

Synthesis, Structural, Thermal and Photo-Physical Properties of Triazine Based NLO Material

M. Shyamala Devi · P. Tharmaraj · C. D. Sheela · R. Ebenezer

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Abstract Three novel triazine based organic chromophores with D- π -A (Donor- π system- Acceptor) push-pull type have been synthesized from 2, 4-diamino-6-phenyl-1,3,5-triazine as a starting material. Structures of all the three compounds have been confirmed by UV-Visible absorption, FT-IR, NMR and Mass spectral techniques. Their photo physical and thermal properties have been investigated. Among the three compounds, 6-phenyl-2,4-((4-amino-1,5-dimethyl-2-phenyl pyrazol-3-ylidene)(4-nitro benzylidene))-diamino-1, 3, 5-triazine (NDP) showed positive solvatochromism compared to the other two compounds. The absorption in the UV region of these three compounds were found to be less dependent on solvent polarities, whereas the red shifted fluorescence was strongly dependent on solvent polarities. The TGA data indicates that all the three compounds are stable up to 160 °C. Measurement of non linear optical properties showed that there is an increased second harmonic generation (SHG) efficiency with respect to urea indicating the existence of high molecular nonlinearity in NDP.

Keywords Fluorescence · Solvatochromism · Intra molecular charge transfer · SHG

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M. S. Devi · P. Tharmaraj (✉) · R. Ebenezer
Department of Chemistry, Thiagarajar College,
Madurai 625 009, India
e-mail: sheelatharmaraj@gmail.com

C. D. Sheela
Department of Chemistry, The American College,
Madurai 625 002, India

Introduction

Recently the field of molecular nonlinear optics has attracted the attention of the researchers to search for nonlinear optical materials [1] and to improve the NLO efficiency of the known materials. Moreover, molecular nonlinearity deals with the essential issues such as charge transfer, hyper polarizabilities, conjugation and various applications in different fields including telecommunications [2], optical data storage and information processing [3], micro fabrication [4–6] and biological imaging [7, 8]. The strategy used to design π -electron chromophores for second-order NLO applications is to end-cap a suitably conjugated bridge with donor (D) and acceptor (A) groups. So it has been better understood that the second order molecular non linearity can be enhanced by large delocalized π -electron systems with the strong push-pull chromophores [9, 10] at two non equivalent ends. The triazine derivatives end-capped with donor/acceptor can produce high molecular nonlinearity.

It has been investigated that the D- π -A dipolar chromophores exhibit intense, low energy absorption bands due to intra molecular charge transfer (ICT) between two groups of opposite nature [11] and electron donors such as triphenyl amine [12], diphenyl amine [13], carbazole [14], and 1,3,5-triazines [15] with high electron mobility, thermal and photo chemical stability have commonly been used as hole transporting materials or light emitting materials, since they have a wide range of applications in photovoltaic cells [16], organic light emitting diodes (OLED) [17] and polymer fields [18].

Based on the above strategy, we have designed and synthesized a set of three donor-acceptor substituted conjugated systems in which we have used 4-amino antipyrine and 4-methyl acetophenone as donor moieties functionalized with thiophenyl and nitro acceptor groups. This study opens a new route for designing efficient materials for non linear optics.

Experimental

Materials and Methods

All solvents including acetonitrile, dichloromethane (DCM), dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (ETOH) and ethyl acetate (ETOAC) were of analytical grade and were procured from SD fine chemicals Limited (India) and were used without purification. All the measurements were carried out at room temperature.

