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# Synthesis and photo-physical properties of fluorescent 1,3,5-triazine styryl derivatives

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## Abstract

**Background:** Organic fluorophore contains well-defined D- $\pi$ -A (Donor- $\pi$  system-Acceptor) push-pull system have wide application in the field of NLO, OLED and high tech application. Electron donor diphenyl, triphenyl and carbazole conjugated with electron acceptor terminal through  $\pi$ -system were reported recently for high-tech applications. *N,N*-Dialkyl substituted 1,3,5-triazine also acts as donor keeping this idea in mind we developed D- $\pi$ -A styryl dyes.

**Results:** Novel "Y"-shaped acceptor- $\pi$ -donor- $\pi$ -acceptor type of compounds were synthesized from 4,4'-((6-(4-(diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy)) dibenzaldehyde (DIPOD) as electron donors and different active methylene compounds as electron acceptors by conventional Knoevenagel condensation reaction. Their photophysical and thermal properties were investigated.

**Conclusion:** It was found that the strong electron acceptor-donor chromophoric system of these compounds showed high Stoke's shift and excellent thermal stability. Compounds showed positive solvatofluorism behavior from nonpolar to polar solvent. All compounds have good thermal stability.

## Background

Organic fluorescent heterocyclic chromophores have a wide range of applications in molecular probes [1], fluorescent markers [2], organic light-emitting diodes (OLED)[3], photovoltaic cells [4] and in traditional textile and polymer fields [5]. Electron donors like triphenylamine [6], diphenylamine [7] 1,3,5-triazines [8] and carbazoles [9] with high electron mobility, thermal and photochemical stability are commonly used as hole-transporting materials or light-emitting materials for balanced charge injection for above mentioned application.

*N,N*-Dialkyl substituted 1,3,5-triazine fluorescent styryl derivatives have not been exploited much in the past, but attract increasing interest as they exhibit better solubility in common organic solvents, excellent thermal and electron donating ability of *N,N*-alkyl groups. The presence of electron donating *N,N*-dialkyl group increases the electron flow towards the electron acceptor moieties present in the molecules. From the viewpoint of

molecular design, structural features such as the long  $\pi$  conjugation style, molecular planarity and length of the conjugated bridge play important roles in functional chromophores, which are highly promising for electronic applications like photonic materials [10,11], holographic optical data storage [12] and organic photorefractive materials.

4-(4,6-Dichloro-1,3,5-triazin-2-yl)-*N,N*-diethylaniline is structurally similar to 4,4'-disubstituted diphenylamine and 3,6-disubstituted carbazoles with planar structure. The 4-(4,6-dichloro-1,3,5-triazin-2-yl)-*N,N*-diethylaniline nucleus can be easily functionalized at 4,6- positions and covalently linked to other molecular groups. A typical push-pull chromophore consists of a polar A- $\pi$ -D system with a planar  $\pi$ -system end-capped by a strong electron donor (D) and a strong electron acceptor (A). The  $\pi$ -conjugated system ensuring intramolecular charge transfer (ICT) between the donor (D = *N,N*-dialkyl group) and the acceptor (A = -CN, -COOEt group etc.) is the most common of conjugated double or triple bonds in aromatic and heteroaromatic rings as well as their combinations [13,14].

There has always been an effort to design and synthesize novel and well-defined organic push-pull

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system with prospective applications as chromophores for nonlinear optics (NLO), electronic and photonic devices, organic light-emitting diodes (OLED) and functional polymers [15]. In this paper, synthesis of fluorescent styryl dyes, their structure elucidation and the photophysical and thermal properties are reported.

## Results and Discussion

### Synthesis and Characterization of compounds

The six novel fluorescent triazine based styryl compounds were prepared Figure 1 by classical Knoevenagel condensation of 4,4'-((6-(4-(diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** with active methylene compounds **6a-6f** as shown in Scheme 1. In the first step, the 4-(4,6-dichloro-1,3,5-triazin-2-yl)-*N,N*-diethylaniline (**3**) was synthesized from cyanuric chloride **1** and *N,N*-diethyl aniline **2**. Finally aldehyde **5** and suitable active methylene compound **6a-6f** were stirred in absolute ethanol containing a catalytic amount of piperidine to yield desired styryl triazines **7a-7f**. The structures of the compounds were confirmed by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and Mass spectral analysis. The <sup>1</sup>H NMR spectra of compounds **5** showed singlet peak at  $\delta$  10.04 which indicates the confirmation of compounds **5** and singlet  $\delta$  7.76 to 8.46 in **7a-7f** which indicates the ethylenic protons at styryl group.

