

NONLINEAR OPTICAL PROPERTIES OF Λ-SHAPED NITROPYRIMIDINE DERIVATIVES AND ITS POLYMERIC FILMS*

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ABSTRACT

Three Λ-shaped nitropyrimidine derivatives with benzyl or furfuryl as bridge have been synthesized. They possess shorter absorption wavelengths ($\lambda_{\text{cut-off}} < 400$ nm) and higher $\beta\mu$ values (around 10^{-46} esu). The second order nonlinear optical coefficient d_{33} of poled BNPMOPMDA/PMMA doped film is $1.2\text{--}2.0 \times 10^{-9}$ esu obtained by in-situ SHG measurements. It can be expected that the chromophore-functionalized polymer containing higher number density of synthesized chromophore as side chain will be the potential blue-light transparent frequency doubling materials.

INTRODUCTION

Second harmonic generation (SHG) is one of the essential nonlinear optical phenomena, and its attractive application is to make frequency doubling of semiconductor laser to obtain a new high power blue coherent light source, which is required for the optical data storage of high density, color image processing and optical measurements. As well known, besides the high second order nonlinearity a material applied to SHG must have complete transparency at both the fundamental and doubling frequency wavelength of used laser. Based on the principle of the molecular engineering of organic nonlinear optics the first hyperpolarizability (β) of organic molecules depends on their conjugation length and intramolecular charge transfer. The increase of the molecular β value will lead to red-shift of its absorption wavelength. So to solve this contradiction is one of the key in this field. Several attempts to address the transparency/nonlinearity tradeoff issue have been proposed, and some progresses had been reported^[1,2]. Nevertheless the results are almost invariably the same: the compounds are always more or less colored. It seems possible to get a reliably easy tuning between red and yellow colored materials, but getting a still highly SHG efficient and uncolored material remains a somewhat problematic challenge.

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In this paper the syntheses and their molecular nonlinearities of three kinds of new Λ -shaped nitropyrimidine derivatives (the molecular formulas shown in Fig. 1) are reported. They both are blue-light transparent and possess higher $\beta\mu$ (μ is the dipole moment of the chromophore) product values which are comparable to that of *p*-nitroaniline (*p*-NA). In order to investigate the possibility for device application, the second order coefficient of the poled film of synthesized chromophore BNPMOPMDA doped in PMMA is studied. The results suggested that Λ -shaped nitropyrimidine derivatives and its polymers seem to be the potential blue-light transparent frequency doubling materials.

EXPERIMENTAL

The reagents used in this research are commercial CP or AR grade reagents without further purification. The starting compound 5-nitro-2-aminopyrimidine (NAPyr) was synthesized according to Ref. [3]. The characterizations were performed with a Varian Unity 200 MHz NMR spectrometer and AEI MS-50 mass spectrograph. Melting points were measured with X-4 micro-melting point apparatus. Elemental analyses of the products were carried out by Heraeus CHN-Rapid method.

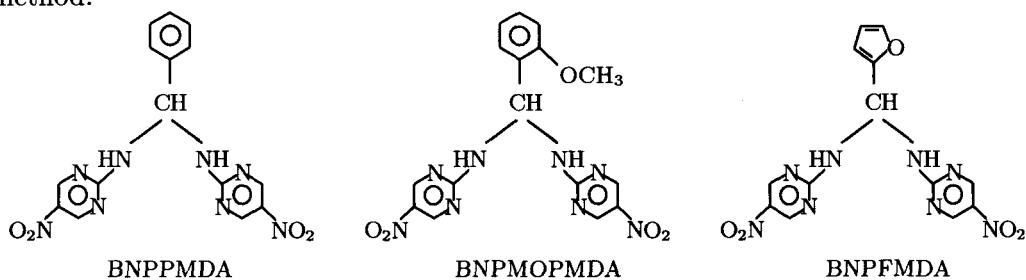


Fig. 1. Molecular structures of three synthesized Λ -shaped nitropyrimidine derivatives

1. Syntheses of Λ -shaped nitropyrimidine derivatives

1) N, N'-bis (5-nitropyrimidyl-2)-phenylmethanediamine (BNPPMDA)

0.28 g NAPyr (2 mmol) and 0.4 ml benzaldehyde (around 4 mmol) were dissolved in 10 ml cumene in a round-bottom flask with magnetic stirrer and condenser which was connected with a water segregator. The mixture was refluxed for 4 hours and around 0.23 ml water was collected in water segregator. Longer refluxing did not cause an increase in water amount. Thereafter, after cooling the solid was collected with filter and washed with ethanol for several times. Yield 0.48 g (65%). mp. $> 250^{\circ}\text{C}$ (decomp.).