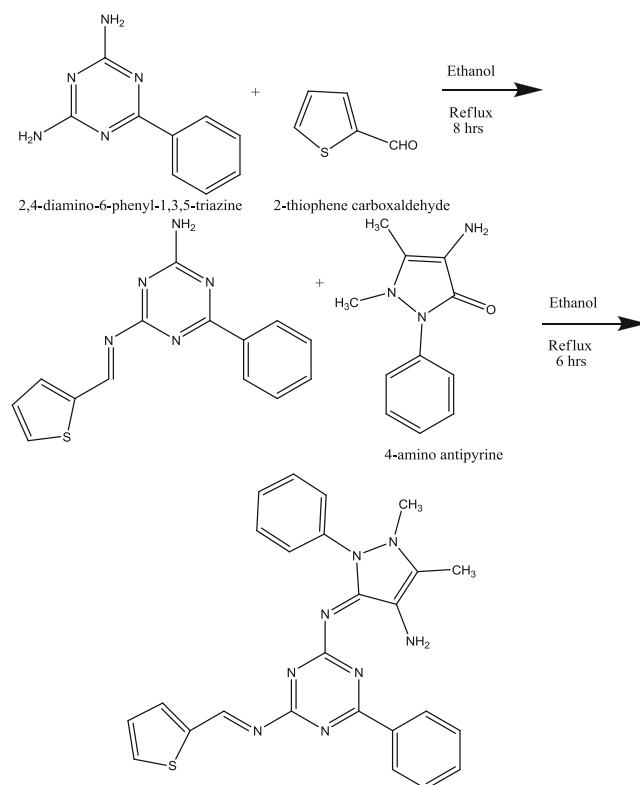
The absorption spectra of the compounds were recorded on a THERMO FISHER SPECTRONIC 6 HEXIOS α . Fluorescence spectrum was performed on ELICO SL174 spectrofluorometer. The FT-IR spectra were recorded on Perkin-Elmer 257 spectrophotometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on BRUKER 400-MHz instrument (USA) using TMS as an internal standard. GEOL GC MATE-2 mass spectrometer was used to record EI Mass spectra. TGA measurements were made on TA Q-50 instrument and 2–3 mg sample was taken for analysis. The sample purge was oxygen free, dry nitrogen gas at the flow rate of 60 cc/min and the balance purge was nitrogen gas at the flow rate of 40 cc/min. [19]. A heating rate of 20 $^\circ\text{C}/\text{min}$ was maintained for all the samples.

Synthesis and Characterization of Compounds

Synthesis of 6-phenyl-2,4-((4-amino-1,5-dimethyl-2-phenyl pyrazol-3-ylidene)(thiophen-2-ylmethylene))-diamino-1,3,5-triazine (TDP) A solution of 3.74 g (20 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine in ethanol (20 ml) was added slowly to 2.24 g (20 mmol) of 2-thiophene carboxaldehyde. The reaction mixture was refluxed under stirring for 8 h and then cooled to room temperature. The resulting mixture on filtration gave yellow precipitate. A solution of 1.96 g (7 mmol) of the above precipitate in ethanol (20 ml) was added drop wise to an ethanol (20 ml) solution of 1.42 g (7 mmol) of 4-amino antipyrine with continuous stirring. After refluxed for 6 h the light yellow precipitate TDP obtained was filtered, dried and recrystallized from ethanol.

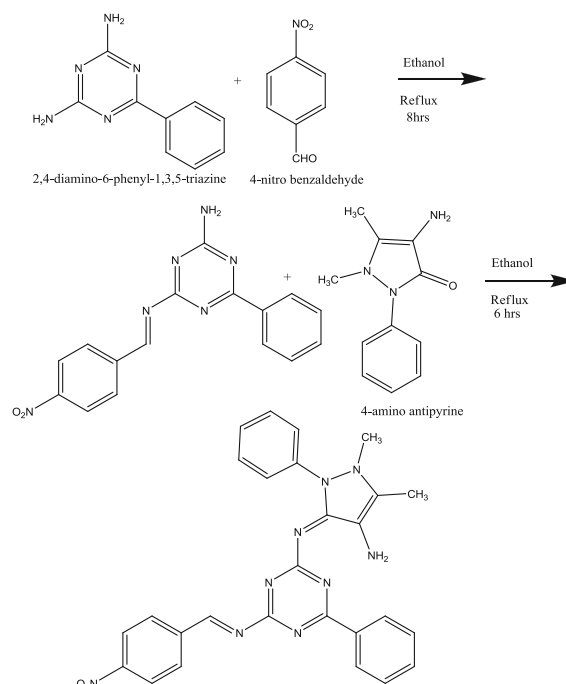
FT-IR (KBr) ν_{max} cm^{-1} : 3066 (Ar-H, stretch), 1612 (HC = N), 1541 (C = N), 2846 (C-H, stretch), 617 (C-S) [20, 21] **^1H NMR (400 MHz, CDCl_3) (δ : ppm):** 8.7 (s, 1H, CH = N), 7.34–8 (m, 9H, Ar-H), 3.26 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 6.66 (s, 2H, NH_2) [22] (Online Resource, Fig. 1) **^{13}C NMR (400 MHz, CDCl_3) (δ : ppm):** 171.51, 168.04, 160.84, 159.7, 137.47, 132.5, 130.45, 128.69, 35.78, 8.2 [23] (Online Resource, Fig. 2) **Mass m/z :** 466.17 (Online Resource, Fig. 3) (Scheme 1).

