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Novel nonlinearity–transparency–thermal stability trade-off of thiazolylazopyrimidine chromophores for nonlinear optical application

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Novel, nonlinear optical thiazolylazopyrimidine chromophores were synthesized and characterized by UV–vis spectroscopy, hyper-Rayleigh light scattering and thermogravimetric analysis. The thiazolylazopyrimidine chromophores exhibited large molecular hyperpolarizabilities which were larger than that of a chromophore derived from 4-nitroaniline, owing to the presence of the electron-deficient thiazole ring at the acceptor end of the molecule. Moreover, in comparison with an analogous aniline based chromophore, the thiazolylazopyrimidine chromophores displayed a large blue shift due to the presence of the electron-poor pyrimidine ring at the donor end molecule, resulting in an improvement in optical transparency. The thiazolylazopyrimidine chromophores displayed high thermal stability owing to the presence of the thiazole and pyrimidine rings. Such novel, nonlinear optical thiazolylazopyrimidine chromophores are distinguished by good nonlinearity–transparency–thermal stability trade-off for nonlinear optical application.

1. Introduction

Chromophore-containing polymeric electro-optic materials have been intensively studied during the past two decades due to their promising applications in information processing and fiber communication. This interest is motivated not only by the large NLO response but also by the versatility, ease of processing, and possibility of tailoring the physicochemical properties by the molecular engineering approach. For the application of NLO polymers, it is important to optimize the comprehensive properties, especially the transparency. The transparency in the near-infrared region (1.0–1.7 μm), such as 1.3 μm and 1.5 μm, is required, rather than that in the visible range. Usually, NLO chromophores, the active components in the NLO polymers, must possess a good nonlinearity–transparency–thermal stability trade-off for nonlinear optical application. In spite of different types of chromophores used for NLO application, azo chromophores have attracted much attention because they can be readily prepared with a wide range of donor and acceptor groups and also because the planarity of the azo bridge versus non-planarity of other systems such as stilbenes should contribute to larger π electron transfer properties of the system and result in larger NLO responses. Although there has been tremendous progress in enhancing the first hyperpolarizability of the chromophore, the harmony and balance of the aforementioned three issues for NLO chromophore remain unsolved, which limits its practical applications in photonics.

Recently, some authors reported the synthesis and characterization of new chromophores in which heteroaromatic rings, such as thiazole [1–4], benzothiazole [5–15] and thiophene [16–20] are employed as conjugating units, which exhibit good nonlinear optical properties. However, the color chemistry studies have evidenced that the replacement of a benzene ring by a less aromatic heterocycle will result in a significant bathochromic shift of the visible absorption band due to the deficiency of electron density on the heterocycle C-atom [21]. Hence the hetarylazo chromophores, which exhibit larger molecular hyperpolarizabilities than that of their benzenoid analogues, are generally accompanied by a large bathochromic shift of the visible absorption band. In the past years we have synthesized some hetarylazo chromophores derived from amino-substituted thiazole [22] and benzothiazole [23–25] as diazo components and aniline derivatives as coupling components. The hetarylazo chromophores possess large β values but produce a pronounced bathochromic shift when compared to the corresponding benzenoid compounds.

To overcome bathochromic shifts of the visible absorption band of conventional azo chromophores, it has been shown in the literature [26] that nitrogen heterocycles were introduced into NLO chromophores to improve optical transparency and thermal stability. However, some chromophores with high transparency and good thermal stability are generally accompanied by low β responses. In continuation of our work, in order to improve optical transparency,

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thermal stability and maintain good nonlinearity, the pyrimidine ring was introduced into the chromophores and some novel thiazolylazopyrimidine chromophores were prepared through an azo coupling reaction. These new NLO chromophores are distinguished by good transparency, thermal stability and large optical nonlinearity for nonlinear optical application. Furthermore, the thiazolylazopyrimidine chromophores containing amino groups and hydroxyl groups can be easily incorporated into polymers through covalent bonds to improve relaxation behavior, which gives these chromophores broad applications.

2. Experimental

2.1. Materials

C.I. Disperse Red 1 (**DR1**, purity >95%), 2-amino-5-nitrothiazole, 4-nitroaniline, 2-chloropyrimidine, 2-aminopyrimidine and *N*-ethyl-*N*-(2-hydroxyethyl) aniline were obtained from Aldrich Chemical Co. All the regents and solvents were analytically pure and used without further purification.

