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Synthesis and characterization of triphenylamino-substituted chromophores for nonlinear optical applications

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Abstract

Two triphenylamino-substituted chromophores containing hydroxy group, which can be easily incorporated into polymer backbone or sol–gel matrix through covalent bond, were synthesized via Vilsmeier–Haack reaction and Knoevenagel condensation. These stilbene-type chromophores with different electron acceptors were characterized by elemental analysis, ^{1}H NMR, FTIR, UV–vis spectra and thermogravimetric analysis (TGA). The hyperpolarizabilities were characterized through solvatochromic method. Compared with commercially available nonlinear optical dyes such as C.I. Disperse Red 1 (DR1), C.I. Disperse Orange 3 (DO3) and C.I. Disperse Red 19 (DR19), triphenylamino-substituted chromophores possess higher thermal stability and display better transparency in operating wavelength of electronic devices.

Keywords: Thermal stability; Stilbene derivates; Triphenylamine; Solvatochromic method; Nonlinear optics; Chromophore; Synthesis

1. Introduction

Organic polymers have been extensively studied for nonlinear optical (NLO) applications [1–3] such as electro-optical (EO) modulation and frequency doubling because of their large optical nonlinearity, fast response time, and easy processing for integrated assembly. These NLO polymers could be acquired by doping NLO chromophores into amorphous polymer matrices (guest–host systems) or covalently incorporating NLO moiety onto polymer backbone [4]. The guest–host NLO polymer materials have some fatal disadvantages such as low solubility of the chromophore in the polymer host, fast decay of nonlinear optical activity due to orientational relaxation and sublimation of the chromophore.

On the other hand, incorporation of the NLO chromophores into a polymer structure by connecting them covalently to the polymer backbone (side-chain type, main-chain type) results in an enhanced chromophore density without phase separation and therefore in high NLO effects. Sol–gel silica materials have rigid inorganic networks and smaller free volume for the nonlinear optical chromophore molecules, which can potentially help freeze the chromophore molecules and, as a result, improves the thermal stability of the electro-optic devices [5]. To form covalent linking sol–gel materials, an alkoxysilane dye, which can be copolymerized via sol–gel processing, should be yielded before hand by reaction of the chromophore and a polymerizable silane [6]. In the strategies mentioned above, chromophores should be designed and synthesized with reactive groups such as hydroxyl or amino, which could be readily covalent bonded to the host matrix.

Normally, despite large optical nonlinearity and good solubility (processability), the thermal stability has been a major concern for NLO chromophore molecule [7]. Chromophoric orientation is obtained by applying a static electric field or by optical poling. The temporal stability of the poling-induced alignment of the chromophores is important for long-term device efficiency and is increased if high T_g host materials are used. However, the chromophores must then be sufficiently thermally robust at these high temperatures to withstand the

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poling process and other fabrication steps for those devices. Replacement of dialkylamino donors in chromophores with diarylamino functionalities has been shown to improve the thermal stability dramatically [8]. NLO chromophore with bulky triphenylamino-substituted group embedded in small free volume of sol–gel materials after heat treatment may potentially increase the temporal stability of the poling-induced orientation [9]. Among the various classes of NLO chromophores, triphenylamine derivatives were good candidates for NLO chromophores because of their multifunctional properties, such as two-photon absorption and hole-conducting properties [10,11]. To obtain large first molecular hyperpolarizability, the triphenylamine can be connected with strong acceptor by an ethylene-conjugated bridge.

In this article, we describe in details the synthesis of two triphenylamino-substituted stilbene-type chromophores containing hydroxy group, named (4-((4-(4-nitrostyryl)phenyl)(phenyl)amino)phenyl)methanol (TPA-H) and 3-(4-((4-(hydroxymethyl)phenyl)(phenyl)amino)phenyl)-2-(4-nitrophenyl)acrylonitrile (TPA-CN). Characterizations of TPA-H and TPA-CN are presented by element analysis, FTIR, ^{1}H NMR, UV–vis spectra, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The composite magnitude ($\beta_{CT}\mu_g$) of the chromophores was experimentally derived using a solvatochromic method. These two chromophores displayed better transparency and higher thermal stability.