Calcd for $C_{15}H_{12}N_8O_4$ C 48.91 H 3.28 N 30.43;

Found C 49.16 H 3.27 N 30.54

^1H NMR (DMSO- d_6) 3.22 (s, 2H), 7.29 (s, 1H), 7.37 (m, 2H), 7.52 (m, 2H), 9.07 (s, 4H), 9.34 (d, 1H)

MS⁺ 368 (4.1), 229 (100), 183 (26.7), 140 (20.6), 125 (28.1) 104 (58.5), 79 (18.8), 77 (16.8)

2) N, N'-bis (5-nitropyrimidyl-2)-2-methoxyphenylmethanedianiline (BNPMOP-MDA)

0.28 g NAPyr (2 mmol) and 0.27 g 2-methoxybenzaldehyde (2 mmol) were mixed well in a round-bottom flask with magnetic stirrer. Five drops of acetic acid were dropped into the mixture. It was stirred and heated at about 160°C for two hours. The solid was cooled down to room temperature, 30ml water was added and stirred, the aqueous layer was poured, 30 ml acetone added. Under stirring the white solid was precipitated, then it was collected with filter and washed with acetone for several times. Yield 0.52 g (70%). mp. > 250°C (decomp.)

for Calcd. $C_{16}H_{14}N_8O_5$ C 48.24 H 3.52 N 28.14;

Found C 48.10 H 3.47 N 28.16

^1H NMR (DMSO- d_6) 3.22 (s, 2H), 3.80 (s, 3H), 6.91–7.05 (m, 2H), 7.28–7.51 (m, 2H), 9.07 (s, 4H), 9.22 (d, 1H)

MS⁺ 398 (3.4), 259 (71.5), 227 (22.5), 213 (14.0), 140 (37.5), 134 (16.1), 118 (100), 107 (23.9), 104 (11.3), 91 (48.2), 79 (22.0), 77 (12.8)

3) N, N'-bis (5-nitropyrimidyl-2)-furanmethanedianiline (BNPFMDA)

To a 50 ml two-neck round-bottom flask with a condenser, 0.28 g NAPyr (2mmol) and 6 ml cumene were added. The mixture was heated at 130°C and refluxed about 30 mins to form a solution. 0.19 g furfuraldehyde (2 mmol) was dropped and refluxed for more than 8 hours. The solid was collected after cooling down to room temperature with filter and washed with 20ml isopropyl alcohol for three times. Yield 0.35 g (49%) mp. > 200°C (decomp.)

for Calcd. $C_{13}H_{10}N_8O_5$ C 43.58 H 2.79 N 31.28

Found C 43.20 H 2.71 N 30.59.

^1H NMR (DMSO- d_6) 3.31 (s, 2H), 6.45 (d, 2H), 7.36 (m, 1H), 9.07 (s, 4H), 9.50 (d, 1H)

MS⁺ 358 (16.5), 218 (50.0), 190 (100), 140 (69.7), 125 (26.5), 120 (14.6), 94 (19.2), 79 (27.7), 67 (23.1)

2. Measurements of $\beta\mu$ of synthesized chromophores

The $\beta\mu$ values of synthesized Λ -shaped nitropyrimidine derivatives were mea-

sured by the solvatochromic method based on the quantum mechanical two-level model reported previously^[4]. The parameters required in the calculation include the molecular ground-state dipole moment μ_g , transition frequency ω_{eg} , transition dipole moment μ_{eg} , the difference between the excited-state and ground-state dipole moment $\mu_e - \mu_g$ and the positions and intensities of molecular maximum absorption bands. They can be determined through measuring the molecular dielectric constants in the desired solutions of various chromophore concentrations and the electric absorption spectra in different polar solvents. Used instruments were TNP KB-1 Q-meter (made in the former USSR) and Hitachi 340 spectrometer.

3. Preparation of thin film of BNPMOPMDA doped in PMMA

Uniform films were made by casting the twice-filtered solution of BNPMOPMDA and PMMA in DMSO, in which molar ratio of chromophore with PMMA was 1.2 mol%, onto ITO conducting glass under heating at about 80°C. The formed films were dried in vacuum (10^{-2} torr) at 60°C for one day and night to remove residual solvent completely.

4. In-situ poling and SHG measurements of the doped films

As described in Ref. [5], the dried films were poled at 110°C using a corona-discharge setup under in-situ conditions. The second order nonlinearity of poled films was measured with Nd:YAG system simultaneously.