Synthesis of 6-phenyl-2,4-((4-amino-1,5-dimethyl-2-phenyl pyrazol-3-ylidene)(4-nitro benzylidene))-diamino-1,3,5-triazine (NDP) A solution of 4.67 g (25 mmol) of 2,4-

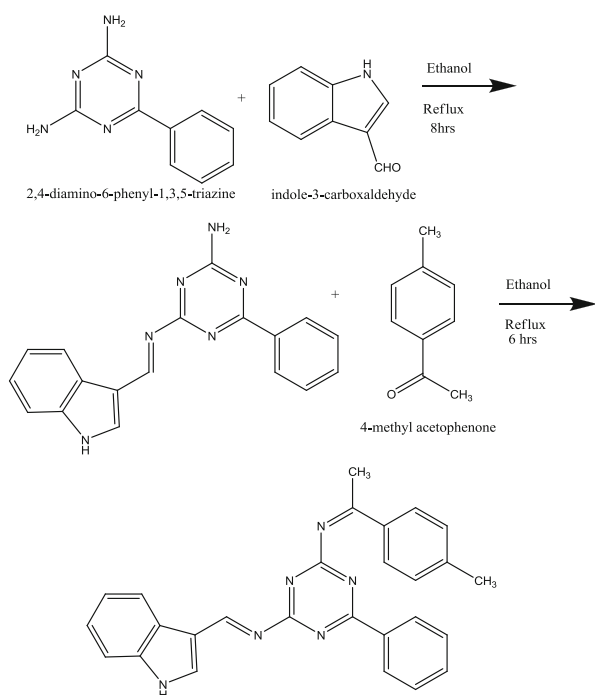


Scheme 1 6-Phenyl-2,4-((4-amino-1,5-dimethyl-2-phenylpyrazol-3-ylidene)(thiophen-2-ylmethylene))-diamino-1,3,5-triazine (TDP)

diamino-6-phenyl-1,3,5-triazine in ethanol (25 ml) was added slowly to 3.77 g (25 mmol) 4-nitro benzaldehyde in ethanol (10 ml). The reaction mixture was refluxed



Scheme 2 6-Phenyl-2,4-((4-amino-1,5-dimethyl-2-phenyl pyrazol-3-ylidene)(4-nitro benzylidene))-diamino-1,3,5-triazine (NDP)



Scheme 3 6-Phenyl-2,4-((indol-3-yl) methylene)((1-*p*-tolylethylidene))-diamino-1, 3, 5-triazine (IDM)

under stirring for 8 h. On cooling, a yellow precipitate was obtained. A solution of 2.72 g (8.5 mmol) of the yellow precipitate was added to an ethanol (20 ml) solution of 1.72 g (8.5 mmol) of 4-amino antipyrine. Allow the reaction mixture to reflux for 6 h and the yellow precipitate NDP obtained was recrystallized from ethanol.

FT-IR (KBr) ν_{max} cm^{-1} : 3059 (Ar-H, stretch), 1616 (HC = N), 1546 (C = N), 2852 (C-H, stretch), 634 (C-S), 1558, 1498 (NO₂) ¹HNMR (400 MHz, CDCl₃) (δ : ppm): 9.811 (s, 1H, CH = N), 7.45–8.2 (m, 8H, Ar-H), 3.236 (s, 3H, CH₃), 2.155 (s, 3H, CH₃), 5.15 (s, 2H, NH₂) [24] (Online Resource, Fig. 4) ¹³C NMR (400 MHz, CDCl₃) (δ : ppm): 170.58, 167.87, 152.6, 131.47, 128.57, 128.09, 35.2, 8.3 (Online Resource, Fig. 5) Mass *m/z*: 505.2 (Online Resource, Fig. 6) (Scheme 2)