2. Experimental

2.1. Materials and measurements

Triphenylamine (purity > 98%) was purchased from ACROS Organics. 4-Nitrophenylacetic acid (purity > 98%) and 4-nitrophenylacetonitrile (purity > 98%) were obtained from Alfa Aesar. Phosphorus oxychloride ($POCl_3$, AR) was purchased from Shanghai Tingxin Chemical & Reagent Co. Reagent grade solvents were dried when necessary and purified by distillation.

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 and chloroform-*d* ($CDCl_3$) as solvents. 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 in nitrogen atmosphere.

2.2. Synthesis

The synthesis route of TPA-H and TPA-CN is depicted in Scheme 1.

2.2.1. Synthesis of 4,4′-(phenylazanediyl)dibenzaldehyde (**1**) [12,13]

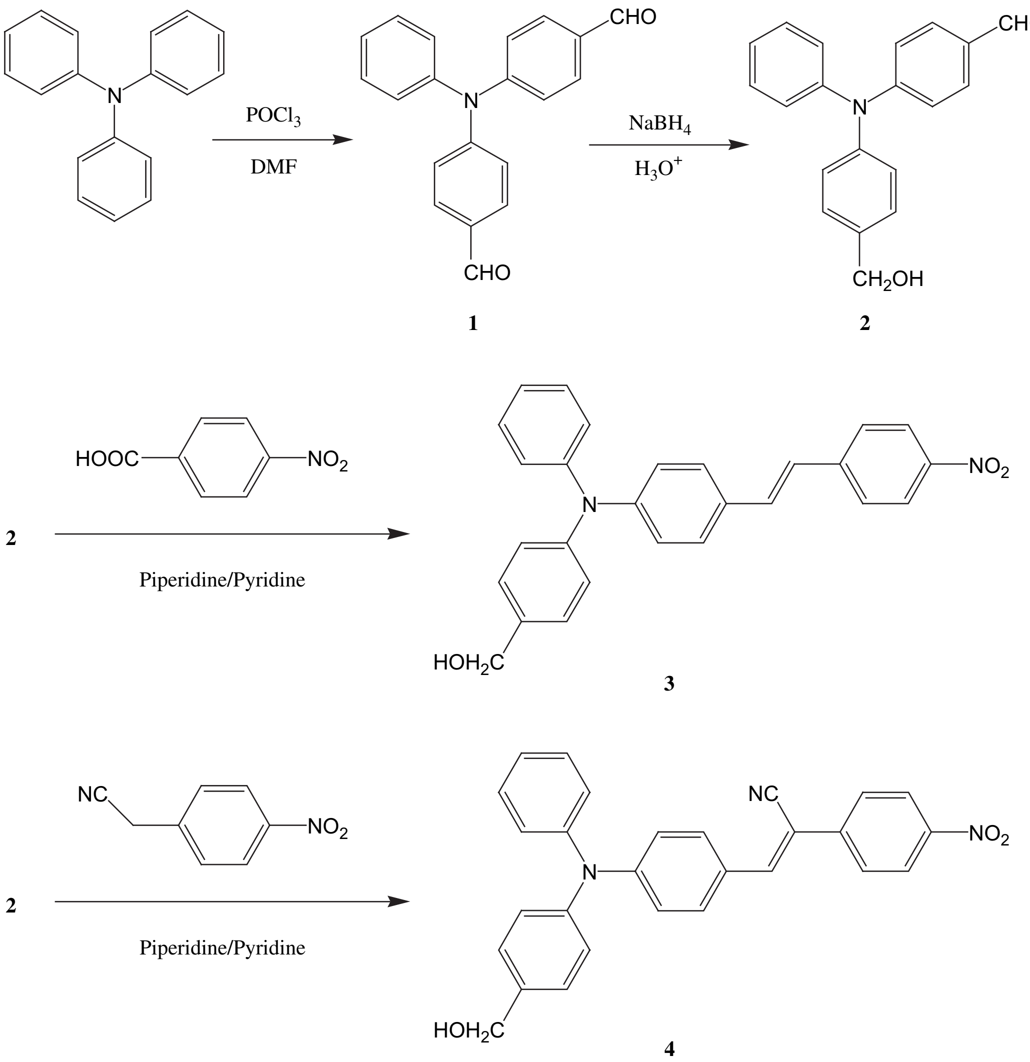
To 8.25 ml (90 mmol) of $POCl_3$ in an ice bath an equimolar amount of DMF (6.9 g) was added dropwise with vigorous stirring for 0.5 h to form Vilsmeier reagent. Then, 5 g (20 mmol) of triphenylamine was added, followed by stirring at 85 °C under N_2 atmosphere for 12 h, cooled, and then poured slowly into ice water. The mixture was then neutralized with 10% NaOH solution, and then extracted with dichloromethane, filtered, washed with water, and dried. After evaporation of dichloromethane, the crude product, dark-green oil, was first purified by column chromatography using neutral alumina and toluene as eluent. After evaporation of the solvent the remaining reaction product was recrystallized from toluene/petroleum ether three times to give yellow crystal. Yield: 63%. ^{1}H NMR (500 MHz, δ ppm): δ 7.17–7.19 (m 6H, $J = 13$ Hz), δ 7.25–7.28 (t 1H, $J = 14.8$ Hz), δ 7.38–7.41 (t 2H, $J = 15.6$ Hz), δ 7.76–7.78 (d 4H, $J = 8.6$ Hz), 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.