RESULTS AND DISCUSSION

As mentioned, higher $\beta\mu$ values and good transparency in fundamental and doubling frequency of used laser are the essential requirements for second order nonlinear optical materials in the frequency doubling applications. The concept of Λ -shaped molecule was suggested by Miyata^[6] at first. In the molecules two independent hyperpolarizable moieties are linked by σ -bonds, so that the intramolecular charge transfer contributing to β has almost a two-dimensional character. Therefore, the largest molecular hyperpolarizability tensor β_{ijk} is a nondiagonal component. It had been shown in their experiments that synthesized Λ -shaped molecules stack easily along one direction. In addition, these molecules in their most stable conformation display an internal angle of about 120° between the two charge transfer axes, the higher β value will be obtained according to the vector addition. For example, N, N'-bis (4-nitrophenyl)-methanediamine (NMDA) possess large second order nonlinearity (80 times that of urea). In organic chemistry, Dewar's rules^[7] has suggested that the molecular absorption wavelength can be adjusted through introducing substituent and heteroatom substitution at different position of conjugated backbone of intramolecular charge transfer molecules, when the placement of

more electronegative atom at the β positions of electronic donor in chromophore the absorption wavelength of the compound will produce a large hypsochromic shift. These rules pointed out the more favorable transparency/nonlinearity tradeoff by replacing benzene ring with pyridine ring or pyrimidine ring. It can be well illustrated from the maximum absorption wavelength of p-NA, 2-amino-5-nitropyridine and NAPyr, which are 375, 342 and 316nm, respectively. To combine the concept of Λ -shaped molecular structure and Dewar's rules the Λ -shaped nitropyrimidine derivatives have been designed and synthesized. In these compounds two NAPyr moieties are bonded together via a benzyl or furfuryl bridge. As similar to Miyata's NDMA, pure products can be easily obtained by condensation between one mole relative aldehyde and two moles amine of NAPyr. Sometimes small amount of acid needs to be used as catalyst. All of synthesized compounds possess higher decomposition temperature ($> 200^\circ\text{C}$).

Table 1 gives the results of the solvatochromic measurements of synthesized Λ -shaped nitropyrimidine derivatives. For comparison, the relative values of p-NA, NAPyr and NMDA are listed, too.

Table 1 Comparison of λ and $\beta\mu$ of synthesized Λ -shaped compounds with its analogues

Compound	λ_{max} (nm) (in 1, 4-dioxane)	$\beta\mu(\times 10^{-46}\text{esu})$ (1064nm)	mp. ($^\circ\text{C}$)	Ref.
BNPPMDA	319	0.39	>250 (dec.)	this work
BNPMOPMDA	327	1.27	> 250 (dec.)	this work
BNPFMDA	318	1.36	> 200 (dec.)	this work
NMDA	367	1.39	240	[6]
p-NA	353	1.21		[5]
NAPyr	295	0.48	238	this work

From Table 1, it can be seen that the maximum absorption wavelengths of synthesized Λ -shaped compounds are blue-shifted about 40–50 nm from that of benzene ring analogous NMDA. The cut-off absorption wavelengths of synthesized compounds are all shorter than 400 nm. These coincide with the prediction of Dewar's rules well. The $\beta\mu$ of BNPMOPMDA and BNPFMDA possess almost the same values with that of NMDA although they have shorter absorption wavelengths. It indicates that Λ -shaped molecular configuration plays an important role in determining their first order hyperpolarizability. The above results show that these new Λ -shaped compounds could be a good nonlinear optical chromophore for blue-light emission by frequency doubling of semiconductor laser.

For the application of molecular nonlinear optics the poled polymer is one of the

most important and effective materials. The thin film of BNPMOPMDA doped in PMMA has been prepared and its poling properties investigated. Poling temperature was set at 110°C, where rapid onset of SHG signal was observed. In-situ SHG measurements showed that second order nonlinear optical coefficient d_{33} of poled films are in the range of $1.2\text{--}2.0 \times 10^{-9}$ esu. It is worthy to notice that the chromophore concentration in the measured films is 1.2 mol% only. Based on the one-dimensional rigid orientation gas model (1D ROGM), which is always used to describe nonlinearity of poled polymer films, d_{33} of poled film is proportional to the contained number density of chromophore. So it can be expected that d_{33} will be increased significantly if the higher number density chromophore-functionalized polymer containing synthesized Λ -shaped nitropyrimidine derivatives as side chain can be synthesized. It will be hopeful to meet the application requirements of 10^{-8} esu.

In summary, three new Λ -shaped nitropyrimidine compounds with benzyl or furfuryl as bridge have been synthesized and their first hyperpolarizabilities have been measured by solvatochromic method. They display similar $\beta\mu$ values to p-NA, however their absorption wavelengths have been blue-shifted obviously. The poling experiments of BNPMOPMDA doped in PMMA film show that the chromophore-functionalized polymer may be a promising material for the frequency doubling of semiconductor laser.

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Keywords:

Blue-light transparent materials; Λ -shaped compounds; Nitropyrimidine derivatives; Second harmonic generation; Poled polymer

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