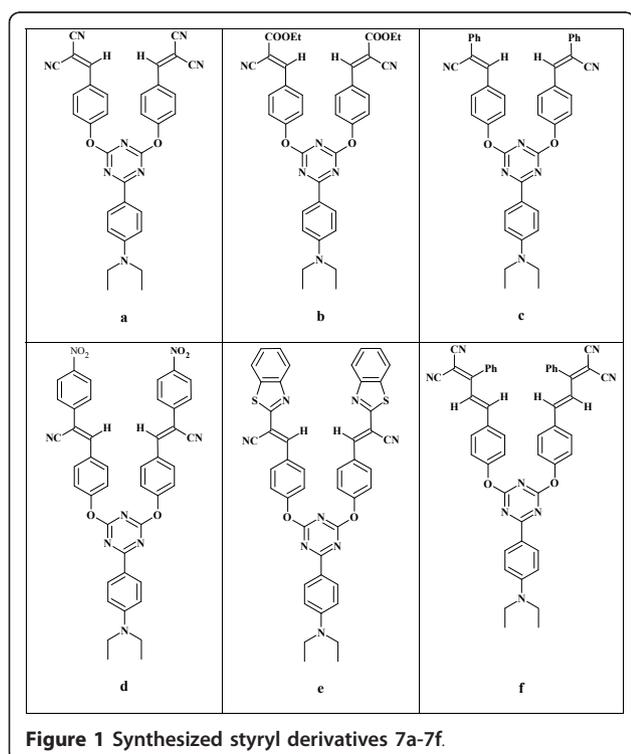
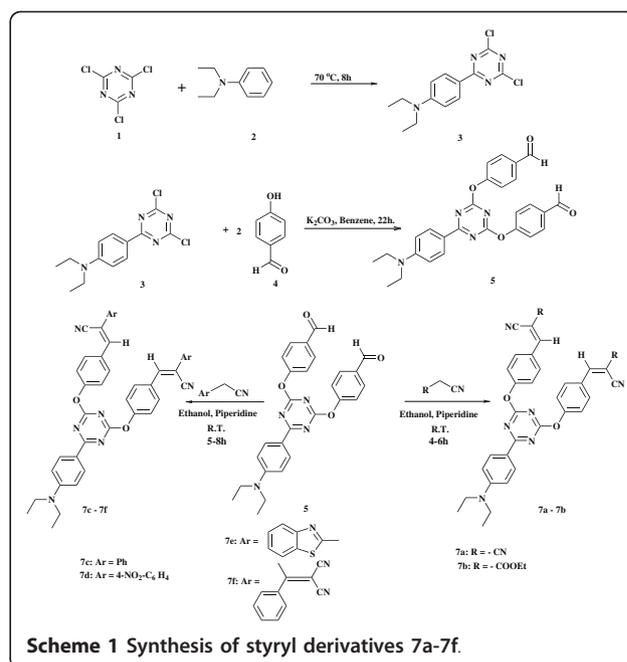


Figure 1 Synthesized styryl derivatives 7a-7f.



Scheme 1 Synthesis of styryl derivatives 7a-7f.

### Photo-physical properties

The UV-Vis absorption and emission spectra of styryl derivatives (**7a-7f**) were recorded in acetonitrile at room temperature and the compound concentration is  $1 \times 10^{-6}$  M. The  $\lambda_{max}$  (absorbance) values of compounds (**7a-7f**) were obtained as (**7a** = 381; **7b** = 378; **7c** = 354; **7d** = 354; **7e** = 354; **7f** = 369) nm Figure 2 and fluorescence emission of compounds **7a-7f** were obtained as 422, 413, 408, 413, 399 and 403 nm respectively with difference in fluorescence intensity Figure 3.

To evaluate the effect of solvent polarity on absorption-emission properties of synthesized compounds. Absorption, emission properties of compound **7a-7f** were studied in different solvents of varying polarity and

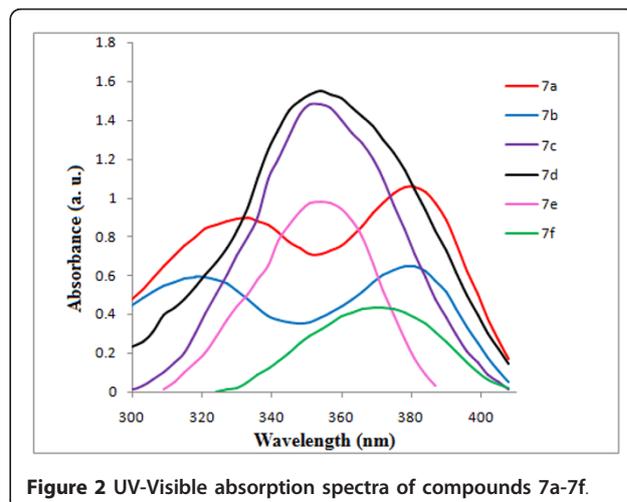


Figure 2 UV-Visible absorption spectra of compounds 7a-7f.

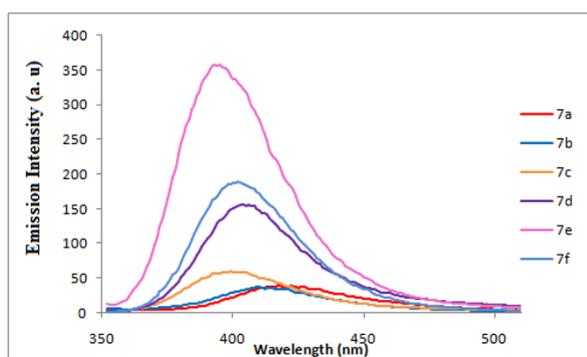


Figure 3 Fluorescence emission spectra of compounds 7a-7f.

hydrogen bonding capability as shown in Table 1. Six solvents are tested for effect of solvent on their absorption-emission characteristics. The absorption-emission spectra of 7a-7f are not affected much by a change in polarity and hydrogen bonding capacity of the solvent.