2.2.2. Synthesis of 4-((4-(hydroxymethyl)phenyl)-(phenyl)amino)benzaldehyde (**2**)

To a solution of 2 g (6.64 mmol) of 4,4′-(phenylazanediyl)-dibenzaldehyde (**1**) in 25 ml of dry THF, 64 mg (0.08 mmol) of sodium borohydride in 4 ml of ethanol was added dropwise under stirring. After stirring for 1.5 h at room temperature, the reaction mixture was neutralized with diluted hydrochloric acid, extracted with dichloromethane, the extract washed out with water and dried. After filtration the solvent was evaporated and the residue purified by column chromatography (silicagel) using petroleum ether/ethylacetate (4/1, v/v) as eluent. Light yellow oil was obtained. Yield: 72%. ^{1}H NMR (500 MHz, δ ppm): δ 4.69 (s 2H, –Ph–C*H*$_2$–OH), δ 7.15–7.18 (t 5H, $J = 14.4$ Hz), δ 7.32–7.35 (t 4H, $J = 16.5$ Hz), δ 7.66–7.68 (d 2H, $J = 8.7$ Hz), δ 9.80 (s 1H, C*H*O).

2.2.3. Synthesis of (4-((4-(4-nitrostyryl)phenyl)(phenyl)-amino)phenyl)methanol (TPA-H, **3**) and 3-(4-((4-(hydroxymethyl)phenyl)(phenyl)amino)phenyl)-2-(4-nitrophenyl)acrylonitrile (TPA-CN, **4**) [14]

To a solution of 2.5 g (8.3 mmol) of 4-((4-(hydroxymethyl)phenyl)(phenyl)amino)benzaldehyde (**2**) and 1.9 g (10 mmol) of 4-nitrophenylacetic acid in 20 ml of pyridine, a few drops of piperidine were added. The reaction mixture was heated for 3 h under stirring, cooled, poured onto ice, extracted with dichloromethane and dried. After filtration the solvent was evaporated and the crude reaction product was purified first by column chromatography onto silicagel and dichloromethane as eluent. After evaporation of the solvent the remaining reaction product was recrystallized from ethanol to obtain pure chromophore **3**. Yield: 42%. Anal. Calcd for $C_{27}H_{22}N_2O_3$ (422.48): C, 76.76; H, 5.25; N, 6.63; O, 11.36. Found: C, 76.78; H, 5.24; N, 6.58. The synthesis procedure of chromophore TPA-CN (**4**) was similar to the synthesis of TPA-H (**3**) with the replacement of 4-nitrophenylacetic acid



Scheme 1. Synthesis route of TPA-H (**3**) and TPA-CN (**4**).

by 4-nitrophenylacetonitrile. Yield: 53%. Anal. Calcd for $C_{28}H_{21}N_3O_3$ (447.48): C, 75.15; H, 4.73; N, 9.39; O, 10.73. Found: C, 74.82; H, 4.69; N, 9.14. The structures of two final products were characterized by FTIR and ^{1}H NMR as presented below.