2.2. Synthesis of 2-2′-hydroxyethylaminopyrimidine

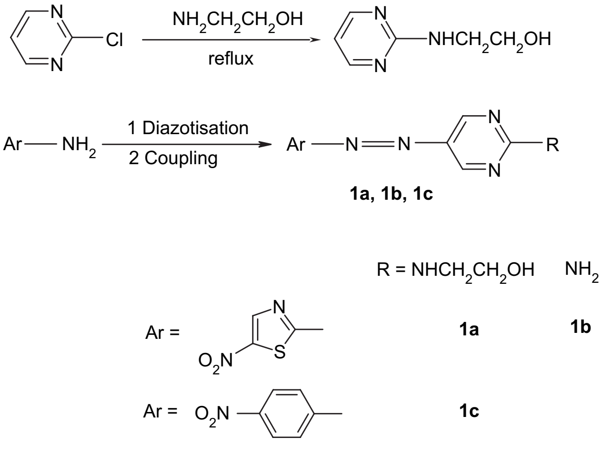
2-Chloropyrimidine (26 g, 1 mol) and ethanolamine (34.5 g, 2.5 mol) in ethanol (150 mL) were refluxed for 1 h, the solvent evaporated, the residue poured into cold water (100 mL), saturated with sodium chloride, the pH adjusted to 11 with 5 mol/L sodium hydroxide, and the whole extracted with chloroform (12 × 75 mL). The dried extract was evaporated and the residue crystallized from benzene–light petroleum to provide 2-2′-hydroxyethylaminopyrimidine (21.8 g, 70%).

2.3. Synthesis of azo chromophores **1a**,**b** and **c** (Scheme 1)

Azo chromophores were prepared by diazotization of the variously substituted amines followed by coupling with pyrimidine derivatives (Scheme 1). The completion of diazotization was checked by checking for the presence of excess nitrous acid using starch-iodide paper. The progress of the coupling reaction was checked according to the literature [27].

2.3.1. Diazotisation

2-Amino-5-nitrothiazole (14.5 g, 0.1 mol) was dissolved into 100 mL of 1:5 propionic–acetic acid mixtures. Sodium nitrite (7.6 g, 0.11 mol) was added to 98% concentrated sulfuric acid (50 mL) slowly at 0–5 °C with stirring, and then the temperature was increased to 30 °C to dissolve the $NaNO_2$. The temperature was reduced to 0 °C again and the propionic–acetic acid mixtures were added 120 mL dropwise while controlling the temperature below 10 °C. After that, it was stirred for 0.5 h, cooled down to 0 °C, and then the solution of 2-amino-5-nitrothiazole was added at 0–5 °C. The resulting mass was stirred for 2 h at 0 °C to afford a dense solution of 2-amino-5-nitrothiazole diazonium salt.



Scheme 1. Synthesis of chromophores **1a**,**b** and **c**.

4-Nitroaniline (13.8 g, 0.1 mol) was dissolved into 18% hydrochloride solution (60 mL) and stirred overnight at room temperature. The mixture was cooled to 0 °C, a solution of sodium nitrite (6.9 g, 0.1 mol) dissolved in 30 mL cold water was added dropwise to the reaction mixture and the mixture was stirred for a further 1 h at 0–5 °C to afford a clear solution of 4-nitroaniline diazonium salt.

2.3.2. Coupling

A solution of the pyrimidine derivative (0.1 mol) dissolved in glacial acetic acid (50 mL) was added slowly dropwise to the diazonium solution at 0 °C with vigorous stirring. The reaction mixture was then stirred for 2 h at 0–5 °C, followed by neutralization (pH 5–6) with ammonia, and stirred for 1 h. The precipitate was filtered off and washed with plenty of water.

*2.3.2.1. Chromophore **1a**.* Yield of crude product 55%, blue brown crystals purified by recrystallization (acetone). m.p. 220 °C. ^1H NMR (DMSO): $\delta = 1.99$ (s, 1H, O*H*), 2.29 (t, 2H, NHCH_2), 2.50 (t, 2H, CH_2O), 7.06 (s, 1H, N*H*), 8.35 (s, 1H, pyrimidine-*H*), 8.36 (s, 1H, pyrimidine-*H*), 8.99 (s, 1H, thiazole-*H*). IR (KBr, cm^{-1}): 3392 (–OH), 1520 (–NO_2, ν_{as}), 1350 (–NO_2, ν_s), 1473 (N=N). Anal. Calcd for $C_9H_9N_7O_3S$ (295.3): C, 36.61; H, 3.07; N, 33.20. Found: C, 36.66; H, 3.06; N, 33.25.

