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Nonlinear optical chromophores with good transparency and high thermal stability

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Abstract

In order to improve the transparency and thermal stabilities of nonlinear optical (NLO) chromophores, new materials based on the azo benzene chromophore having 1,3,5-triazine groups were prepared. Their NLO properties were experimentally derived using a two-level model. Compared with corresponding NLO chromophores *p*-nitroaniline (PNA) and C.I. Disperse Red 1, the newly synthesised chromophores displayed better transparency and higher thermal stability. The reaction of a new NLO chromophore with a dianhydride resulted in polyimide that was converted to a poled polymer which had a d_{33} value of 69 pm/v, a T_g of 225°C, decomposition temperature of 354°C and an absorption cut-off below 450 mm, indicating its ability for harmonic generation application in the blue and green regions.

Keywords: 1,3,5-Triazine; Nonlinear optical chromophores; Solvatochromism; AM1/FF; Good transparency; High thermal stability

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1. Introduction

The major challenge in the design of nonlinear optical chromphores for frequency-doubling devices is simultaneously achieving acceptable nonlinearity, transparency and thermal stability. In this paper, the 1,3,5-triazine group was linked to a NLO chromophore that is used in the field of frequency-doubling. Two such molecules **1** and **2** (in Scheme 1) were synthesized and characterized. 1,3,5-Triazine groups have been used intensively in dyes to obtain a hypsochromic effect, which is required for the present work. Apart from this, amino-substituted 1,3,5-triazines have high thermal stability which is favoured in the design of NLO chromophores.

Many methods, including electric-field-induced second harmonic generation (EFISH) [1,2] and hyper-Rayleigh scattering (HRS) [3] techniques, have been used to determine the second order nonlinearity of molecules. In this paper, a simple two-level model [4] was used to rationalize the trends in β. This simplified approach is particularly useful for examining a series of related molecules, as in the present study. Using this approach, the value for static β reduces to a simple expression:

$$\beta(-2\overline{\omega};\overline{\omega},\overline{\omega}) = \beta_{\overline{CT}} = \frac{3\Delta\mu_{eg}\mu_{eg}^{2}}{2_{\overline{\varepsilon}0}\left(\hbar\overline{\omega}_{eg}\right)^{2}} \frac{\overline{\omega}_{eg}^{4}}{\left(\overline{\omega}_{eg}^{2}-\overline{\omega}^{2}\right)\left(\overline{\omega}_{eg}^{2}-4\overline{\omega}^{2}\right)} \tag{1}$$

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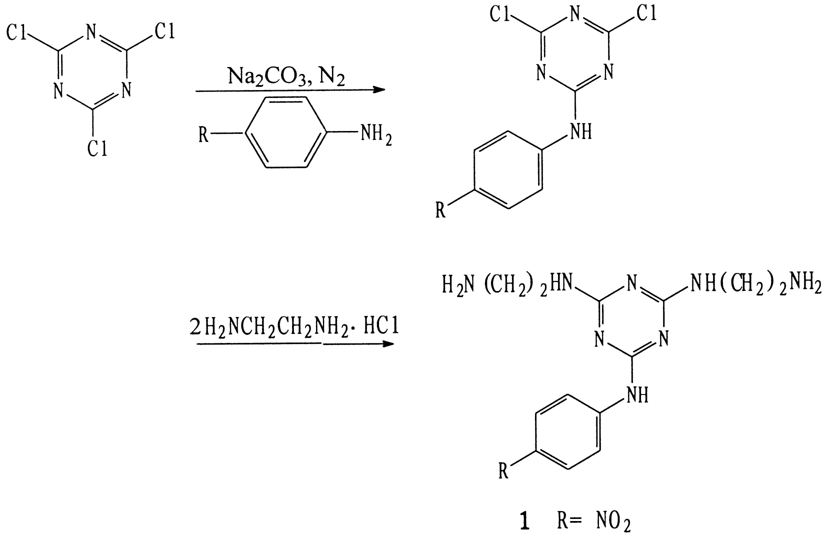

1 R= NO_2

2 R= $N{=}N{-}C_6H_4NO_2$

Scheme 1. Synthesis of molecules **1** and **2**.

where μ_{ge} is the transition moment between the ground and excited state, $\Delta\mu_{ge}$ is the corresponding difference in dipole moments ω_{eg} is the transition frequency and ω is the laser wavelength.