These compounds with A- $\pi$ -D structure consist of an electron-donating *N,N*-diethyl group on triazine moiety and electron withdrawing cyano or carboethoxy group. The results showed that these compounds do not show strong solvatochromic and solvatofluoric properties. The introduction of electron accepting groups in the triazine moiety causes intramolecular charge transfer and mesomeric dipole moment. Depending upon the electron affinity of acceptor groups, the CT band was slightly shifted

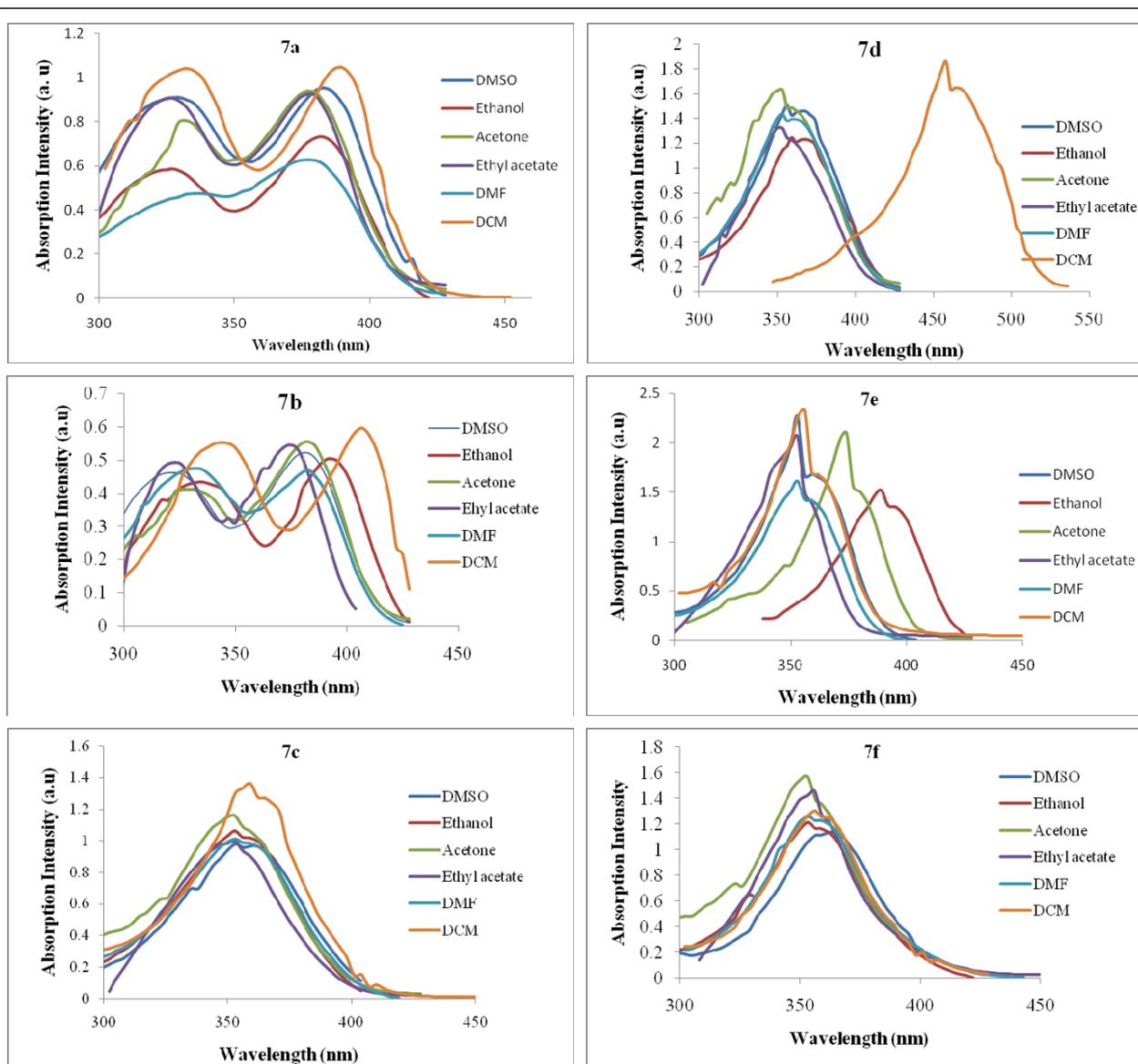


Figure 4 Effect of solvent polarity on absorption spectra of compounds 7a-7f.

**Table 1 Fluorescence absorption and emission maxima of compound 7a-7f in various solvents.**

Solvents	7a			7b			7c		
	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$
DCM	329(1.030) 389(1.048)	408(079)	79	341(0.549) 404(0.589)	403(149)	62	359(1.361)	408(482)	49
EtOAc	323(0.898) 377(0.852)	403(490)	80	320(0.488) 371(0.531)	392(201)	87	356(0.956)	403(490)	47
Acetone	329(0.793) 377(0.927)	406(688)	77	323(0.375) 380(0.550)	410(108)	72	354(1.157)	403(216)	49
EtOH	326(0.585) 380(0.727)	428(288)	102	332(0.420) 389(0.503)	424(131)	92	353(1.061)	410(166)	57
DMF	329(0.458) 377(0.628)	401(487)	72	332(0.475) 380(0.461)	392(183)	60	350(0.994)	411(132)	61
DMSO	326(0.908) 383(0.982)	428(087)	102	323(0.455) 377(0.539)	418(229)	95	353(0.979)	418(164)	65

Solvents	7d			7e			7f		
	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$	$\lambda_{max}$	$\lambda_{em}$	$\Delta\lambda$
DCM	410(1.864)	458(1000)	48	356(2.322)	400(1000)	44	356(1.305)	416(1000)	60
EtOAc	353(1.319)	410(1000)	57	350(1.992)	410(1000)	60	353(1.424)	416(1000)	63
Acetone	350(1.621)	410(1000)	60	374(2.099)	400(1000)	26	353(1.571)	408(684)	55
EtOH	362(1.209)	418(600)	56	389(1.521)	408(1000)	19	353(1.213)	413(937)	57
DMF	356(1.380)	413(561)	57	353(1.616)	403(681)	50	353(1.229)	413(363)	60
DMSO	356(1.507)	420(400)	64	353(2.252)	408(476)	55	359(1.166)	416(359)	57

DCM: Dichloromethane; EtOAc: Ethyl acetate; EtOH: Ethyl alcohol; DMF: Dimethylformamide; DMSO: Dimethylsulphoxide.

in DMF with decrease Stoke's shift as shown in Table 1. The absorption and emission spectra of dye **7a-7f** in several solvents having different polarities are shown in Figures 4 and 5. Compound **7a** and **7b** shows dual absorption in dichloromethane and ethanol, while compound **7d** shows red shift in dichloromethane and **7e** shows red shift in acetone and ethanol. The negative solvatochromism observed in **7d** indicates that there is no charge transfer character in the molecule after excitation; therefore presence of nitro group does not lower the energy of the excited state by solvation. In the case of **7e** presence of benzothiazolyl ring gives a charge transfer characteristic to the system and thus exhibits positive solvatochromism.