*2.3.2.2. Chromophore **1b**.* Yield of crude product 50%, blue brown crystals purified by recrystallization (acetone). m.p. 210 °C. ^1H NMR (DMSO): $\delta = 7.50$ (s, 2H, NH_2), 8.38 (s, 1H, pyrimidine-*H*), 8.37 (s, 1H, pyrimidine-*H*), 8.98 (s, 1H, thiazole-H). IR (KBr, cm^{-1}): 3425 (–NH), 1525 (–NO_2, ν_{as}), 1353 (–NO_2, ν_s), 1477 (N=N). Anal. Calcd for $C_7H_5N_7O_2S$ (251.2): C, 33.47; H, 2.01; N, 39.03. Found: C, 33.51; H, 2.03; N, 39.09.

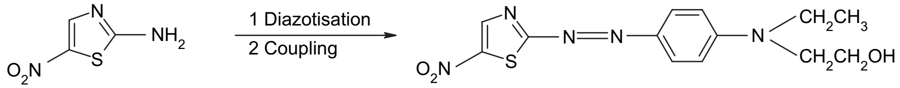
*2.3.2.3. Chromophore **1c**.* Yield of crude product 50%, yellow crystals purified by recrystallization (ethanol). m.p. 190 °C. ^1H NMR (DMSO): $\delta = 2.10$ (s, 1H, O*H*), 2.27 (t, 2H, NHCH_2), 2.50 (t, 2H, CH_2O), 7.24 (s, 1H, N*H*), 7.75 (d, 2H, Ar-*H*), 8.35 (d, 2H, Ar-*H*), 8.70 (s, 1H, pyrimidine-*H*), 8.71 (s, 1H, pyrimidine-*H*). IR (KBr, cm^{-1}): 3396 (–OH), 1508 (–NO_2, ν_{as}), 1342 (–NO_2, ν_s), 1470 (N=N). Anal. Calcd for $C_{12}H_{12}N_6O_3$ (288.3): C, 49.99; H, 4.20; N, 29.15. Found: C, 50.03; H, 4.22; N, 29.20.

2.4. Synthesis of azo chromophore **2a** (Scheme 2)

The synthesis of chromophore **2a** was described in a previous article (Scheme 2) [22]. Yield of crude product 50%, green crystals purified by recrystallization (ethanol). m.p. 184 °C. ^1H NMR ($CDCl_3$): $\delta = 1.30$ (t, 3H, CH_3), 2.07 (s, 1H, O*H*), 3.63 (m, 2H, CH_2CH$_3$), 3.75 (t, 2H, NCH_2), 3.96 (t, 2H, CH_2O), 6.83 (d, 2H, Ar-*H*), 7.93 (d, 2H, Ar-*H*), 8.60 (s, 1H, N–C*H*=C). IR (KBr, cm^{-1}): 3396 (–OH), 2981, 2924 (–CH_3, –CH_2), 1602 (–C_6H_4), 1517 (–NO_2, ν_{as}), 1347 (–NO_2, ν_s), 1486 (N=N). Anal. Calcd for $C_{13}H_{15}N_5O_3S$ (321.4): C, 48.58; H, 4.70; N, 21.79. Found: C, 48.50; H, 4.67; N, 21.70.

2.5. Characterization

UV–vis spectra were recorded on a Shimadzu UV 2201 spectrometer from chromophores solutions in tetrahydrofuran (THF) or *N*,*N*-dimethylfomamide (DMF) at a concentration of 1.667×10^{-5} mol/L. Fourier transform-infrared spectra (FT-IR) were recorded on a Nicolet 750 series in the region of 4000–400 cm^{-1} using KBr pellets. ^1H NMR data were obtained with a Bruker 300 MHz



2a

Scheme 2. Synthesis of chromophore **2a**.

spectrometer using dimethyl sulphoxide (DMSO) or $CDCl_3$ as solvent and tetramethyl silane (TMS) as internal standard. Elemental analysis was obtained using a Perkin–Elmer Lambda 6 elemental analyzer. Thermal degradation temperature was obtained with SDT Q600 thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen atmosphere. Melting points were obtained with a WRS-2A microcomputer melting point apparatus.