3. Results and discussion

3.1. Characterization

TPA-H and its analogue TPA-CN with cyano (CN) group were synthesized via Vilsmeier–Haack reaction, selective reduction of an aldehyde group and Knoevenagel condensation. It is important to purify crude product of **1** by column chromatography using neutral alumina and toluene as eluent before recrystallization. It should also be noted that aldehyde condensation in product **1** would lead to some kind of polymerization, which could be detected by thin-layer chromatogram (TLC). The elemental analysis values of the compounds are generally in good agreement with the calculated values for the proposed structures.

The structures of TPA-H and TPA-CN were confirmed by FTIR and ^{1}H NMR spectroscopies. Fig. 1 shows FTIR spectra of TPA-H and TPA-CN. For both of them, the stretching vibration of the hydroxyl group was observed around 3420 cm^{-1}, and the C–H stretching vibration of CH_2 and =CH was observed around 2855, 2927 and 3040 cm^{-1}. In addition, the C=C stretching of phenylene, asymmetric stretching and symmetric stretching of NO_2 were observed around 1580, 1500 and 1330 cm^{-1}, respectively. In spectrum of TPA-CN, the sharp absorption peak corresponding to CN stretching was observed at 2210 cm^{-1}.These results indicate that TPA-H and TPA-CN were obtained.

^{1}H NMR spectra of TPA-H and TPA-CN are shown in Fig. 2. In ^{1}H NMR spectrum of TPA-H, the lines assigned to the phenylene protons of nitrobenzene group are as follows: 8.19–8.21 and 7.58–7.60 ppm. In ^{1}H NMR spectrum of TPA-CN, the lines assigned to the phenylene protons of nitrobenzene groups, combining two phenylene protons of triphenylamino groups which are closest to CN group are as follows: 8.26–8.28 and 7.78–7.83 ppm. The lines 1.56, 4.67 ppm in TPA-H and 1.61, 4.70 ppm in TPA-CN are assigned to the hydroxyl

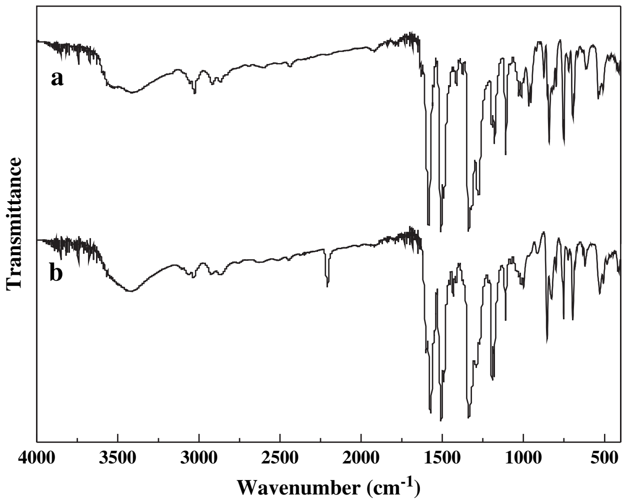


Fig. 1. FTIR spectra of TPA-H (a) and TPA-CN (b).

group $(-\mathrm{O}H)$ and the methylene nearby $(-\mathrm{C}H_2-\mathrm{OH})$, respectively. The lines at 7.39–7.41 ppm were assigned to vinyl groups $(\mathrm{C}H{=}\mathrm{C}H)$ in TPA-H, and the line 7.55 ppm in TPA-CN was assigned to vinylene groups $(-\mathrm{C}H{=}\mathrm{C(CN)})$. We can assign other lines to the phenylene protons of triphenylamino group. No proton assigned to aldehyde group was found in these two spectra, it implied the effective condensation between aldehyde and active methylene. CN group is a deshielding group in relation to both aliphatic and aromatic hydrogens, and thus its presence in TPA-CN molecule could be inferred from the observed chemical shifts compared to TPA-H.