An effective fluorescent dyes for biological application should have good fluorescence intensity, high quantum yield and high photostability. Quantum yield of compounds **7a-7f** were determined by using anthracene as standard. Absorption and emission characteristics of standard as well as unknown samples were measured at different concentration of unknown samples and standard at (2, 4, 6, 8 and 10 ppm level). Graphs were plotted absorbance intensity values against emission intensity values. A linear plot was obtained. Gradients were calculated for each unknown compound and for standards. All the measurements were done by keeping the parameters constant such as solvent and slit width. Relative quantum yield of all

synthesized compounds **7a-7f** were calculated by using **Formula 1**[16].

**Formula 1:** Relative fluorescence quantum yield

$$\Phi_x = \Phi_{ST} (\text{Grad}_x/\text{Grad}_{ST}) (\eta^2_x/\eta^2_{ST})$$

Where:  $\Phi_x$  = Quantum yield of unknown sample

$\Phi_{ST}$  = Quantum yield of standard used

$\text{Grad}_x$  = Gradient of unknown sample

$\text{Grad}_{ST}$  = Gradient of standard used

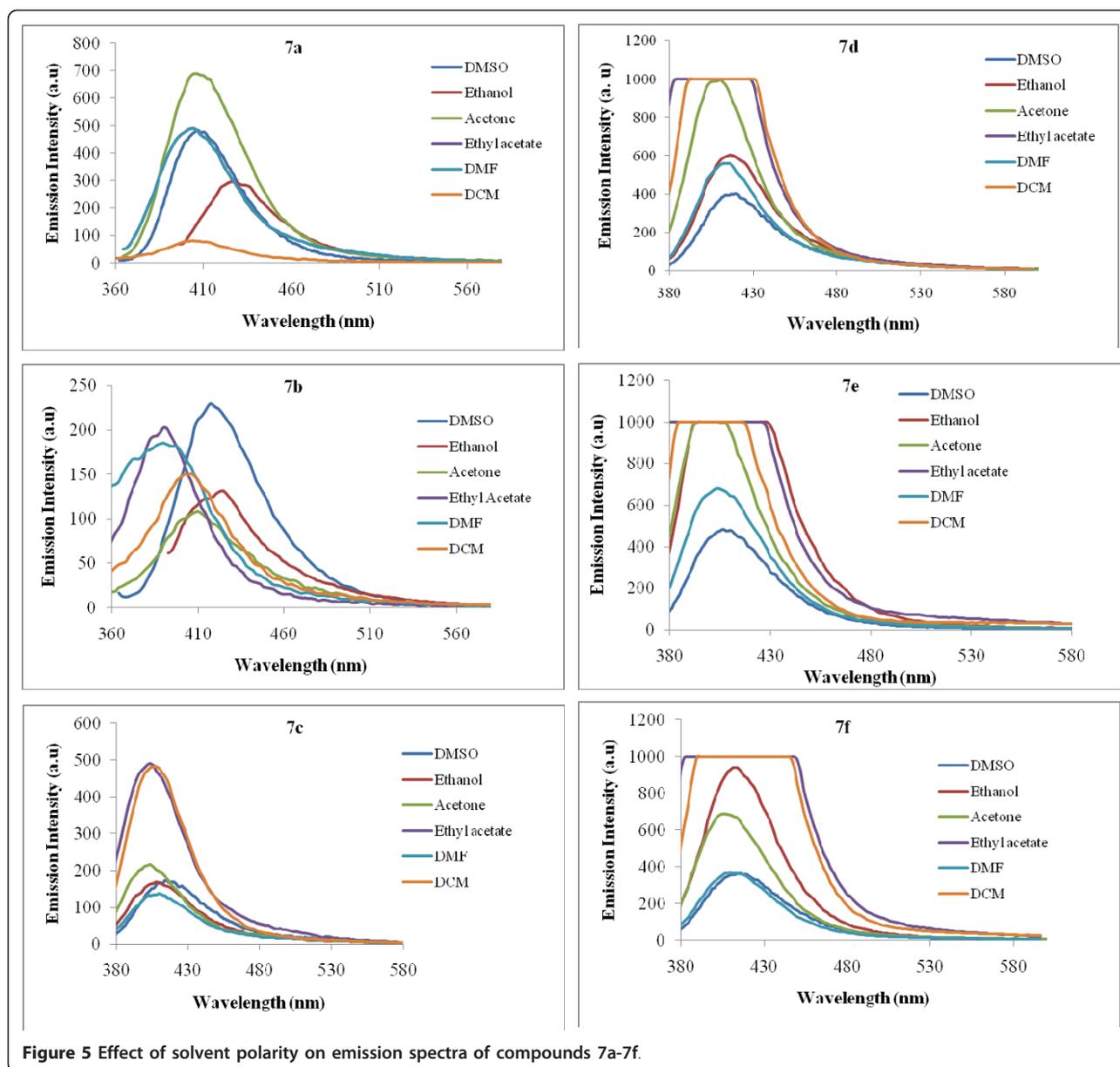
$\eta^2_{ST}$  = Refractive index of solvent for standard sample

