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Fluorescent azo disperse dyes from 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol and comparison with 2-naphthol analogs

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ABSTRACT

Five novel fluorescent azo disperse dyes were synthesized using different diazotized aromatic amines followed by coupling with 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol. These dyes were characterized by FT-IR, ¹H NMR and mass spectroscopy. These azo disperse dyes were applied on polyester and their fastness properties were evaluated. A parallel series of dyes using 2-naphthol in place of benzothiazolyl were made to investigate the effect of benzothiazolyl moiety on the fastness properties. This investigation showed that the dyes containing benzothiazolyl residue have better fastness properties than that of the azo disperse dyes based on 2-naphthol. Effect of pH on photo physical properties was also studied. © 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Azo dyes represent the single largest chemical class of industrial colorants. They are the most versatile and robust group of synthetic dyes, which cover the full range of shades of colors. The ease of preparation of azo dyes by diazotization and azo coupling reactions and economy of the reaction have led to the synthesis of many dyes in the past. Replacement of anthraquinone dyes with equivalent azo dyes has great importance [1,2]. Azo disperse dyes containing aromatic heterocyclic moiety have been investigated due to their superior properties in general, and the use of heterocyclic diazo or coupling components in particular has made possible the production of colorants with brilliant color and chromophoric strength, high level-dying property and excellent fastness properties [3–7]. Azo dyes based on heterocyclic compounds have been reviewed comprehensively [4,8–10]. Heterocyclic azo disperse dyes are used to dye hydrophobic fibers especially polyester and polyamide fabrics due to their excellent properties; they have also been utilized in non-textile applications such as lasers and non-linear optical systems [11], photodynamic therapy, reprography [12], dye sensitized solar cells [13], and metallochromic indicators [14]. Among them thiazolyl and benzothiazolyl azo compounds are the most popular ones in the production of red azo dyes having better fastness properties [15–18]. Benzothiazolyl azo disperse dyes are used for dyeing polyester fabrics due to their better fastness and high level-dyeing properties [19–24]. Azo disperse dyes containing thiazole unit have been investigated due to their excellent properties [25].

The photo stability and hence light fastness of mono azo disperse dyes can be enhanced by the presence of hydroxyl, amino, or acetamido groups at ortho position relative to the azo bridge [26] which is attributed to the hydrogen bonding between hydroxyl and azo groups. However mono azo disperse dyes derived from 2-naphthol as coupling component are reported to have poor light fastness [27]. Many a times UV absorber-finish is given to prevent photo degradation of dyed fabrics, or UV absorbing unit is deliberately introduced into the dye molecule [28–32]. The commonly used UV absorbers or substituted benzophenones, benzotriazole and their exceptional photo stability are attributed to the presence of hydrogen bonding [32].

In this paper we have reported azo disperse dyes using 3-(1,3benzothiazol-2-yl) naphthalen-2-ol as a coupler. The benzothiazolyl group present adjacent to the hydroxyl group is known to enter into an excited state intramolecular proton transfer (ESIPT) as shown in Fig. 1 [33] conferring extra photo stability. It was





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E = enol form in ground state; K = keto form in ground state;

 E^* = enol form in excited state; K^* = keto form in excited state.



envisaged that presence of such an ESIPT in mono azo dyes will lead to dyes with superior light fastness properties. It is also known that azo disperse dyes having an inbuilt ESIPT unit fluoresce in highly polar solvents [34], although the fluorescence intensity is suppressed due to presence of azo bridge [35–38]. It is also to be noted that 3-(1,3-benzothiazol-2-yl) naphthalen-2-ol has been used in the preparation of mono azo pigments [39,40] and bisazo dyes [41,42].

2. Materials and methods

2.1. Materials

Aniline, 2-aminothiophenol, 3-hydroxynaphthalene-2carboxylic acid, 4-chloroaniline, 4-nitroaniline, 4-methoxyaniline, 4-nitroaminophenol, sodium carbonate, sodium hydroxide, metamol (dispersing agent) and conc. HCl were purchased from S.D. fine chemicals Ltd, Mumbai, India. Solid reagents were characterized by melting point and used without purification. Liquid reagents distilled at their boiling points and used thereafter. Solvents were used after necessary purification and drying according to standard processes.

