

The synthesis and characterizations of NLO-tricyanopyrroline chromophore derivative and the substituent effect on the electro-optical coefficients

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Four chromophores contained tricyanopyrroline (TCP) acceptor were designed and synthesized for investigating the substituent effect on the second order nonlinear. The chromophores were characterized using FT-IR, Uv-vis, NMR, and MS; and thermal gravimetric analysis revealed that the chromophores have excellent thermal stability. Poly(Bisphenol A Carbonate) polymer doped with these chromophores have been poled to afford large electrooptic coefficients (γ_{33}) at the measuring wavelength of 1310nm, and the highest γ_{33} was 61pm/V.

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1. Introduction

Over the past two decades, researchers have shown a great deal of interest in organic nonlinear optical (NLO) active chromophores. A wide variety of structural modifications on the donor, acceptor and π -conjugated moieties have been carried out [1-6]. Major research efforts have focused on developing NLO chromophores possessing large molecular nonlinearity and good thermal stability as well as improved solubility and processing ability. It is well known that the second order molecular nonlinear optical hyper polarizability increases with increasing donor and acceptor strengths and with increasing length of conjugation [7, 8]. Recently, very large microscopic nonlinearities were achieved by employing a tricyanopyrroline acceptor to synthesize highly efficient planar NLO chromophores [9]. When the dipole moment of a chromophore is sufficiently high to align it in an antiparallel manner, the planar chromophore molecules do not dissociate easily and get aligned even under a poling field. In order to disturb the intermolecular aggregation of chromophores and reduce the electrostatic attraction among the chromophores, bulky substitutes are usually tethered to the secondary amine in the TCP acceptor and the donor group. [4, 10-12]

In this paper, we report on the synthesis and NLO properties of the 4 TCP-based chromophores. And we found that the γ_{33} was becoming larger with the substituent groups increasing because of the reduced intermolecular forces.

2. Experimental section

2.1 Materials and characterization

All the reagents were used as received unless stated. DMF was freshly distilled prior to use; TCP acceptor and chromophore 1 were prepared according to the article [9]. ¹H NMR spectra were determined by Avance II-400 (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). FT-IR spectra were recorded on BIO-RAD FTS-165 spectrometer; MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) BIFLEX III (Bruker Inc.) spectrometer. UV-vis spectra were performed on Hitachi U2001 photo spectrometer. TGA was determined by TA5000-2950TGA (TA co) and DSC was taken on Perkin-Elmer DSC-7 with a heating rate of 10°C/min under the protection of nitrogen.

2.2. Synthesis

2.2.1 Synthesis of chromophores

Chromophore 1(or Chromophore 2) and sodium carbonate were mixed in 50ml of Acetonitrile under argon. After heating the solution at 70°C, benzyl bromide was added dropwise and the reaction mixture was stirred for 0.5 hour. It was poured into ice water to obtain the greenish solid product. The solid was filtered and dried at 60 °C in vacuum. The resulting product was purified by silica-gel column chromatography to yield.

2.2.2 Chromophore 1a

Yield 93%, UV-Vis (CH₂Cl₂): λ_{\max} = 734 nm; IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 2928(C-H), 2856(C-H), 2225(CN), 1734(C=C); MS (MALDI-TOF), m/z : 694(M⁺); ¹H NMR (300 MHz, CD₃COCD₃), δ : 8.50(d, 1H, =CH-), 7.76(d, 2H, Ar-H), 7.35(t, 2H, Ar-H), 7.28(d, 2H, Ar-H), 7.26(t, 1H, Ar-H), 7.11(d, 1H, -CH=), 7.00(d, 2H, Ar-H), 5.34(s, 2H, ArCH₂-N), 3.94(t, 4H, CH₂-CH₂-N), 3.83(t, 4H, O-CH₂-CH₂), 0.85(s, 18H, Si-C-CH₃), 0.02(s, 12H, Si-CH₃).