$\eta^2_x$  = Refractive index of solvent for sample

The fluorescence quantum yields of **7a-7f** were recorded in ethanol at room temperature. It was observed that the quantum yield of **7d** and **7e** in ethanol (0.0039 for **7a**, 0.0026 for **7b**, 0.0082 for **7c**, 0.0689 for **7d**, 0.0291 for **7e** and 0.0034 for **7f**) are higher than **7a-7c** and **7f** in the same solvent. The details are given in the Table 2. Quantum yield results summarized in Table 2 indicate that, compounds **7d** and **7e** show high quantum efficiency as compared to compound **7a**, **7b**, **7c** and **7f**. This difference in quantum efficiency is may be due to conjugation through aromatic system as well as strong hydrogen bonding between nitro of **7d** and ethanol, and thiazole of **7e** and ethanol.

#### Thermal Properties

In order to examine the thermal stability of these compounds **7a -7f** thermo gravimetric (TG) and differential



**Figure 5** Effect of solvent polarity on emission spectra of compounds 7a-7f.

scanning calorimeter (DSC) analysis were carried out between 40-600°C under a nitrogen atmosphere. The TG curves of the compounds are shown in Figure 6. The TG results indicates that the frame work of the synthesized compounds are stable up to 300°C. Above 250°C the thermo gravimetric curves of the synthesized compounds show a loss in weight. The comparisons of the  $T_d$  (decomposition temperature) showed that the thermal stability of **7a-7f** decreases in the order **7c** > **7a** > **7f** > **7b** > **7d** > **7e**. Thermal stability graph as shown in Figure 6. Compound **7a** is thermally more stable, it does not decompose completely upto 600°C (65% stable up to temperature 600°C). Compounds **7a** and **7b** are 40% stable up to temperature 600°C. Compounds **7c**, **7e** and **7f** decompose almost

**Table 2** Absorption, emission and quantum yield of compounds **7a-7f**.

Compounds	Absorption <sup>a</sup> Intensity (a.u.) $\lambda_{max}(nm)$	Emission <sup>a</sup> Intensity (a.u.) $\lambda_{max}(nm)$	Stoke Shift ( $\Delta\lambda$ )	Quantum Yield <sup>b</sup>
<b>7a</b>	381(1.056)	422(038)	41	0.0039
<b>7b</b>	378(0.645)	413(036)	35	0.0026
<b>7c</b>	354(1.509)	408(057)	54	0.0082
<b>7d</b>	354(1.547)	413(149)	59	0.0689
<b>7e</b>	354(1.025)	399(344)	45	0.0295
<b>7f</b>	369(0.434)	403(182)	34	0.0034

<sup>a</sup> Absorption and Emission were measured in acetonitrile.

<sup>b</sup> Solvent for quantum yield measurement in ethanol.

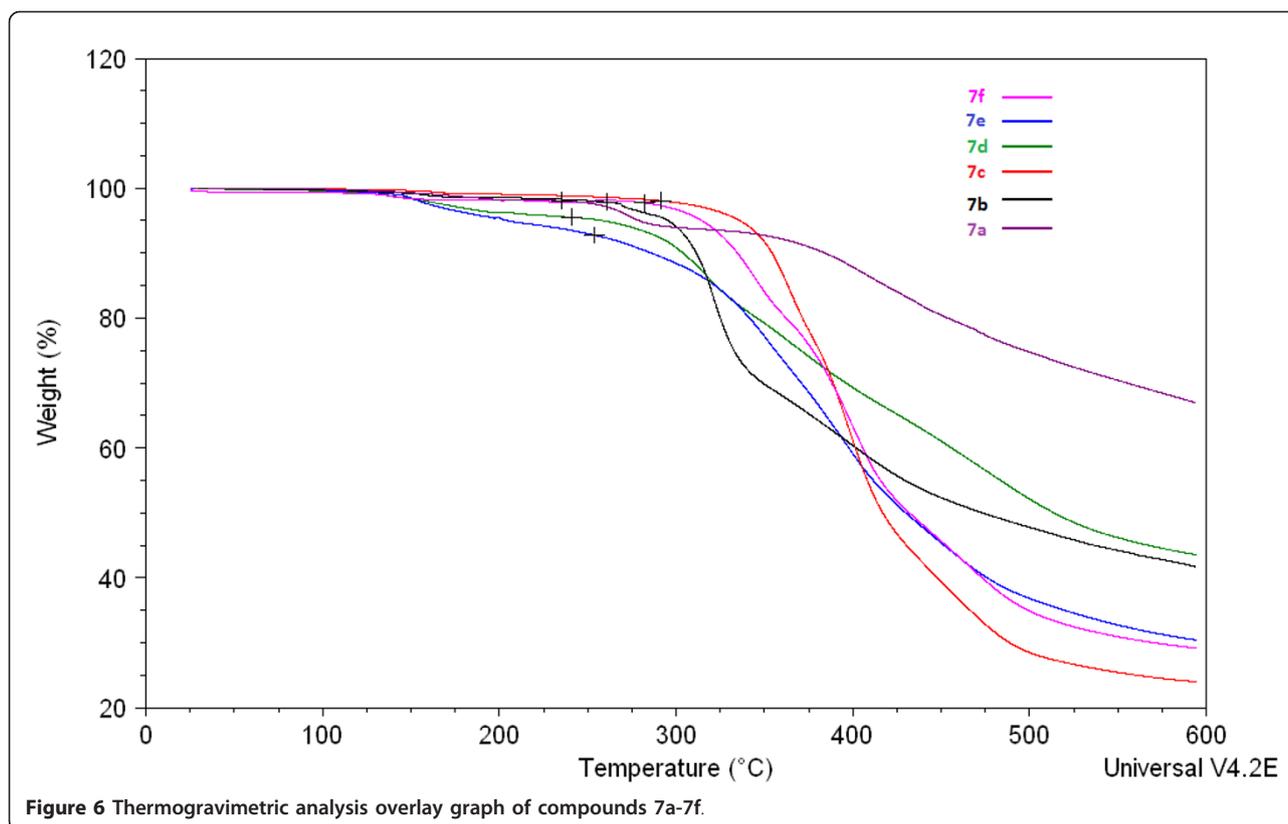


Figure 6 Thermogravimetric analysis overlay graph of compounds 7a-7f.

completely beyond temperature 600°C. 7d and 7e starts decomposing at 120°C but after 300°C its decomposition behavior is same like 7a, 7b, 7c and 7f.