2.6. Nonlinear optical measurements

The molecular first hyperpolarizabilities were measured by HRS method. In the HRS experiment, a fundamental wavelength of 1064 nm from a Q-switched Nd:YAG laser (10 ns, 10 Hz, pulse energy: $\leq$10 mJ) was used for the nanosecond HRS experiments. The well-studied NLO chromophore *p*-nitroaniline (PNA) was used as an external reference ($\beta = 3.7 \times 10^{-29}$ esu in DMF). Samples were dissolved in DMF and filtered through 0.2 μm filters before being measured. A series of the solutions of different concentrations for each compound were obtained by serial dilution of a concentrated standard.

3. Results and discussion

3.1. Preparation of the azo chromophores

The synthetic procedures of the azo chromophores (**1a**,**b**,**c** and **2a**) are shown in Schemes 1 and 2. The chromophores were obtained by coupling pyrimidine derivatives and aniline derivatives, respectively, with relevant diazotised amines.

Two types of nitrosating reagent, nitrosyl chloride from $NaNO_2$/HCl solution and nitrosylsulphuric acid from $NaNO_2$/concentrated H_2SO_4, were used for diazotisation of the variously substituted amines. Most of the mono-substituted carbo-aromatic anilines were diazotized by $NaNO_2$/HCl solution since the mild acidity of this reagent resulted in relatively smaller amount of by-products. More weakly basic heteroaromatic amines, such as 2-amino-5-nitrothiazole, demand the use of $NaNO_2$/concentrated H_2SO_4. Due to the weak basicity of heteroaromatic amines and the protonation of the heterocycle *N*-atom in acid, the formation of stable diazonium salts becomes difficult. Thus the nitrosyl sulfuric acid with high reactivity is selected as a diazotizing agent.

By adding a glacial acid solution containing coupling component continuously to the resulting diazonium salt, subsequent coupling reaction took place readily on when keeping the coupling temperature below 5 °C. The pH of the reaction mixture was eventually adjusted to approximately 5–6 by ammonia in order to complete the coupling.

3.2. The linear optical properties

The absorption spectra of the chromophores dissolved into both THF and DMF were used to determine the wavelength of the maximum absorption peak. The values of maximum absorption wavelength in UV–vis spectra are shown in Table 1. It can be seen that these chromophores show red shifts in stronger polar solvent (DMF) than in the weaker polar solvent (THF) and display positive solvatochromism as the polarity of the solvents increased.

UV–vis absorption spectra of the chromophores **1a**,**b**,**c** and **2a** in THF are shown in Fig. 1. Comparing the absorption maxima of chromophores **1a** and **b**, replacement of NH_2 group by $NHCH_2CH_2OH$ group produces slight bathochromic shifts of λ_{max} in THF, reflecting the higher electron-releasing property of the $NHCH_2CH_2OH$ group.

Heterocyclic systems containing sulphur as the π-excessive heteroatom afford very electronegative diazo components and, consequently, provide a pronounced bathochromic effect in comparison with the corresponding benzenoid compounds. In Fig. 1 the λ_{max} of chromophore **1a**, which contains a nitrothiazole moiety as the acceptor ring, shows significant bathochromic shifts in THF compared to corresponding chromophore **1c**, derived from 4-nitroaniline. Similar red shifts are apparent for chromophore **2a**, which absorbs at longer wavelength than **DR1**, as shown in Table 1. The reason of the large red shifts peculiar to these heterocyclic systems is that an electron-withdrawing NO_2 group is appended to an electron-deficient thiazole ring to enhance the acceptor ability of the acceptor substituent and thus lead to large bathochromic shift. However, this large bathochromic shift is beneficial to give large NLO response.

Examination of the chromophores **1a**,**b** and **2a** allows us to examine the role of the pyrimidine ring in the molecules in relation to the linear optical properties. As shown in Fig. 1, thiazolylazopyrimidine chromophores **1a** and **b** display more blue-shifted absorption maxima in THF than analogous aniline based chromophore **2a**. Similar observations have also been made for chromophores **1c** and **DR1** from Table 1. The aromatic six-membered heterocyclic pyrimidine is termed electron-deficient since the heteroatom is more electronegative than carbon. The electron-poor heterocyclic pyrimidine strongly withdraws excessive electron density from electron-donating NH_2 and $NHCH_2CH_2OH$ groups through inductive effects, thereby decreasing the donor ability of the donors. Thus the intermolecular charge transfer between the donor and acceptor groups is reduced and the absorption maxima are significantly blue-shifted. The deviation of the absorption band from the operating wavelengths of the laser for telecommunication may help to decrease the absorption optical loss. Therefore, thiazolylazopyrimidine chromophores **1a** and **b** exhibit improved optical transparency and their absorption optical loss are reduced greatly. In addition it has been shown in Table 1 that the cut-off wavelengths of the chromophores **1a**,**b**,**c** and **2a** in both THF and DMF are below 735 nm exhibiting good optical transparency.

