wavelength (nm)		633	1300	1549	532	1064
Refractive index	TIOH	1.6491	1.5622	1.5576	1.959	1.567
	TI	1.6276	1.5504	1.5465	1.905	1.556

Therefore, both of the poled films with almost the same molecular hyperpolarizability, do not exhibit similar d_{33} values, and the film doped with TIOH shows remarkably higher d_{33} than the film doped with TI whether absorption effect was considered or not. This result can be explained by studying the molecular structure. The possible reason is that the introduction of hydroxyl substituent group might increase the molecular compatibility with hybrid film, preventing the aggregation of the chromophores or phase separation in the materials, which strongly influences the optical nonlinearity.

4. Conclusions

Two push–pull type triphenylamino-substituted chromophores with high thermal stability for second-order NLO application were synthesized to be with/without hydroxyl group and characterized by elemental analysis, ^{1}H NMR, FTIR, UV–vis spectra and thermogravimetric analysis (TGA). Optical-quality films by spin coating were obtained after incorporation of these two chromophores. Refractive index dispersions of hybrid films doped with TIOH or TI at different wavelengths were obtained. The nonlinear optical properties of chromophores and poled hybrid film were measured by solvatochromic method and SHG measurement, respectively. The introduction of methanol group could increase the molecular hyperpolarizability, enhance the compatibility with hybrid film, increase the refractive index of doped film and finally strongly influence the macroscopical optical nonlinearity as a result.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from the National Natural Science Foundation of China (under Grant No. 50530026) and the Foundation for the Author of National Excellent Doctoral Dissertation of P.R. China (No. 200134).

References

[1] Marder SR, Beratan DN, Cheng LT. Science 1991;252:103.
[2] Yesodha SK, Sadashiva Pillai CK, Jsutsumi N. Prog Polym Sci 2004;29:4.
[3] Zhang C, Ren AS, Wang F, Zhu JS, Dalton LR. Chem Mater 1999;11:1966.
[4] He MQ, Leslie TM, Sinicropi JA. Chem Mater 2002;14:4662.
[5] Suresh S, Zengin H, Spraul BK, Sassa T, Wada T, Smith DW. Tetrahedron Lett 2005;46:3913.
[6] Verbiest T, Houbrechts S, Kauranen M, Clays K, Persoons A. J Mater Chem 1997;7:2175.
[7] Moylan CR, Twieg RJ, Lee VY, Swanson SA, Betterton KM, Miller RD. J Am Chem Soc 1993;115:12599.
[8] Matsui M, Suzuki M, Hayashi M, Funabiki K, Ishigure Y, Doke Y, et al. Bull Chem Soc Jpn 2003;76:607.
[9] Sanchez C, Lebeau B, Chaput F, Boilot JP. Adv Mater 2003;15:1969.
[10] Innocenzi P, Kidchob T, Yoko T. J Sol–Gel Sci Technol 2005;35:225.
[11] Innocenzi P, Miorin E, Brusatin G, Abbotto A, Beverina L, Pagani GA, et al. Chem Mater 2002;14:3758.

[12] Lemke R. Synthesis 1974;359.
[13] Kreuder W, HoÈrhold H-H, Rost H, Hoest AG. PCT Int Appl. WO 97 09394; 1997.
[14] Broeck KV, Verbiest T, Degryse J, Beylen MV, Persoons A, Samyn C. Polymer 2001;42:3315.
[15] Li JY, Liu D, Hong ZR, Tong SW, Wang PF, Ma CW, et al. Chem Mater 2003;15:1486.
[16] Song HC, Chen YW, Zheng XL, Ying BN. Spectrochim Acta Part A 2001;57:1717.
[17] Bilot VL, Kaski AZ. Naturforsch A 1962;17:621.
[18] Chen LJ, Cui YJ, Mei XN, Qian GD, Wang MQ. Dyes Pigments 2007;72:293.
[19] Naoto T, Mikio M, Wataru S. Macromolecules 1998;31:7764.
[20] Luo JD, Qin JG, Kang H, Ye C. Chem Mater 2001;13:927.
[21] Jerphagnon J, Kurtz SK. J Appl Phys 1970;41:1667.
[22] Amano M, Kaino T. J Appl Phys 1990;68:6024.
[23] Karunakaran YS, Chennakkattu KSP, Masataka S, Naoto T. Macromol Chem Phys 2002;203:1126.