2.2. Methods

2.2.1. General procedure of dyeing [43,44]

Disperse dyeing of polyester fabric was carried out using high temperature high pressure method in Rossari Labtech Flexi Dyer dyeing machine at a material to liquor ratio of 1:20. Fabric was dyed using 2% dye (calculated on weight of the fabric). All synthesized azo disperse dyes are having poor solubility in water. Initially dye was dissolved in 5 mL N,N-dimethylformamide and diluted with 15 mL buffered solution of pH 5 made by using sodium acetate and acetic acid in water. Solution was ultrasonicated for 15 min to obtain fine dispersion. Metamol was used as a dispersant. Polyester fabric was dyed using above solution. Dyeing was commenced at room temperature. The dye bath temperature was raised at a rate of 3 °C min⁻¹ to 130 °C, maintained at this temperature for 60 min, and rapidly cooled to room

2.2.2. Fastness to washing

A specimen of dyed polyester fabric was stitched between two pieces, one of undyed polyester and other of cotton fabric having equal length. This fabric was washed in solution (3 g L^{-1} Na₂CO₃, 1 g L^{-1} NaOH) with 1:50 fabric to solution ratio at 60 °C for 30 min. The staining on the undyed adjacent fabric or change in tone was assessed according to the following international geometric gray scale (1 for poor and 5 for excellent).

2.2.3. Fastness to light

Light fastness was evaluated by exposing a dyed fabric to highenergy radiation (Q-SUN Xenon Test Chamber, Q-LAB, USA) in a fade-o-meter for 24 h and compared with unexposed fabric. AATCC Test method was used for evaluation (scale: 1 for poor and 8 for outstanding).

2.2.4. Fastness to sublimation

Sublimation fastness was measured with a sublimation fastness tester (R. B. Electronics and Engineering Pvt. Ltd.). The sample was prepared by stitching a piece of dyed polyester fabric between two pieces, one of undyed polyester and other of cotton fabric having equal length and then treated at 180 °C for 30 s. Any staining on the undyed adjacent fabric or change in tone was assessed according to the following international geometric gray scale (1 for poor and 5 for excellent).

2.2.5. Color assessment

The color coordinates of azo disperse dyes were determined on CE-7000A Gretag-Macbeth computer color matching system. The color values were expressed by using CIE 1976 Color Space method. The coordinates used to determine color values are "*L**" for lightness, "*a**" for redness (positive value) and greenness (negative value), "*b**" for yellowness (positive value) and blueness (negative value), "*c**" for chroma and "ho" for hue angle in the range of 0° -360°. "K/S" value is directly associated with the dye concentration on polyester fabrics.

2.2.6. Spectrophotometer measurements

UV–visible spectral studies were carried on Spectrophotometer (Model–8500, TECHCOMP, Hong Kong) with 1 cm quartz cells. The concentration used was 100 ppm.

2.2.7. Fluorescence emission measurements

Fluorescence emission measurements were performed on JASCO-FP 1520 with Borwin software.

2.3. Experimental

All reactions were monitored on precoated silica gel aluminum based plates kisel gel 60 F_{254} Merck, India. Purification of all compounds was achieved by recrystallization. Purity of compounds was ascertained by thin layer chromatography. Melting points were recorded by using open capillary on instrument from Sunder Industrial Product and are uncorrected. Infrared analysis was carried on an FTIR-8400S spectrophotometer, SHIMADZU. ¹H NMR spectra were recorded on 400 MHz on Varian mercury plus spectrometer. Chemical shifts are expressed in δ ppm using TMS as an internal standard and CDCl₃ as a solvent.

2.4. Synthesis

2.4.1. General procedure for preparation of 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol

Phosphorus trichloride (2.6 mL, 4.13 g, d = 1.57 g mL⁻¹, 0.03 mol) was added drop wise to a mixture of the 3-hydroxynaphthalene-2carboxylic acid (6.2 g 0.033 mol) and 2-aminothiophenol (3.85 mL, 4.5 g, d = 1.17 g mL⁻¹, 0.036 mol) in toluene (50 mL). Slight exotherm was observed. The temperature was maintained below 45–50 °C during the addition of phosphorus trichloride. The mixture was refluxed vigorously for 4 h and then cooled solution was made alkaline using 20% sodium carbonate solution. Solid was filtered. Crude solid was slurred in methanol and filtered to remove methanol-soluble impurities followed by washing with (25 mL) 80% aqueous acetone. Homogenous spot was obtained on TLC. This was used as a coupler. Yield: 65%; m.p.: 182 °C (literature 183 °C) [45].