3.3. The nonlinear optical properties

The method we have chosen to determine the first hyperpolarizability of the chromophores is based on HRS technique. The

Table 1
Linear and nonlinear optical properties of the chromophores at 1064 nm measurement and their thermal stabilities

Chromophore	$\lambda_{max}/\lambda_{cut\text{-}off}$ (nm)		$\beta \times 10^{-30}$ (esu)	T_d (°C)
	THF	DMF		
1a	527/680	544/731	510	285
1b	520/680	540/731	500	280
1c	464/649	475/684	80	255
2a	567/688	590/733	560	224
DR1	491[a]	503[a]	90	250[b]

[a] λ_{max} Value of **DR1** is from Ref. [11].
[b] T_d Value of **DR1** is from Ref. [2].

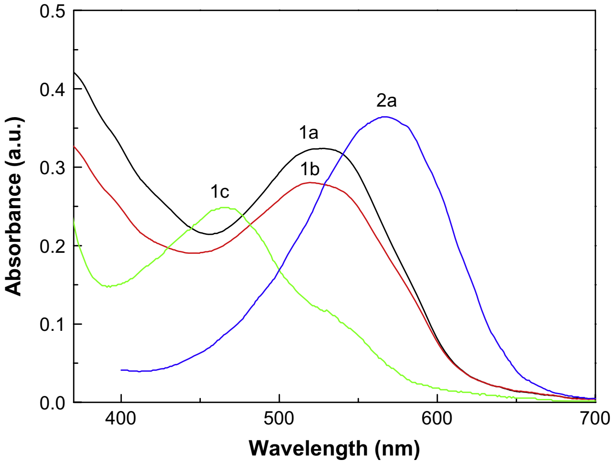


Fig. 1. UV–vis spectra of chromophores **1a**,**b**,**c** and **2a** in THF.

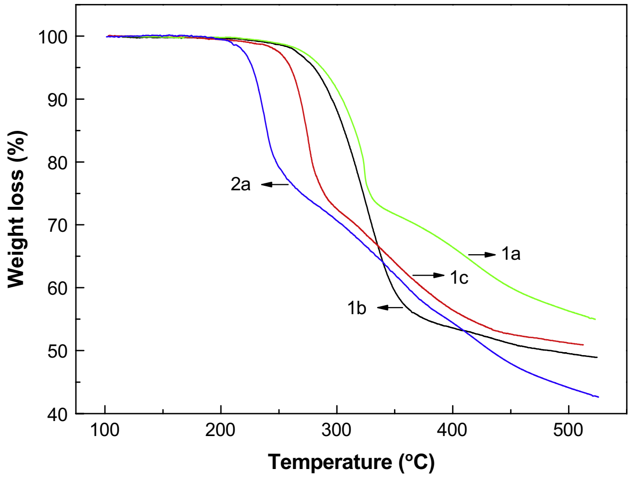


Fig. 2. TGA of chromophores **1a**,**b**,**c** and **2a**.

HRS technique has a lot of advantages over the electric field induced second harmonic generation (EFISH); it has been demonstrated as a useful and simple method to characterize the β values. β Values for these chromophores at the fundamental wavelength of 1604 nm are listed in Table 1. β Value of chromophore **1a** is larger than that of chromophore **1b**. It can be concluded that the $NHCH_2CH_2OH$ group is a strong electron-donating group in comparison with the NH_2 group and the strong electron-donating group on the donor side should be responsible for the high β value.