The UV–vis absorption spectra of TPA-H and TPA-CN in ethanol are shown in Fig. 3. It was obvious that the absorption was hypsochromically shifted in TPA-CN compared to TPA-H. This can be explained as follows: the UV–vis absorption maximum peak mainly results from n–π* electronic transitions of the NLO chromophore. TPA-H has a donor group (diarylamino) and an acceptor group $(-\mathrm{NO_2})$ at separated positions, respectively. If an additional strong electron-withdrawing

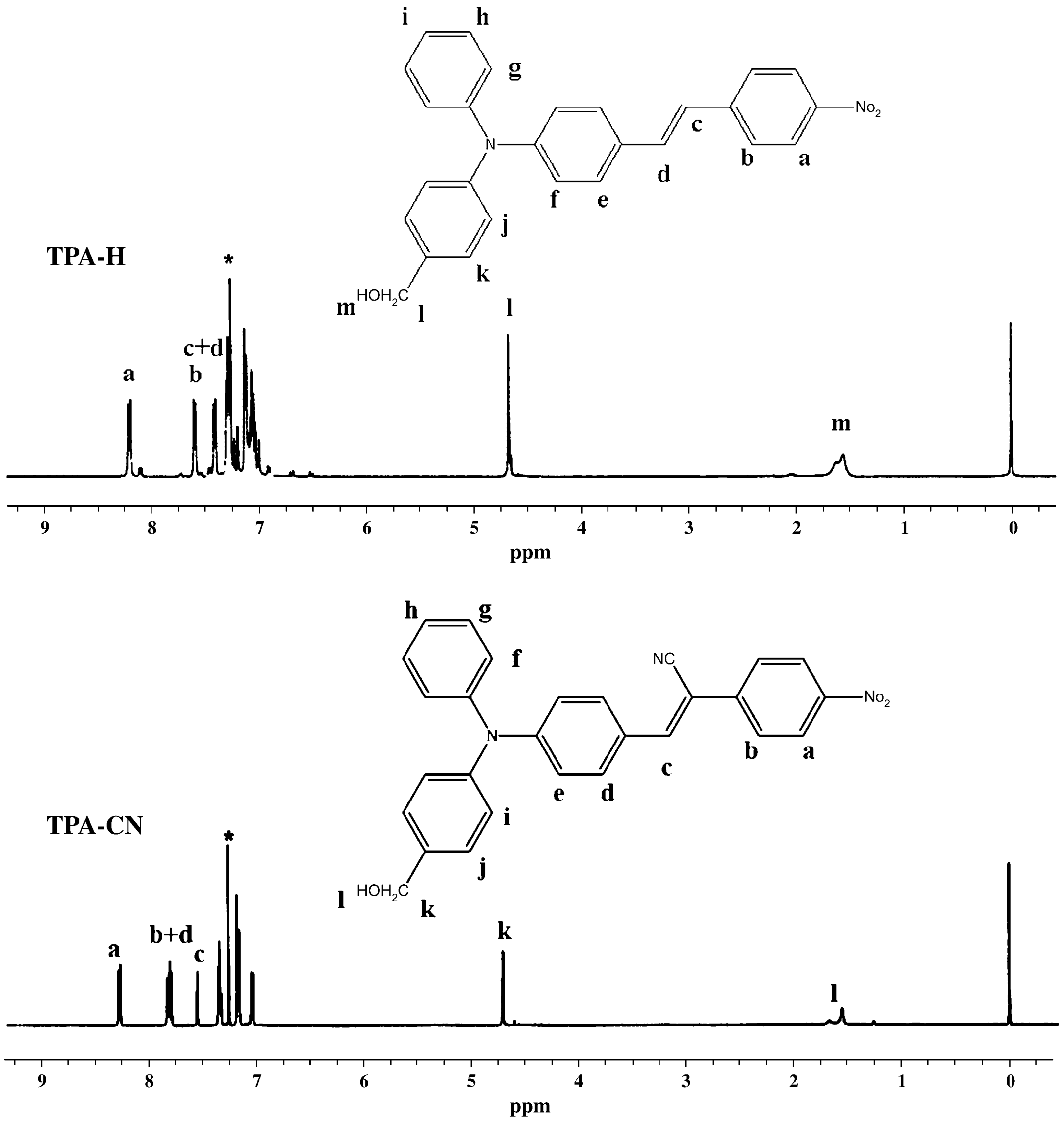


Fig. 2. ^{1}H NMR spectra (500 MHz) of TPA-H (a) and TPA-CN (b) in $\mathrm{CDCl_3}$ (the signal marked with * is caused by the solvents) and the assignment of peaks.