Synthesis of 6-phenyl-2,4-((indol-3-yl) methylene)((1-*p*-tolylethylidene))-diamino-1, 3, 5-triazine (IDM) A solution of 4.67 g (25 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine in

Table 1 Absorption and emission maxima λ_{max} of compounds in acetonitrile

Compounds	Absorption λ_{max} (nm)	Emission λ_{emi} (nm)
TDP	296	305.5
NDP	396	407.5
IDM	300	312

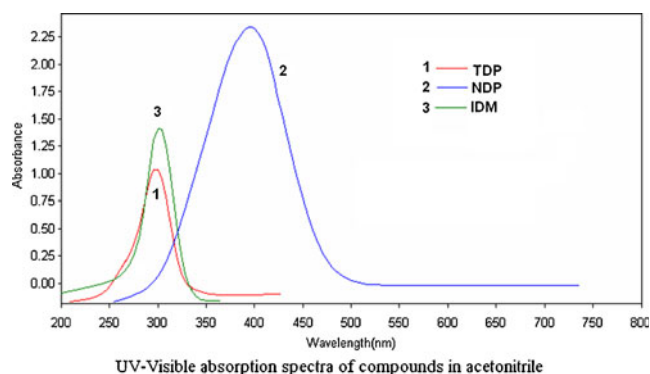


Fig. 1 UV-Visible absorption spectra of compounds in acetonitrile

ethanol (25 ml) was added slowly to 3.62 g (25 mmol) of indole-3-carboxaldehyde in ethanol (10 ml) and refluxed under stirring for 8 h thoroughly. It was kept aside for cooling and the white precipitate was filtered out. A solution of 3.14 g (10 mmol) of the above precipitate was added to an ethanol (20 ml) solution of 1.34 g (10 mmol) of 4-methyl acetophenone with continuous stirring. After refluxed for 6 h, the white precipitate IDM was filtered out, dried and recrystallized from ethanol.

FT-IR (KBr) ν_{max} cm^{-1} : 3148 (Ar-H), 2915 (CH₃), 1614 (C = C), 1539 (C = N) [25] ¹HNMR (400 MHz, CDCl₃) (δ : ppm): 8.265 (s, 1H, CH = N), 7.48 (d, 1H, NH), 6.807–7.47 (m, 8H, ArH), 2.442 (s, 3H, CH₃) [26] (Online Resource, Fig. 7) ¹³C NMR (400 MHz, CDCl₃) (δ : ppm): 170.65, 167.87, 156.3, 137.51, 131.5, 128.5, 128.12, 21.3, 18.4 (Online Resource, Fig. 8) Mass *m/z*: 430.19 (Online Resource, Fig. 9) (Scheme 3)

Non Linear Optical Activity

The SHG efficiencies of the compounds were measured by the powder method developed by Kurtz and Perry [27]. The compound was ground into powder with an average particle size of