## Experimental

### Materials and equipments

All commercial reagents and solvents were procured from s. d. fine chemicals (India) and were used without purification. The reaction was monitored by TLC using on 0.25 mm E-Merck silica gel 60 F<sub>254</sub> precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai, and are uncorrected. The FT-IR spectra were recorded on Perkins-Elmer 257 spectrometer using KBr discs. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra were recorded on VARIAN 400-MHz instrument (USA) using TMS as an internal standard. Mass spectra were recorded on Finnigan mass spectrometer. The visible absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV-Visible spectrometer. Simultaneous DSC-TGA measurements were performed out on SDT Q 600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd.

## Synthesis and characterization

### Synthesis of 4-(4,6-dichloro-1,3,5-triazin-2-yl)*N,N*-diethylaniline 3

A mixture of *N,N*-diethylaniline **1** (27.0 g, 0.2 mol) and cyanuric chloride **2** (18.4 g, 0.1 mol) was heated at 70°C for 8 h under a slow stream of dry nitrogen. After completion of reaction monitored by TLC, the mixture was extracted with hot chloroform (200 mL) and the white crystalline hydrochloride salt of *N,N*-diethylaniline removed by filtration. Slow cooling and evaporation of the chloroform extract to a volume of 50 mL yielded good crystals of **3**. The product was recrystallized two times from acetone.

Yield: 11.68 g, 40%; m.p.: 156°C. (Recrystallized from acetone)

**FT-IR (KBr)  $\nu$  max:** 567, 715, 824, 839, 1164, 1232, 1515, 1610, 2967, 3411 cm<sup>-1</sup>

**<sup>1</sup>H NMR (400 MHz) ( $\delta$ : ppm):** 1.22-1.25 (t, 6H, -CH<sub>3</sub>), 3.44-3.46 (q, 4H, -CH<sub>2</sub>), 6.65-6.69 (dd, 2H, *J* = 9.2, 2.8 Hz, Ar-H), 8.29-8.33 (dd, 2H, *J* = 9.2, 2.8 Hz, Ar-H).

**<sup>13</sup>C NMR (100 MHz) ( $\delta$ : ppm):** 15.6, 49.0, 114.6, 125.6, 130.7, 154.2, 172.3, 179.5.

**Mass:** m/e = 298 (M + 1), 299 (M + 2)

**4,4'-((6-(4-(*N,N*-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl)bis(oxy)) dibenzaldehyde 5** *p*-Hydroxybenzaldehyde **4** (2.42 g, 0.022 mol) and 4-(4,6-dichloro-1,3,5-triazin-2-yl)-*N,N*-diethylaniline **3** (3.0 g, 0.011 mol) were added to a suspension of K<sub>2</sub>CO<sub>3</sub> (3.04 g, 0.022 mol) in 50 mL of benzene. The mixture was refluxed for 22 h. The reaction mixture was then cooled and the solid was removed by filtration and washed with hot ethyl acetate twice. The filtrate was extracted with 10% Na<sub>2</sub>CO<sub>3</sub> solution (20 mL) twice and with H<sub>2</sub>O once. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The white powder was recrystallized from 20 mL of ethanol to afford 3.31 g of 4,4'-((6-(4-(*N,N*-diethylamino)phenyl)-1,3,5-triazine-2,4 diyl)bis(oxy)) dibenzaldehyde **5** as a white fluffy precipitate (80%).

Yield: 3.31 g, 80%; m. p.: 150°C.

**FT-IR (KBr) v max.:** 505, 726, 831, 1565, 1705(C = O), 2729, 2929(Aldehyde CH), 2972 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz) (δ: ppm):** 1.19 (t, 6H, -CH<sub>3</sub>), 3.43 (q, 4H, -CH<sub>2</sub>), 6.58 (d, 1H, *J* = 9.17, 2.71 Hz, Ar-H), 6.61 (d, 1H, *J* = 9.17, 2.71 Hz, Ar-H), 7.41 (d, 2H, *J* = 8.43, 1.83 Hz, Ar-H), 7.44 (d, 1H, *J* = 8.43, 1.83 Hz, Ar-H), 7.95 (d, 1H, *J* = 8.80, 1.83 Hz, Ar-H), 7.98 (d, 1H, *J* = 8.80, 1.83 Hz, Ar-H), 8.05 (d, 1H, *J* = 9.17 Hz, Ar-H), 8.08 (d, 1H, *J* = 9.17 Hz, Ar-H), 10.04 (s, 2H, Aldehyde H).

**<sup>13</sup>C NMR (100 MHz)(δ: ppm):**12.37, 43.92, 110.72, 119.13, 122.56, 130.91, 131.13, 133.76, 151.58, 156.25, 171.53, 174.40, 192.04.