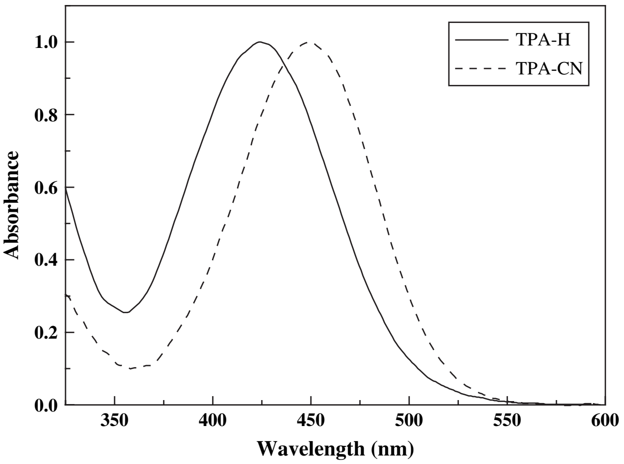


Fig. 3. UV−vis absorption spectra of TPA-H and TPA-CN in ethanol.

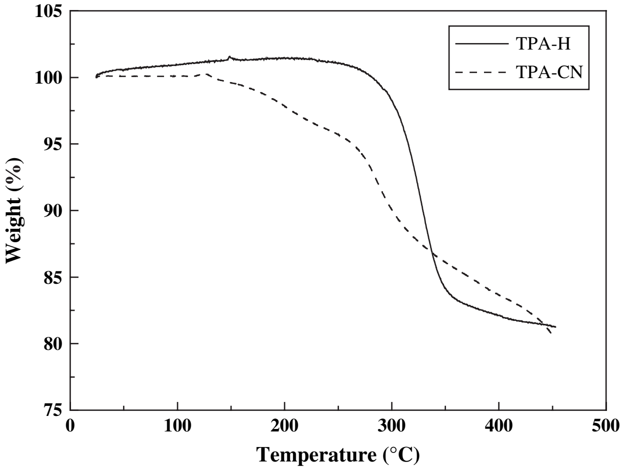


Fig. 4. TGA curves of TPA-H and TPA-CN.

group (−CN) is designed to be introduced at the position of vinyl, the structure change of the acceptor can cause an increased electron-release behavior and change the resonance absorption. As a result, the red shift of absorption can possibly occur. In summary, these analytical results clearly show the successful formation of TPA-H and TPA-CN via Vilsmeier−Haack reaction and Knoevenagel condensation.

3.2. Thermal stability

The decomposition temperatures (T_d) are defined as shown in Fig. 4, being 298.4 °C for TPA-H and 300.7 °C for TPA-CN. It revealed that TPA-CN has almost the same thermal stability as TPA-H. It should be pointed out that the TGA result of TPA-CN reveals two stages of weight reduction. The first stage beginning at 175.9 °C maybe caused by the sublimation of the chromophore [15], and the onset of the second stage was defined as the decomposition of TPA-CN. These triphenylamino-substituted chromophores are more stable than commercially available NLO dyes, such as DR1 ($T_d = 254$ °C) [9], DO3 ($T_d = 235$ °C), and DR19 ($T_d = 260$ °C) [16]. This indicates that the replacement of aliphatic dialkylamino donor groups with diarylamino groups in nonlinear optical chromophores results in the increase in thermal stabilities. But the T_d of TPA-H is about 50 °C lower than its analogue without methanol group reported before [8]. We regard it as a tradeoff between thermal stability and the property of bearing a reactive group which could be readily bonded to the host matrix.

3.3. Experimental nonlinear optical properties

The method we have chosen to determine the first-order hyperpolarizability of the chromophores is based on solvatochromism [17−19]. For most organic chromophores the two-level model was a good approximation because the energy difference between the ground state and first excited state is considerably less than that between the ground state and higher excited state. Typical NLO chromophores have an electron-donor group and an acceptor group linked through a conjugated system. As a result, the first excited state is often a low-lying charge-transfer state, usually in the visible or near-UV region of the spectrum. As a consequence the dominant component of the first-order hyperpolarizability β_{ijk} is β_{xxx}, often referred as β_{CT}.