2.2.3 Chromophore 2a

Yield 94%, UV-Vis (CH₂Cl₂): λ_{\max} = 729 nm; IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 2926, 2856, 2220, 1727; MS (MALDI-TOF), m/z : 549(M⁺); ¹H NMR (300 MHz, CD₃COCD₃), δ : 8.57(d, 1H, =CH-), 7.79(d, 2H, Ar-H), 7.35(t, 2H, Ar-H), 7.28(d, 2H, Ar-H), 7.26(t, 1H, Ar-H), 7.11(d, 1H, -CH=), 7.00(d, 2H), 5.34(s, 2H, ArCH₂-N), 3.94(t, 2H, CH₂-CH₂-N), 3.83(t, 2H, O-CH₂-CH₂), 2.05(s, 3H, N-CH₃), 0.83(s, 9H, Si-C-CH₃), 0.02(s, 6H, Si-CH₃).

2.2.4 Chromophore 1b

Yield 73%, UV-Vis (CH₂Cl₂): λ_{\max} = 731 nm; IR(KBr), $\nu_{\max}/\text{cm}^{-1}$: 2928, 2857, 2224, 1734, 1528, 1175, 1059; MS (MALDI-TOF), m/z : 951.3(M⁺); ¹H NMR(300 MHz, CD₃COCD₃), δ : 8.50(d, 1H, =CH-), 7.81(d, 2H, Ar-H), 7.12(d, 1H, -CH=), 6.93(d, 2H, Ar-H), 6.43(s, 1H, Ar-H), 6.39(s, 2H, Ar-H), 5.30(s, 2H, ArCH₂-N), 3.93(t, 4H, CH₂-CH₂-N), 3.85(t, 8H O-CH₂-), 1.65(m, 2H, CH₂-CH-(CH₂)₂), 1.37(m, 16H, CH-CH₂-CH), 0.90(t, 12, CH₂-CH₃), 0.85(s, 18H, Si-C-CH₃), 0.02(s, 12H, Si-CH₃).

2.2.5 Chromophore 2b

Yield 70%, UV-Vis (CH₂Cl₂): λ_{\max} = 726 nm; IR(KBr), $\nu_{\max}/\text{cm}^{-1}$: 2927, 2857, 2224, 1734, 1537, 1252, 1061; MS (MALDI-TOF), m/z : 805(M⁺); ¹H NMR(300 MHz, CD₃COCD₃), δ : 8.56(d, 1H, =CH-), 7.78(d, 2H, Ar-H), 7.12(d, 1H, -CH=), 6.97(d, 2H, Ar-H), 6.43(s, 1H, Ar-H), 6.41(s, 2H, Ar-H), 5.25(s, 2H, ArCH₂-N), 3.93(t, 2H, CH₂-CH₂-N), 3.86(d, 4H, O-CH₂-CH), 3.77(t, 2H, O-CH₂-CH), 3.27(s, 3H, N-CH₃), 1.68(m, 2H, CH₂-CH-(CH₂)₂), 1.27(m, 16H, CH-CH₂-CH), 0.90(t, 12, CH₂-CH₃), 0.85(s, 9H, Si-C-CH₃), 0.02(s, 6H, Si-CH₃).

2.3 Film preparation

For the γ_{33} measurements, the films were prepared by a spin-coating method. Firstly APC was dissolved in the mixture of dibromomethane, and a given amount of chromophore was then added into the solution, and filtered through a syringe filter (0.44 μm) to remove the undissolved particulates. The indium-tin oxide (ITO)-coated glass was pre-cleaned using acetone, distilled water, and tetrahydrofuran sequentially in ultra sonic bath. The obtained homogenous solution was spin coated on to the ITO-coated glass substrate at room temperature with the spinning rate of 800 rpm to give a film, which was dried in a vacuum oven at 50°C for 12h to remove the residual solvent.

2.4. Corona poling process and NLO measurement

The poling process was carried out for 10 minutes at a temperature of about 5 °C above the T_g of the polymer. The applied voltage is set at 8 kV. The sample was subsequently cooled to room temperature and then the applied voltage was withdrawn.