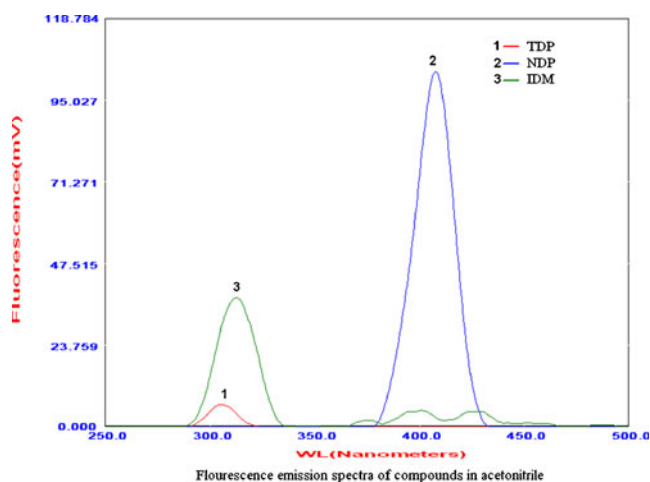


Fig. 2 Fluorescence emission spectra of compounds in acetonitrile

Table 2 Elemental analysis of compounds TDP, NDP and IDM

Compound	Color	Yield %	Molecular formula	Found (calcd.) %			
				C	H	N	S
TDP	Light Yellow	79	C ₂₅ H ₂₂ N ₈ S	64.32 (64.35)	4.78 (4.76)	24.05 (24.03)	6.84 (6.86)
NDP	Yellow	85	C ₂₇ H ₂₃ N ₉ O ₂	64.16 (64.14)	4.62 (4.59)	24.96 (24.94)	–
IDM	White	81	C ₂₇ H ₂₂ N ₆	75.34 (75.32)	5.15 (5.17)	19.51 (19.53)	–

100–150 μm and was packed in a micro capillary of uniform pore size. This was then exposed to laser radiations of Q-switched Nd: YAG laser beam wavelength of 1064 nm. The emission of green radiation confirms the SHG and the parent ray was filtered using IR filter. The photomultiplier with digitalizing oscilloscope set up measures the amplitude of the SHG output voltage. The efficiency of the sample was compared with KDP and Urea, powdered to the same particle size as the experimental sample and were taken as a reference material for SHG efficiency. The input beam energy used for TDP was 3.15 mJ/pulse and for NDP and IDM, it was 8.0 mJ/pulse.

Results and Discussion

Photo-physical Properties

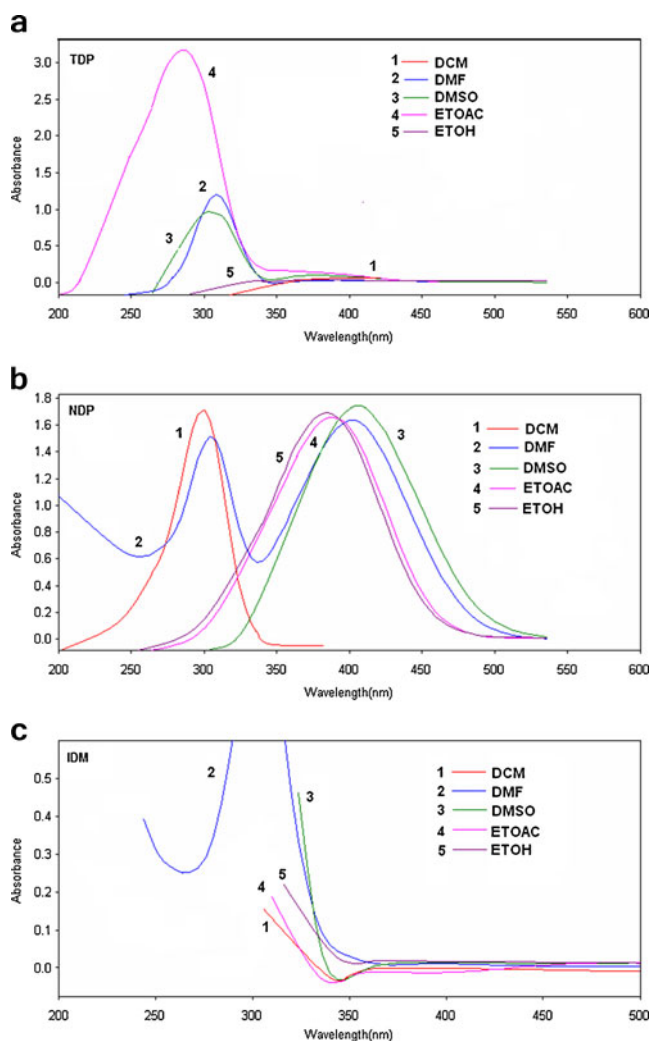
The absorption spectral data (λ_{max}) of compounds TDP, NDP and IDM are presented in Table 1. The above compounds absorb at 296, 396, and 300 nm respectively (Fig. 1). They exhibit fluorescence emissions at 305.5, 407.5 and 312 nm respectively (Fig. 2) with varying fluorescence intensity. Elemental analysis of compounds TDP, NDP and IDM were given in Table 2.

Absorption-emission characteristics of the compounds have been studied in five different solvents of varying polarity (Table 3) to evaluate the effect of solvent polarity on absorption-emission properties (Figs. 3 and 4). It has been investigated that change of polarity of solvents has little influence on absorption-emission behavior.