As previously described in literature [17,18], the value for β_{CT} reduces to a simple expression:

$$\beta_{CT} = \frac{3(2\pi)^2}{2\varepsilon_0 h^2} \frac{\omega_{eg}^2}{\left(\omega_{eg}^2 - \omega^2\right)\left(\omega_{eg}^2 - 4\omega^2\right)} \left(\mu_e - \mu_g\right)\mu_{eg}^2 \tag{1}$$

where $\mu_e - \mu_g$ is the difference between the excited and ground state dipole moment, μ_{eg} is the transition dipole moment between the ground and excited state, ε_0 is dielectric constant in vacuum, h is the Plank constant and ω_{eg} is the transition frequency. Here, the ω_{eg} could be obtained simply from the band maximum of the UV−vis absorption spectrum of the molecule: $\omega_{eg} = 2\pi c/\lambda$.

The transition dipole moment μ_{eg} is related to the intensity of the transition and can be obtained from the area under the band by means of Eq. (2) [17]

$$\int \varepsilon \, d\omega = \frac{2\pi\omega_{eg} N n \mu_{eg}^2}{3 \ln 10 \varepsilon_0 c h} \tag{2}$$

where N, n and c are Avogadro's constant, solvent refractive index and speed of light in a vacuum, respectively.

If we assume μ_e and μ_g to be parallel to each other and if changes of the solvent polarizability and reorientation of the solvent dipoles upon excitation are neglected, the solvatochromic shift is given by a modification of Abe's theory [19]:

$$\hbar\left(\omega_{eg}^{s} - \omega_{eg}\right) = -\frac{1}{4\pi\varepsilon_0 a^3}\left[2\left(\mu_e^u - \mu_g^u\right)\mu_g^u\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \left[\left(\mu_e^u\right)^2 - \left(\mu_g^u\right)^2\right]\frac{n^2 - 1}{n^2 + 2}\right] \tag{3}$$

where ω_{eg}^{s} is the transition frequency in the solvent, ω_{eg} is the transition frequency in diluted vapor, ε and n are the dielectric constant and refractive index of the solvent, a is the radius of a

Table 1
Experimental properties of studied molecules

Compound	λ_{max}[a] (nm)	$\varepsilon \times 10^4$ (mol^{-1} L cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	λ_{max}[b] (nm)	$\Delta\nu$ (cm^{-1})	a (nm)	$\beta_{CT}\mu_g$ $\times 10^{-30}$ (esu D)
TPA-H	434	2.65	4951	427	377	0.9	891
TPA-CN	455	3.38	4178	449	293	0.9	1096
DR1	503	2.87	3819	477	1083	0.62	4340

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

spherical cavity occupied by the molecules. The index u refers to the solute.

According to Eq. (4) [18], the values of $\beta_{CT}\mu_g$ can be found:

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

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 mol^{-1} L cm^{-1} and unit of D is Debye.

The experimental values of TPA-H, TPA-CN and DR1 are listed in Table 1, where DR1 data measured under identical experimental conditions have been enclosed as reference. It can be found that the $\beta\mu$ values of TPA-H and TPA-CN were 89.1×10^{-29} esu D and 109.6×10^{-29} esu D, respectively, lesser than that of DR1 [20]. These maybe attributed to weaker electron-donating ability and less coplanarity of triphenylamino group. TPA-CN shows higher $\beta\mu$ values than TPA-H by incorporation of an additional strong electron-withdrawing group (CN). Although TPA-H and TPA-CN bear lower $\beta\mu$ values, they possess higher decomposition temperature and better transparency in visible region, which make it more suitable for use in second-harmonic generation (SHG) in the visible spectrum and thermally robust at high temperatures to withstand fabrication steps for those devices.

4. Conclusions

In summary, two NLO active chromophores bearing reactive hydroxyl group namely TPA-H and TPA-CN, which could be readily covalent bonded to the host matrix, were synthesized and confirmed by means of elemental analysis, FTIR, ^{1}H NMR, etc. The products exhibit a comprehensive combination of good transparency, high thermal stability and nonlinearity, indicating the ability for second-order nonlinear optical applications in the visible spectrum.

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