2.4.2. General method of diazotization

One of the substituted aromatic amines $4\mathbf{a}-\mathbf{e}$ (0.015 mol) was taken in water. Conc. HCl (0.045 mol, 1.64 g, d = 1.1 g mL⁻¹, 4.98 mL of 30% HCl) was added to dissolve completely. Then reaction mixture was cooled to 0–5 °C by using ice–salt mixture. Cold 20% solution of NaNO₂ (0.015 mol, 1.03 g) was added drop wise over the period of 10 min. Reaction mixture was stirred for 30 min. Completion of diazotization was checked using starch iodide paper. 0.01 g of urea was added to consume excess of nitrous acid [46].

2.4.3. General method of coupling

3-(1,3-Benzothiazol-2-yl)naphthalen-2-ol (0.01 mol, 2.77 g) was dissolved in (50 mL) 80% of methanol in water having 0.4 g NaOH (0.01 mol). Clear yellow solution was obtained. Reaction mixture was then cooled to 5 °C. Above diazotized amine was added slowly with constant stirring and maintaining temperature at 5 °C and pH between 9 and 10. Dyes **6a**–**e** were collected and purified by using methanol.

2.4.3.1. 3-(1,3-Benzothiazol-2-yl)-1-[(E)-(4-chlorophenyl)diazenyl] naphthalen-2-ol **6a**. Color: red. Yield: 88%; m.p.: 248–250 °C. ¹H NMR (CDCl₃, δ ppm): 16.72 (s, 1H, Hydrogen bonding), 9.03 (s, 1H, Ar–H), 8.36 (d, 1H, Ar–H, *J* = 8 Hz), 8.10 (d, 1H, Ar–H, *J* = 8 Hz), 7.95 (d 1H, Ar–H, *J* = 8 Hz), 7.72 (d, 1H, Ar–H, *J* = 8 Hz), 7.58 (t, 2H, Ar–H, *J* = 3 Hz), 7.52 (t, 2H, Ar–H, *J* = 9 Hz), 7.37 (d, 4H, Ar–H, *J* = 8 Hz), 1.60 (s, 1H, OH). FT-IR (KBr, cm⁻¹): 3442 (–OH), 1607 (–C=N), 1555 (–N=N), 1498 (aromatic ring), 821 (–C–Cl), 755 (–C–S). Mass: *m*/ *z*: 416.5 (M + 1).

2.4.3.2. 3-(1,3-Benzothiazol-2-yl)-1-[(E)-phenyldiazenyl]naph-

thalen-2-ol **6b**. Color: red. Yield: 92%; m.p.: 272–274 °C. ¹H NMR (CDCl₃, δ ppm): 16.88 (s, 1H, Hydrogen bonding), 9.11 (s, 1H, Ar–H), 8.85 (d, 1H, Ar–H, J = 8 Hz), 8.14 (d, 1H, Ar–H, J = 8 Hz), 8.02 (d, 1H, Ar–H, J = 7 Hz), 7.82 (d, 1H, Ar–H, J = 7 Hz), 7.78 (d, 1H, Ar–H, J = 7 Hz), 7.62 (t, 1H, Ar–H, J = 7 Hz), 7.53 (t, 3H, Ar–H, J = 7 Hz), 7.44 (d, 2H, Ar–H, J = 7 Hz), 7.31 (d, 1H, Ar–H, J = 8 Hz), 1.25 (s, 1H, OH). FT-IR (KBr, cm⁻¹): 3439 (–OH), 1604 (–C=N), 1557 (–N=N), 1499 (aromatic ring), 758 (–C–S). Mass: m/z: 382 (M + 1).