Table 3 Absorption, emission maxima of compounds in various solvents

Solvents	TDP		NDP		IDM	
	λ_{max} (nm)	λ_{emi} (nm)	λ_{max} (nm)	λ_{emi} (nm)	λ_{max} (nm)	λ_{emi} (nm)
DCM	368	372	301	410	396	403.5
ETOAC	284	298.5	388	399.5	364	368.5
ETOH	376	375.5	384	392.5	372	371
DMF	308	323	304,400	316,360	304	427.5
DMSO	376	385	404	409	384	384.5

The compound NDP showed dual absorption peak around 304 and 400 nm in more polar dimethyl formamide, whereas a single absorption peak was observed at 301 nm in non polar dichloro methane. Moreover, a distinct red shifted peak was observed for NDP in acetonitrile. It also exhibited positive solvatochromic behavior in polar solvents indicating a greater stabilization of the excited state as compared to the ground state by a polar solvent. It is clearly understood that the molecule is solvated significantly in the S_1 excited state, resulting in a

**Fig. 3** Effect of solvent polarity on absorption spectra of compounds

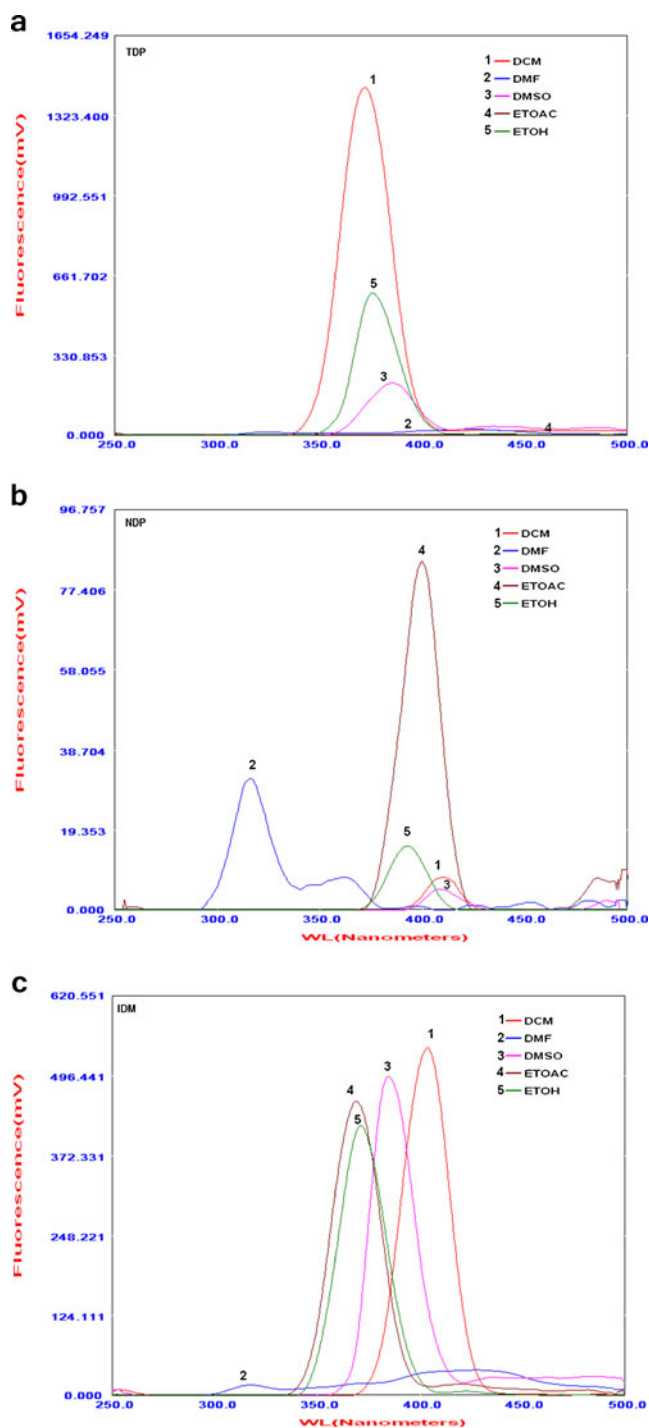


Fig. 4 Effect of solvent polarity on emission spectra of compounds

Table 4 SHG parameters of TDP, NDP and IDM

Compound	Measured SHG efficiency (mV)	SHG Efficiency of KDP (mV)	SHG Efficiency with respect to KDP	SHG Efficiency of urea (mV)	SHG Efficiency with respect to Urea
TDP	255	41	6.2	260	0.98
NDP	118	10.3	11.5	90	1.3
IDM	41	10.3	4	90	0.45