The transition frequency ω_{eg} and the transition dipole moment can be determined from a UV–Visible absorption spectrum of the substance in solution in which ω_{eg} is the frequency of maximum absorption, and μ_{eg} can be determined by numerical integration of the absorption band [5], wherein a Lorentz local field correction [6,7],

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

$$f^2/n = \left(n^2+2\right)^2/9n,$$

is included; ε is the molar extinction coefficient, ω_{eg} is the transition frequency in the solvent, ε_0 is the vacuum permittivity, N_A is Avogadro's number, h is Planck's constant and c is the speed of light.

The ground-state dipole moment can be determined by measuring the dielectric constant for several concentrations using the Debye–Guggenheim equation [8].

$$\mu_g^2 = \frac{9kT}{4\pi N_A} \frac{3}{(\varepsilon_0+2)\left(n_0^2+2\right)} \frac{\left(\varepsilon - n^2\right) - \left(\varepsilon_0 - n_0^2\right)}{C} \tag{3}$$

where ε_0 and n_0 are the dielectric constant and the refractive index of the pure solvent, ε and n denote the dielectric constant and the refractive index of solution, and C is concentration.

$\Delta\mu_{ge} = \mu_e - \mu_g$ is extracted from the solvatochromic shifts (Δv) of the absorption spectra in solvents with closely matching refractive indexes but different dielectric constants (D) according to the following equation [9],

$$hc(\Delta v) = \frac{2\mu_g\left(\mu_e - \mu_g\right)}{a^3} \Delta\left(\frac{D-1}{D+2}\right) \tag{4}$$

In this study, four solvents were chosen, namely diethylether, ethyl acetate, acetone and ethanol, whose refractive indexes vary between 1.351 and 1.372. The $(D-1)/(D+2)$ values of the solvents are 0.527, 0.625, 0.868 and 0.886. The absorption maximum of molecules **1** and **2** in different solvents are listed in Table 1. The Onsager radius a, is taken to be 5 Å for molecule **1** and 8 Å for molecule **2**, respectively, according to Ye Cheng's method [10].

Table 1
$\lambda_{\max}$ (nm) values of molecules **1** and **2** measured in different solvents

Compound	*p*-Dioxane	Diethylether	Ethyl acetate	Acetone	Ethanol
1	324.7	334.5	346.6	368.1	370.8
2	378.1	385.4	388.7	393.8	394.5

Often, another expression β_{CT} is used [11],

$$\beta_{\mathrm{CT}} \alpha \lambda_{\max}^{3}, f \Delta\mu_{eg} \tag{5}$$

in which expression (5) can be obtained by substituting the following expression [12]

$$f = \left(2m\varpi_{\mathrm{eg}}/3e^{2}\hbar\right)\mu_{\mathrm{eg}}^{2} \tag{6}$$

and

$$\lambda_{\max} \alpha \frac{1}{\varpi_{\mathrm{eg}}} \tag{7}$$

into expression (1), where f is the oscillator strength and m is the electron mass.

2. Results and discussion

2.1. Experimental linear and nonlinear properties

Compounds **1** and **2** containing the NLO chromophores were obtained by the reaction of 2,4,6-trichloro-1,3,5-triazine with *p*-nitro aniline (PNA) or C.I. Disperse Orange 3 (DO3), followed by aromatic nucleophilic substitution, as shown in Scheme 1.

The experimental values of the ground state dipole moment (μ_g, in debye), absorption maximum ($\lambda_{\max}$, in nm), transition moment (μ_{ge}, in debye), oscillator strengths (*f*) and dipole moment difference ($\Delta\mu_{\mathrm{ge}}$, in debye) of PNA, C.I. Disperse Red 1 (DR1), **1** and **2** are presented in Table 2. The melting point (°C) and two-level model derived static hyperpolarizability values (β_0, in 10^{-30} esu) are also shown.

Table 2
Experimental properties of studied molecules

Compound	μ_{ga}	$\lambda_{\max}{}^{\mathrm{a}}$	$\mu_{\mathrm{eg}}{}^{\mathrm{a}}$	f	$\Delta\mu_{\mathrm{eg}}$	β_{o}	Mp
1	6.1	325	5.88	0.50	6.2	7.6	>300
PNA	6.0	354	5.10	0.35	6.8	8.4	150
2	6.8	378	6.60	0.54	12.8	32	>300
DR1	7.0	455	6.1	0.38	13.0	35.7	161

[a] Measured in 1,4-dioxane.