**Mass:** m/e = 469.2 (M<sup>+</sup> + 1).

**Synthesis of Styryl 7a-7f** **Synthesis of 2,2'-((6-(4-(*N,N*-diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy)) bis(4,1-phenylene)bis(methanylylidene)dimalononitrile 7a**

4,4'-((6-(4-(*N,N*-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and malanonitrile (0.33 g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 4 h. filtered the reaction mass to separate out product and recrystallized it from ethanol.

Yield: (0.96 g, 78%), m.p.: 198°C.

**FT-IR (KBr) v max:** 805, 1138, 1174, 1233, 1344, 1541, 2229, 2902, 2986 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz) (δ: ppm):** 1.23 (t, 6H, -CH<sub>3</sub>), 3.44 (q, 4H, -CH<sub>2</sub>), 6.60-6.63 (d, 2H, *J* = 9.4 Hz, Ar-H), 7.43-7.47 (d, 4H, *J* = 1.8, 8.7 Hz, Ar-H), 7.79 (s, 2H, Ethylenic protons), 8.00-8.03 (d, 2H, *J* = 1.8, 8.8 Hz, Ar-H), 8.06-8.07 (d, 2H, *J* = 7.0, 2.5 Hz, Ar-H), 8.10 (d, 2H, *J* = 2.2 Hz, Ar-H).

**<sup>13</sup>C NMR (100 MHz) (δ: ppm):**12.38, 43.94, 81.13, 110.72, 113.28, 114.26, 119.17, 122.94, 128.79, 130.98, 132.28, 151.64, 155.84, 160.40, 171.39, 174.55.

**Mass:** m/e = 565.2 (M + 1), 566.2 (M + 2).

**2E, 2'E-Diethyl-3,3'-((6-(4-(*N,N*-diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy))bis(4,1-phenylene) bis(2-cyanoacrylate) 7b.**

4,4'-((6-(4-(*N,N*-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and ethylcyanoacetate (0.59 g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 5 h filtered the reaction mass to separate out product and recrystallized product from ethanol.

Yield: (1.05 g, 71%), Melting Point: 162-164°C.

**FT-IR (KBr) v max.:** 512, 729, 831, 1134, 1565, 1630, 1729, 2735, 3075, 3390 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz) (δ: ppm):** 1.20 (t, 6H, -CH<sub>3</sub>), 1.42 (t, 6H, -CH<sub>3</sub>), 3.41 (q, 4H, -CH<sub>2</sub>), 4.41 (q, 4H, -CH<sub>2</sub>), 6.60-6.63 (d, 2H, *J* = 9.52 Hz, Ar -H), 7.39 (d, 2H, *J* = 8.8 Hz, Ar -H), 7.42 (d, 2H, *J* = 8.8 Hz, Ar -H), 8.08 (d, 2H, *J* = 8.8, 4.0 Hz, Ar -H), 8.09 (d, 2H, *J* = 4.0 Hz, Ar -H), 8.10 (d, 2H, *J* = 8.8, 4.0 Hz, Ar -H), 8.26 (s, 2H, Ethylenic protons).

**<sup>13</sup>C NMR (100 MHz) (δ: ppm):** 12.40, 14.01, 43.94, 62.41, 102.24, 110.74, 115.68, 122.77, 128.89, 130.95, 132.49, 154.06, 155.17, 161.84, 171.51.

**Mass:** m/e = 659.3 (M + 1), 660.3 (M + 2).

**2E, 2'E-3,3'-((6-(4-(*N,N*-Diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy))bis(4,1-phenylene)bis(2-phenylacrylonitrile) 7c.**

4,4'-((6-(4-(*N,N*-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and phenyl acetonitrile (0.61 g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 6 h filtered the reaction mass to separate out product and recrystallized product from ethanol.

Yield: (1.10 g, 76%), m.p.:160°C.

**FT-IR (KBr) v max.:** 815, 1140, 1187, 1218, 2986, 3102 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz) (δ: ppm):** 1.11 (t, 6H, -CH<sub>3</sub>), 3.33 (q, 4H, -CH<sub>2</sub>), 6.69 (d, 2H, *J* = 9.0 Hz, Ar -H), 6.71 (d, 2H, *J* = 9.1 Hz, Ar -H), 7.49 (d, 2H, *J* = 8.4 Hz, Ar -H), 7.52 (d, 2H, *J* = 8.4 Hz, Ar -H), 8.03-8.16 (d, 6H, *J* = 8.8, 3.2 Hz, Ar -H), 8.39-8.40 (d, 4H, *J* = 8.8, 2.5 Hz, Ar -H), 8.43 (s, 2H, Ethylenic protons).

**<sup>13</sup>C NMR (100 MHz) (δ: ppm):** 15.38, 47.94, 82.13, 115.32, 118.81, 119.06, 121.17, 124.0, 129.23, 133.4, 139.28, 145.43, 149.30, 152.34, 155.13, 164.40, 173.9, 177.3, 181.2.

**Mass:** m/e = 667.9 (M + 1).

**2E, 2'E-3,3'-((6-(4-(*N,N*-Diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy))bis(4,1-phenylene)bis(2-(4-nitrophenyl)acrylonitrile) 7d** 4,4'-((6-(4-(*N,N*-

Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and 4-nitro phenyl acetonitrile (0.84 g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 8 h, filtered the reaction mass to separate out product and recrystallized product from ethanol.

Yield: (1.40 g, 83%, m.p.: 201°C.