difference in dipole moment between the S_1 excited state and the ground state. Due to stronger interaction between molecules in the excited state and the surrounding solvents [28], the intra molecular charge transfer state was stabilized by polar solvents. The red shifted absorption and emission of NDP compared to those of TDP and IDM revealed larger conjugation in NDP. Because based on the π conjugated electron system fluorescence property changes and increase of flow of electrons in a system enhances the fluorescence. The fluorescence intensity of IDM was more intense in all the five solvents and showed red shifted peaks. TDP showed small shift in absorption spectra, but a slightly increased solvent induced shift in emission spectra when the solvent polarity was higher [29]. The fluorescence emission of TDP showed red shift in polar dimethyl sulfoxide. The intense emission peaks were observed in apolar solvents than polar solvents for all the three compounds. Obviously, a highly polar solvent favors ICT relaxation but an apolar solvent helps the fluorescence transition.

From the above observations, the absorption spectra of TDP, NDP and IDM were found to be less dependent on the polarities of the solvent [30]. But the extent of red shifted fluorescence was strongly dependent on solvent polarities. This fluorescent sensitivity of compounds to solvent is mainly due to the formation of intramolecular charge transfer (ICT) state in polar solvent.

Non Linear Optical Properties

The SHG efficiency of the three compounds was found to be greater than the reference materials KDP and Urea [31]. The values obtained for TDP, NDP and IDM were 255 mV, 118 mV, and 41 mV respectively as shown in Table 4. It was found that, NDP had greater SHG efficiency than TDP and IDM indicating the larger delocalized π electron flow from donor to acceptor group in NDP. The compound NDP showed 11.5 times greater SHG efficiency than KDP and 1.3 times greater efficiency than Urea as the NDP system consists of electron donating methyl group and electron withdrawing nitro group on triazine moiety. This was in comparison with the SHG efficiency of similar type of triazine based compound 2,4,6-tristyryl-s-triazine has been reported to exhibit 1.8 times larger SHG efficiency as that of urea [32]. The SHG of IDM was found to be 4 times greater than KDP and 0.5 times greater than Urea. Similarly, TDP showed 6.2 times and

0.98 times greater SHG efficiency with respect to KDP and Urea respectively.

Thermal Properties

Thermal stability of the compounds TDP, NDP and IDM was evaluated through thermo gravimetric analysis [33] between the temperature ranges of 50 °C to 400 °C under nitrogen atmosphere. The TG curves ideally show weight changes during heating. The DTG curve, which is the derivative of

the TG curve, shows changes in the slope that may not be obvious from the TG curve. The TG curves of three compounds were shown in Fig. 5. The TG results indicated that the synthesized compounds started their degradation at about 160 °C. Their initial weight loss was about 4 % in TDP, 1 % in NDP and 1.5 % in TDP. Till 202 °C, a weight loss of only about 7 % was found for NDP. The rate of decomposition increased very rapidly between 250 and 275 °C and the products were decomposed completely beyond 350 °C [34].