Conjugating moieties also have effect on the β values. As shown in Table 1, although the thiazolylazopyrimidine chromophores **1a** and **b** display high molecular hyperpolarizabilities with the values of 510×10^{-30} esu and 500×10^{-30} esu, respectively, the β values of the chromophores **1a** and **b** are lower than that of the analogous aniline based chromophore **2a**. The same results have been obtained for chromophores **1c** and **DR1**. The electron-donating NH_2 and $NHCH_2CH_2OH$ groups are appended to the electron-deficient pyrimidine ring to reduce the donor ability of the donor substituents and hence decrease the NLO responses. Now, let us pay our attention to the large β values of the thiazolylazopyrimidine chromophores **1a**,**b**. From Table 1, the trends in β values of chromophores **1a**,**b** and **c** clearly point out that replacing a benzene ring by a thiazole ring on the acceptor end causes a dramatic enhancement in β values. The β values of chromophores **1a** and **b**, which contains a nitrothiazole moiety as the acceptor ring, are more than 6 times of that of chromophore **1c** derived from 4-nitroaniline; similarly the β value of **2a** is larger than that of **DR1**. Theoretical calculations indicate that lower aromatic delocalization energy and electron-deficient moieties on the acceptor side can enhance NLO response, and the latter plays more important role in this enhancement [28]. Thiazole (25 kcal/mol) possesses lower aromatic delocalization energy than benzene (36 kcal/mol) and, therefore, is expected to be more effective than benzene in promoting charge transmission, thus increasing the β values. However, this description is oversimplified. Theoretical studies reveal that the lower delocalization energy of heterocyclic rings is not the only major factor which determines the first hyperpolarizability and the magnitude of β is determined not only by the nature of the heterocyclic ring but also by its location [29]. The electron-poor thiazole ring, which is substituted by an electron-withdrawing NO_2 group strongly withdraws electron density from acceptor substituent, thus increasing the acceptor ability of the nitro group and acting as auxiliary acceptor. This increased acceptor ability leads to a substantial increase in NLO response. In addition, it is forecast theoretically that β values will be lower if thiazole ring is replaced by thiophene in chromophores **1a** and **b**. As Varanasi et al. [29] said that the presence of electron deficient ring on the acceptor end of the molecular system caused an enhancement in β values. Due to the –C=N– linkage, thiazole ring with two heteroatoms is electron-deficient in nature in contrast to thiophene ring containing one heteroatom. More electron-deficient thiazole rings assist the nitro group resulting in a more pronounced electron-accepting effect in chromophores **1a** and **b**. Comparatively less electron-deficient thiophene ring produces similar but much less pronounced effect. Furthermore, thiazole possesses lower aromatic delocalization energy than thiophene (29 kcal/mol). Therefore, we can predict that β values will be reduced if thiazole ring is replaced by thiophene in chromophores **1a** and **b**. Similarly, Qiu et al. [2] predicted that β values were lower if thiazole moiety was replaced by thiophene in chromophores.

3.4. *Thermal stabilities*

Thermal stability is an important requirement for the incorporation of new chromophores in poled-polymer structures. The thermal stability was evaluated by measuring the decomposition temperatures (T_d) of the chromophores and the results are listed in Table 1. Fig. 2 shows the thermal gravity analysis (TGA) thermograms of the chromophores **1a**,**b**,**c** and **2a**. Comparing the decomposition temperatures of chromophores **1a**,**b** and **2a**, the thiazolylazopyrimidine chromophores **1a** and **b** have higher thermal decomposition temperatures than analogous aniline based chromophore **2a**. It can be concluded that the incorporation of pyrimidine into chromophores has been much effective in enhancing the thermal stability of the chromophores. The decomposition temperatures of the thiazolylazopyrimidine chromophores **1a** and **b** are higher than **1c**, indicating that the thermal stabilities of the chromophores increase when replacing benzene ring with thiazole ring. In addition the chromophores **1a**,**b** and **c** exhibit T_d values higher than **DR1**, thus displaying high thermal stability and making those good chromophores for the incorporation into polymer.

4. Conclusion

The new NLO thiazolylazopyrimidine chromophores have been synthesized by diazo coupling reaction for potential NLO applications. The thiazolylazopyrimidine chromophores **1a** and **b** exhibit large molecular hyperpolarizabilities with the values of 510×10^{-30} esu and 500×10^{-30} esu, respectively, which are larger than that of chromophore **1c** derived from 4-nitroaniline. In comparison with analogous aniline based chromophore **2a**, the thiazolylazopyrimidine chromophores **1a** and **b** display 40–50 nm blue shift of λ_{max}. Thus these chromophores possess an obviously improved optical transparency and the absorption optical loss can be decreased greatly. The thiazolylazopyrimidine chromophores **1a** and **b** possess high thermal stability with the decomposition temperatures of 285 °C and 280 °C, respectively, on account of the introduction of the thiazole and pyrimidine rings into chromophores. Therefore, the thiazolylazopyrimidine chromophores exhibit good nonlinearity–thermal stability trade-off and appear to be the most attractive candidates for electro-optic applications and synthetic design to attach these chromophores to the NLO polymers is in progress.

Acknowledgments

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