The γ_{33} value for a poled film was calculated from the equation: [13]

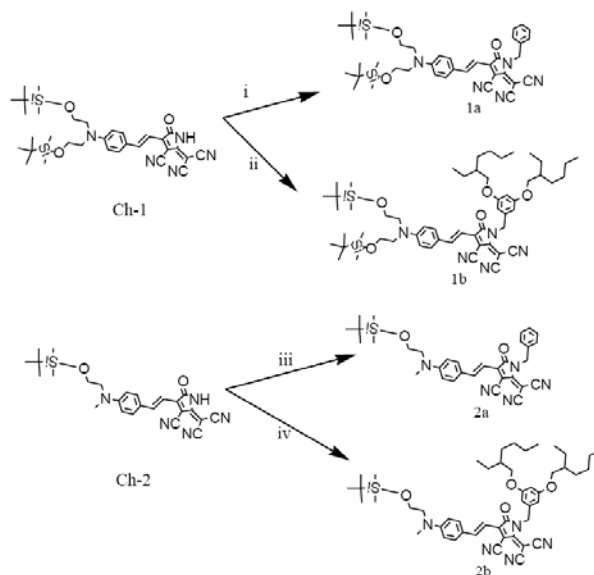
$$\gamma_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \cdot \frac{(n^2 - \sin^2 \theta)^{1/2}}{\sin^2 \theta}$$

where I_m is the amplitude of the modulation, λ is the wavelength of the light, V_m is the modulating voltage, I_c is half the maximum laser intensity, n is the index of refraction, θ is the incident angle.

3. Results and discussion

3.1 Synthesis of chromophore

The structures of the push-pull chromophores were shown in Scheme 1, which were produced by a one-step procedure. We produced the chromophore Ch-1 and Ch-2 according to the related report. The compounds unmentioned in this paper were purchased from Chemical reagent Beijing Co., Ltd. The reaction between TCP acceptor and benzyl bromide have higher yield which is important for its application in NLO material.



Scheme 1. Synthetic procedure of the chromophores 1a,

1b, 2a, 2b

The reaction of the chromophore with benzyl bromide has higher yield than with 3,5-Bis(2'-ethylhexyloxy)benzyl Bromide, and the yield of chromophore 2 was higher than chromophore 1. Maybe the yield has some relation with the stereo effect of the reagents. The yield got lower when the stereo effect increased. The time control is very important in this reaction, if the time is too long the chromophore will be broken up. This reaction can take place in solvent of acetonitrile or dimethylformamide, but the yield will be higher in acetonitrile and the product will be easier to purify.

3.2 The thermal stabilities of the chromophores

Thermal stability is an important requirement for the incorporation of new chromophores in poled polymer structures [14]. The thermal stabilities of the chromophores were investigated by TGA under nitrogen, with a heating rate of 10°C/min. Fig.1 gives the thermogravimetric curves of the chromophores. The results show that all the chromophores are thermally stable with decomposition temperatures (Td) higher than 268 °C. Fig.2 shows the Differential scanning calorimetry curves of the chromophores in APC polymer. And all the glass transition temperatures (Tg) are around 120 °C. The gap between Tg of APC polymer and Td of chromophore is wide enough to allow safe poling procedure at temperature around Tg.

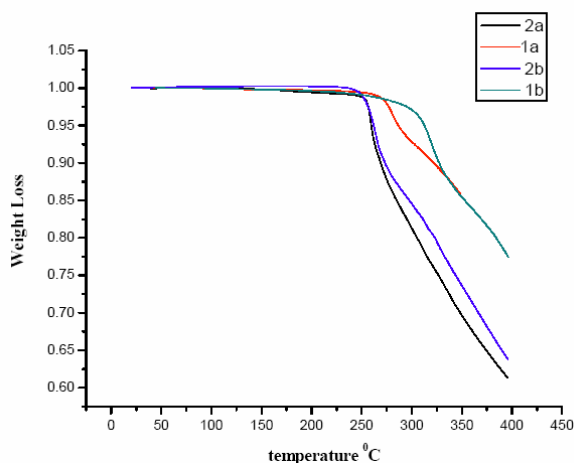


Fig. 1. TGA curves of the chromophores.