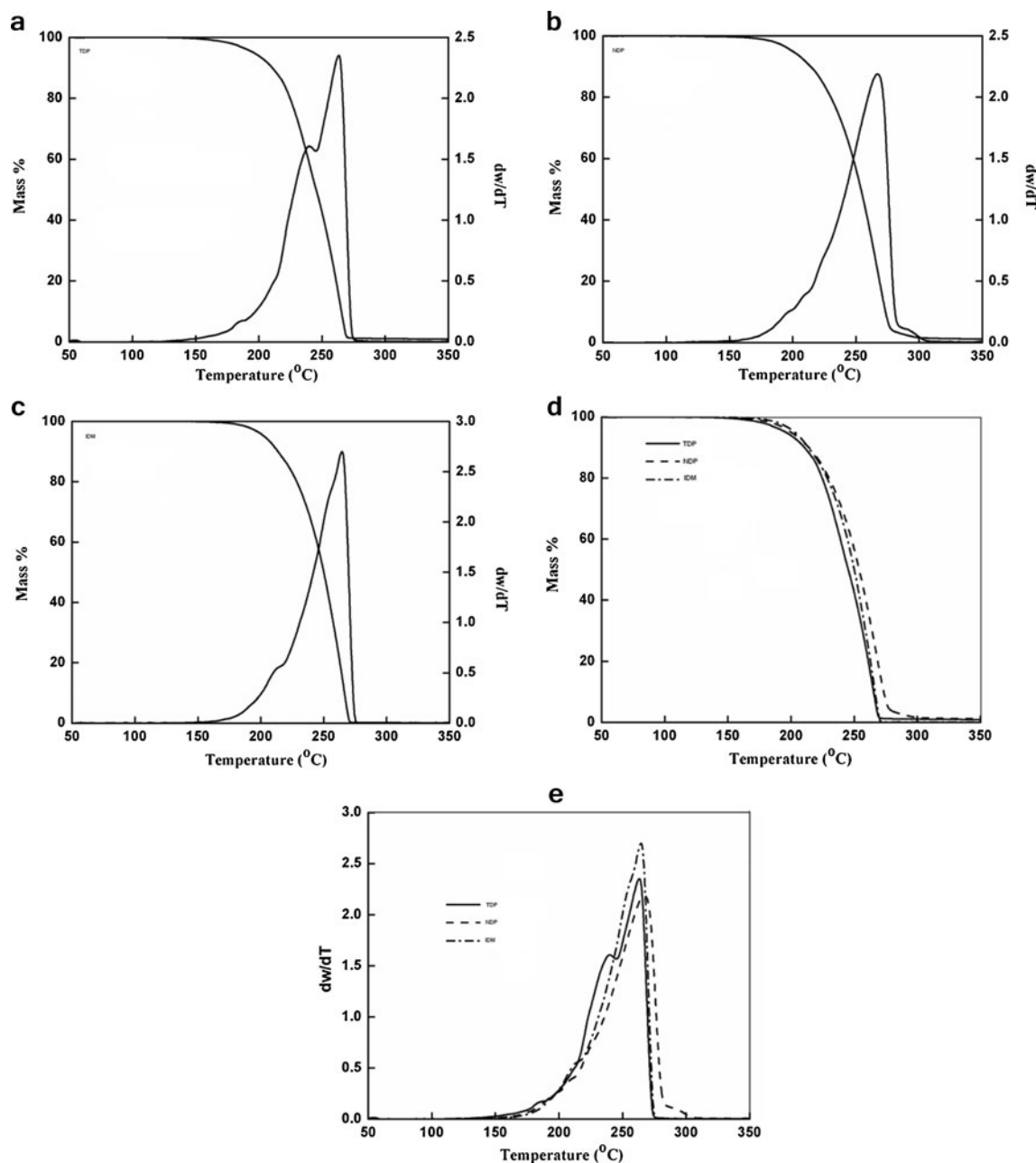


Fig. 5 TGA/DTG curves of compounds TDP, NDP and IDM

Conclusion

Three novel donor-acceptor π -conjugated push-pull systems were synthesized in good yields using simple synthetic procedures starting from easily available, low cost material 2,4-diamino-6-phenyl-1, 3, 5-triazines. Solvent polarity has significant impact on emission properties of the synthesized compounds. They showed good solvatochromic behavior, thermal stabilities and solubility in usual organic solvents. All the three have better SHG efficiency compared to KDP and urea. The NDP system showed excellent SHG efficiency which is suitable for many second order NLO applications. From the applications point of view, it is clear that the non-linearity of NDP is sufficiently high to develop electro-optic materials that can compete with inorganic NLO materials. Based on the results, new trend for the molecular design of novel push-pull chromophores containing triazine moiety for second order NLO applications was proposed. The search for nonlinear optical properties in completely new materials can improve our understanding of the mechanisms behind the NLO effects.

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