**FT-IR (KBr)  $\nu$  max.:** 513, 734, 836, 1562, 1635, 2279, 2309, 2729, 3069, 3390  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz) ( $\delta$ : ppm):** 1.10 (t, 6H,  $-\text{CH}_3$ ), 3.32 (q, 4H,  $-\text{CH}_2$ ), 6.66 (d, 2H,  $J = 9.0$  Hz, Ar -H), 6.69 (d, 2H,  $J = 9.09$  Hz, Ar -H), 7.47 (d, 2H,  $J = 8.5$  Hz, Ar -H), 7.50 (d, 2H,  $J = 8.5$  Hz, Ar -H), 8.03-8.12 (d, 8H,  $J = 8.8, 3.2$  Hz, Ar -H), 8.35-8.36 (d, 4H,  $J = 8.8, 2.5$  Hz, Ar -H), 8.39 (s, 2H, Ethylenic protons).

**$^{13}\text{C}$  NMR (100 MHz) ( $\delta$ : ppm):** 12.38, 43.94, 81.13, 110.72, 113.28, 114.26, 119.17, 122.87, 128.91, 131.4, 132.28, 143.67, 148.30, 151.64, 155.84, 160.40, 171.39, 174.6, 177.5.

**Mass:**  $m/e = 757.3$  ( $M + 1$ ),  $758.3$  ( $M + 2$ ).

**2E, 2'E-3,3'-((6-(4-(N,N-Diethylamino)phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy))bis(4,1-phenylene)bis(2-(benzo[d]thiazol-2-yl)acrylonitrile) 7e** 4,4'-((6-(4-(N,N-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and 2-cyano methyl benzothiazole (0.90 g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 5 h, filtered the reaction mass to separate out product and recrystallized product from ethanol.

Yield: (1.16 g, 67%), m.p.: 196°C.

**FT-IR (KBr)  $\nu$  max.:** 513, 727, 821, 1565, 1600, 2278, 2328, 2729, 3069, 3370  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz) ( $\delta$ : ppm):** 1.12 (t, 6H,  $-\text{CH}_3$ ), 3.32 (q, 4H,  $-\text{CH}_2$ ), 6.67 (d, 2H,  $J = 9.09$  Hz, Ar -H), 6.70 (d, 2H,  $J = 9.09$  Hz, Ar -H), 7.50 (d, 2H,  $J = 7.5$  Hz, Ar -H), 7.52 (d, 2H,  $J = 7.5$  Hz, Ar -H), 7.53-7.57 (d, 8H,  $J = 8.2$  Hz, Ar -H), 8.03-8.22 (d, 4H,  $J = 9.09, 7.6$  Hz, Ar -H), 8.46 (s, 2H, Ethylenic protons).

**$^{13}\text{C}$  NMR (100 MHz) ( $\delta$ : ppm):** 12.38, 43.94, 81.13, 110.72, 113.28, 114.26, 119.17, 122.90, 128.99, 130.92, 132.38, 147.98, 149.31, 151.64, 155.84, 158.32, 160.41, 171.28, 174.89.

**Mass:**  $m/e = 781.9$  ( $M + 1$ ),  $782.9$  ( $M + 2$ ).

**2,2'- (2E, 2E')-((6-(4-(N,N-Diethylamino) phenyl)-1,3,5-triazine-2,4-diyl)bis(oxy)) bis(4,1-phenylene) bis(1-phenyl prop-2-en-3-yl-1-ylidene))dimalononitrile 7f.**

4,4'-((6-(4-(N,N-Diethylamino) phenyl)-1,3,5-triazine-2,4 diyl) bis (oxy)) dibenzaldehyde **5** (1.0 g, 0.0023 mol) and 2-(2-phenylprop-1-en-1-ylidene) malononitrile (0.87

g, 0.0052 mol) were dissolved in absolute ethanol (10 mL). Piperidine (0.1 mL) was added to it and the reaction mixture was stirred at room temperature for 5 h, filtered the reaction mass to separate out product and recrystallized product from ethanol.

Yield: (1.38 g, 74%), m.p.: 146°C.

**FT-IR (KBr)  $\nu$  max.:** 739, 846, 1635, 2309, 3070, 3396  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz) ( $\delta$ : ppm):** 1.12 (t, 6H,  $-\text{CH}_3$ ), 3.35 (q, 4H,  $-\text{CH}_2$ ), 6.69 (d, 2H,  $J = 9.2$  Hz, Ar -H), 6.72 (d, 2H,  $J = 9.2$  Hz, Ar -H), 7.49 (d, 2H,  $J = 8.6$  Hz, Ar -H), 7.51 (d, 2H,  $J = 8.6$  Hz, Ar -H), 8.05-8.14 (d, 10 H,  $J = 8.8, 3.2$  Hz, Ar -H), 8.37-8.39 (d, 6H,  $J = 8.8, 2.5$  Hz, Ar -H), 8.42 (s, 2H, Ethylenic protons).

**$^{13}\text{C}$  NMR (100 MHz) ( $\delta$ : ppm):** 14.12, 45.43, 85.23, 112.72, 114.32, 115.26, 122.17, 124.37, 128.91, 131.4, 135.83, 147.73, 150.30, 151.64, 156.42, 165.41, 173.3, 174.16, 176.15, 179.20

**Mass:**  $m/e = 769.9$  ( $M + 1$ ).

## Conclusion

In summary, we have developed an efficient and simple protocol for the synthesis of fluorescent chromophores containing triazine core moiety and electron withdrawing cyano/carboethoxy groups. The synthesized compounds were confirmed by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectral analysis. From the emissive properties, it was concluded that the electronic coupling between donor and acceptor was sufficient to allow charge transfer in their molecules. Emission properties of synthesized compounds are sensitive towards the solvent polarity; it shows positive solvatochromism with increase in solvent polarity.

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## Authors' contributions

VSP contributed for synthesis, spectral analysis of all compounds under NS; VSP and VSP contributed for photophysical study under the guidance NS. All the authors read and approved the final manuscript.

## Competing interests

The authors declare that they have no competing interests.

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