The decomposition temperature of chromophore 1a and 1b is higher than chromophore 2a and 2b (about 30°C). This may be due to the long carbon chain in the amino which prevent the amino from reacting with acceptor cyano groups when being heated. The thermal degradation is largely related to oxidation whereby the molecular bonds of a chromophore are attacked by oxygen molecules. The core of the chromophore which is a large conjugated group is more easily attacked by oxygen molecules. If the chromophores can have more and larger flexible structures around the core, the probability of the core be attacked will become lower and the chromophores will have better thermal stability. So chromophore 1b has the best thermal stability and this result was proved in Fig.1.

3.3. Solvachromism

Table.1 illustrates the values of maximum absorption of the chromophores in various solvents. It can be seen that these chromophores show blue shifts in stronger polar solvent (THF) than in the weaker polar solvent (dichloromethane) and display positive solvatochromism as the polarity of the solvents increased. This solvatochromic behavior is attributed to an intermolecular charge transfer transition with an increase of the dipole moment upon excitation and is interpreted in terms of predominance of neutral form in the ground state structure. Demartino et al. correlated high solvatochromic effects with a large molecular hyperpolarizability. All the chromophores show great solvatochromic effects, and the chromophore 1a and 1b are a little higher. From the table, all the chromophores exhibit the large λ_{\max} values varying from 694 nm to 734 nm in the aforementioned solvents, which related to low charge transition energy, enhanced second order NLO response.

Table 1. UV-vis data of the chromophores.

chromophore	λ_{\max} (nm) (DCM)	ϵ (DCM) ($\text{Lmol}^{-1}\text{cm}^{-1}$)	λ_{\max} (nm) (THF)	ϵ (THF) ($\text{Lmol}^{-1}\text{cm}^{-1}$)	$\Delta \lambda_{\max}$
1a	734	73840	699	60940	35
1b	731	67643	695	64200	36
2a	729	74049	697	73564	32
2b	726	68103	694	60370	32

3.4. Electro-optic properties of the chromophore doped APC samples

In order to investigate the nonlinear optical properties of the chromophores, guest-host systems were explored. The chromophores were doped into APC [poly (bisphenol A carbonate)] at the same molecular densities (0.1mmol/g), because the γ_{33} value depends on the chromophore density in the films. Solutions of 20% total solids were prepared in Dibromomethane and 2-3 μm thick films were spun cast onto the substrate coated by indium tin oxide (ITO). The films were vacuum dried at 50 °C overnight, and corona poled at 150 °C for 30 minutes under the electric field of 8 kV. Then, the electric field was removed when the films were cooled to room temperature. The electro-optic (EO) coefficients of the films were measured at the fundamental wavelength of 1315 nm by simple reflection technique. In the process of poling, we also researched the stability of the chromophore in electric field. The highest electric field the chromophore can bear was summarized in table 2. We can see that the TCP chromophore with dendron can shows more stable than the chromophore without dendron, and the long carbon chain is also important in improve the stability of the chromophore in the strong electric field.

Table 2. Properties of chromophores

chromophore	E_p	r_{33}	T_d
	V	Pm/V	°C
1a	10000	28	302
1b	11000	61	306
2a	8000	14	268
2b	8500	22	271

The EO coefficients (γ_{33}) of the films are all summarized in Table 2. It is found that the materials containing the chromophore 1b have the highest electro-optic coefficient of 61Pm/V and the chromophore 2a has the lowest electro-optic coefficient. This proves that the protective group in the donor and the dendron groups in the TCP acceptor indeed improved the poling efficiencies by minimizing the electrostatic interactions and aggregation among the chromophore molecular. If we increase the volume of the protective and dendron group, may be the EO coefficient will increase again [15].

4. Conclusions

Four novel TCP acceptor chromophores were

synthesized. These TCP EO-active materials were dispersed into APC and tested as thin-film composites using simple reflection method. The results demonstrate that the EO-coefficient is getting larger as the increase of the modified group. TCP acceptor containing rigid-flexible dendron moiety is ideally suited to EO applications due to the great increase of the EO coefficients and the stability in the high electric field.

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