From Table 2 the following points can be raised. Firstly, the $\lambda_{\max}$ of **1** and **2** were 29 and 77 nm, respectively, lower than that of PNA and DR1. This can be explained by Dewar's rules [13], which are widely used to explain the electronic effects of modifications on chromophores. Accordingly, following Dewar's convention, the benzylic anion (Fig. 1) serves as a model and the atoms in the conjugated backbone of an even, alternate molecule are paired as "starred" or "unstarred" by their positions relative to a terminal donor group which is defined as a starred position. Dewar's rules suggest that the replacement of carbon in a conjugated molecular backbone by a more electronegative atom will produce a large hypsochromic (short-wavelength) shift. From Fig. 1 it can be seen that the three ring nitrogen atoms of molecules **1** and **2** are located in the "star" position, which leads to a considerable hypsochromic effect. Secondly, although molecules **1** and **2** absorbed at much shorter wavelengths, their β_{o} values were similar to those of PNA and DR1. From Table 2 it is evident that the $\Delta\mu_{\mathrm{ge}}$ value of **1** was slightly smaller than that of PNA and the same holds true for **2** and DR1. Thus, the $\Delta\mu_{\mathrm{ge}}$ values cannot explain the superior nonlinear-transparency of molecules **1** and **2**. However, when oscillator strength is considered, the results are clear insofar as the oscillator strengths of **1** and **2** were 0.50 and 0.54, respectively, which was much larger than those of the corresponding PNA and DR1 molecules, whose oscillator strengths were 0.35 and 0.38, respectively. According to expression (5), β_0 values are proportional to λ^3, f and $\Delta\mu_{\mathrm{ge}}$. Hence, while **1** and **2** have absorption maxima that were

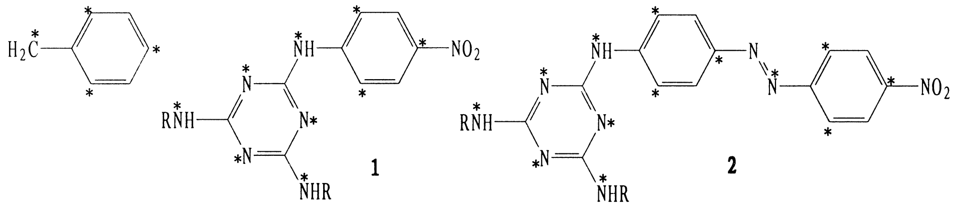

Fig. 1. Starred and unstarred positions of benzylic anion and molecules **1** and **2**.

lower than that of PNA and DR1, their much larger oscillator strengths still ensure their acceptable nonlinearity. Previous studies of the structure–property relationships of molecular nonlinearity found that in most cases, the absorption maximum and, in some cases the absorption maximum together with difference in dipole moment, would predict the order of the nonlinearity of a series of molecules. In this paper it was found that the transition moment or oscillator strength also play an important role in the determination of trends in nonlinearity. Thirdly, from Table 2, molecules **1** and **2** have melting point values above 300°C, which were much higher than PNA and DR1. This finding, to some extent, reflects the superior thermal stabilities of molecules **1** and **2**.

2.2. *Properties of poled polymer with chromophore* 1 *as side-chain chromophore*

Molecule **1** was incorporated as a side-chain in a polyimide backbone to obtain side-chain nonlinear optical polymers (Fig. 2). The polyimide obtained from **1** and 4,4-(hexafluoroisopropylidene) diphthalic anhydride by a traditional two-step process has a T_g of 225°C and a T_d of 354°C. After the polymer was poled using the Corona poling method [14], a d_{33} value of 69 pm/v was obtained using the Maker fringe method employing a Nd: YAG laser as exciting light source and a crystal quartz sample as reference. This high d_{33} value stems from the high poling temperature (up to 280°C) and high poling efficiency. Moreover, this particular poled polymer also had good transparency as evidenced by a cut-off absorption wavelength lower than 450 nm. Further studies of this poled polymer are in progress.

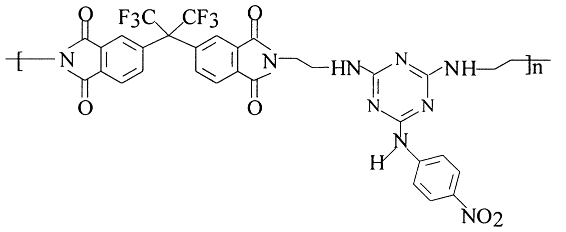

Fig. 2. Structure of polyimide molecule with chromophore **1** as side-chain.

3. Conclusions and outlook

Two new nonlinear optical chromophores (**1**, **2**) containing 1,3,5-triazine groups have been synthesized and characterized. The compounds display acceptable nonlinearity together with high transparency and thermal stability and thus are likely to be used in the field of frequency doubling.

In some cases not only the absorption maximum and dipole difference but also transition moment (oscillator strength) can play an important role in the evolution of molecular nonlinearities.

4. Experimental

4.1. *Equipment*

All melting points (mp) are uncorrected. IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrophotometer, ^{1}H NMR spectra were obtained using a Varian Gemini-300 (spectra referenced to tetramethysilane and recorded in dimethyl sulfoxide-d_6). UV–visible spectra were obtained on a Perkin–Elmer Lambda 20 spectrophotometer. Thermal analysis was performed using a Perkin–Elmer Pyris 1 and a Perkin–Elmer TGA7 system with a heating rate of 20°C/min.

4.2. Materials

2,.4,6-Trichloro-1,3,5-triazine was purchased from Tokyo Chemical Industry Co., Ltd. and was purified by recrystallization from benzene prior to reaction. Ethylene diamine, PNA, C.I. Disperse Orange 3 and 4,4-(hexafluoroisopropylidene)diphthalic anhydride were purchased from Shanghai No. 3 Reagent Company and were used as received.

4.3. Synthesis of 2,4-di(2-aminoethyl)amino-6-(4-nitrobenzyl)amino-1,3,5-triazine **1** *and 2,4-di-(2-aminoethyl)amino-6-(4-nitrophenylazo)amino-1,3,5-triazine* **2**

To a cooled ($< 5°$) solution of *p*-nitroaniline (2.76 g, 0.02 mol) in anhydrous ethanol (30 cm^3), 2,4,6-trichloro-1,3,5-triazine (3.69 g, 0.02 mol) was added. After neutralisation with 40% aqueous sodium carbonate solution, the mixture was stirred for another 6 h and then slowly added to a mixture of ethylenediamine (2.40 g, 0.04 mol), water (30 cm^3) and hydrochloric acid (36%, 3.7 cm^3, 0.043 mol) under nitrogen. The mixture was stirred at 40°C for 5 h and then heated to 80°C to remove ethanol by distillation. The mixture was heated to 100° and refluxed for another 4 h. Upon cooling, the mixture was basified to a pH value of 10 and the resulting solid was collected by filtration and washed with water. Purification was carried out by dissolution in 100 cm^3 of water while keeping the pH at 5. The ensuing mixture was stirred at 50°C for 30 min under nitrogen and then filtered. The filtrate was basified to a pH value of 10 and then extracted with diethyl ether three times. Upon the removal of diethyl ether by distillation, crystals were obtained. Physical and spectral data are shown below:

1: *2,4-Di(2-aminoethyl)amino-6-(4-nitrobenyl)-amino-1,3,5-triazine*

Yield 71%, mp > 300°C. IR: $\nu = 3376$, 3303, 1502, 1326, 1418, 809 cm^{-1}. UV–vis (1,4-dioxane) λ_{max}: 325 nm. ^{1}H NMR $\delta = 1.25$ (t, 4H), 3.20–3.40 (m. 10H), 3.55 (s, IH), 7.90 (d, 4H) ppm.

$C_{13}H_{19}N_9O_2$: calculated: C 46.70, H 5.71, N 35.80; found: C 47.09, H 5.67, N 35.70.

2. *2,4-Di(2-aminoethyl)amino-6-(4-nitrophenylazo)amino-1,3,5-triazine*

Yield 69%, mp > 300°C. IR: $\nu = 3481$, 3355, 1502, 1327, 1415, 808 cm^{-1}. UV–vis (1,4-dioxane).

λ_{max}: 378 nm. ^{1}H MNR $\delta = 1.23$ (t, 4H), 3.22–3.45 (m, 11H), 6.60 (d, 4H), 7.93 (d, 4H) ppm.

$C_{19}H_{23}N_{11}O_2$: calculated: C 52.17, H 5.30, N 35.21; found: C 51.75, H 5.26, N 34.83.

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