2.4.3.3. 3-(1,3-Benzothiazol-2-yl)-1-[(E)-(4-nitrophenyl)diazenyl]

naphthalen-2-ol **6c**. Color: brownish red. Yield: 83%; m.p.: 290–292 °C. ¹H NMR (CDCl₃, δ ppm): 16.31 (s, 1H, Hydrogen bonding), 9.08 (s, 1H, Ar–H), 8.42 (d, 1H, Ar–H, *J* = 8 Hz), 8.36 (d, 2H, Ar–H, *J* = 7.3 Hz), 8.12 (d, 1H, Ar–H, *J* = 8.0 Hz), 8.00 (d, 1H, Ar–H, *J* = 8.0 Hz), 7.84 (t, 2H, Ar–H, *J* = 8.0 Hz), 7.76 (d, 1H, Ar–H, *J* = 7.0 Hz), 7.64 (t, 1H, Ar–H, *J* = 8.2 Hz), 7.54 (m, 2H, Ar–H), 7.42 (m, 1H, Ar–H), 1.57 (s, 1H, OH). FT-IR (KBr, cm⁻¹): 3621 (–OH), 1599

(−C=N), 1557 (−N=N), 1504 (aromatic ring), 748 (−C−S). Mass: *m*/*z*: 427 (M + 1).

2.4.3.4. 3-(1,3-Benzothiazol-2-yl)-1-[(E)-(4-methoxyphenyl)dia-

zenyl]naphthalen-2-ol **6d**. Color: red. Yield: 91%; m.p.: 204–206 °C. ¹H NMR (CDCl₃, δ ppm): 17.25 (s, 1H, Hydrogen bonding), 9.05 (s, 1H, Ar–H), 8.45 (d, 1H, Ar–H, J = 8.2 Hz), 8.09 (d, 1H, Ar–H, J = 8.3 Hz), 7.98 (d, 1H, Ar–H, J = 7.9 Hz), 7.8 (d, 2H, Ar–H, J = 7.9 Hz), 7.69 (d, 2H, Ar–H, J = 8.9 Hz), 7.56 (m, 2H, Ar–H), 7.39 (t, 1H, Ar–H, J = 7.7 Hz), 7.01 (d, 2H, Ar–H, J = 8.9 Hz), 3.93 (s, 3H, –OCH₃), 1.6 (s, 1H, –OH). FT-IR (KBr, cm⁻¹): 3463 (–OH), 1604 (–C=N), 1552 (–N=N), 1508 (aromatic ring), 1258 (–C–O–Ar), 757 (–C–S). Mass: m/z: 412 (M + 1).

2.4.3.5. 3-(1,3-Benzothiazol-2-yl)-1-[(E)-(2-hydroxy-5-nitrophenyl) diazenyl]naphthalen-2-ol **6e**. Color: blackish red. Yield: 78%; m.p.: 312–314 °C. ¹H NMR (CDCl₃, δ ppm): 16.23 (s, 1H, Hydrogen bonding), 9.11 (s, 1H, Ar–H), 8.42 (s, 1H, Ar–H), 8.28 (d, 1H, Ar–H, J = 8.0 Hz), 8.24 (d, 1H, Ar–H, J = 9.0 Hz), 8.11 (d, 1H, Ar–H, J = 3.0 Hz), 8.00 (d, 1H, Ar–H, J = 8.0 Hz), 7.8 (d, 1H, Ar–H, J = 8.3 Hz), 7.65 (t, 1H, Ar–H, J = 7.1 Hz), 7.54 (m, 2H, Ar–H), 7.43 (t, 1H, Ar–H, J = 7.0 Hz), 7.32 (t, 1H, Ar–H, J = 8.3 Hz), 3.49 (s, 1H, OH), 1.25 (s, 1H, OH). FT-IR (KBr, cm⁻¹): 3593, 3462 (–OH), 1586 (–C=N), 1553 (–N=N), 1498 (aromatic ring), 758 (–C–S). Mass: m/z: 443 (M + 1).

3. Results and discussions

The synthesis of target fluorescent azo disperse dyes **6a–e** were accomplished by condensation of 3-hydroxynaphthalene-2-carboxylic acid **1** with 2-aminothiophinol **2** to give 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol **3** as a coupler, followed by coupling with diazotized aromatic amines **4a–e** (Fig. 2).

Synthesized azo disperse dyes **6a**–**e** are having red color with high color strength. All these azo disperse dyes showed weak fluorescence in polar as well as in non-polar solvents. This may be due to the presence of azo group, which is known to quench the fluorescence [35–38]. Absorption and emission spectra of disperse dyes **6a**–**e** in DMF is summarized in Figs. 3 and 4 respectively.

3.1. Effect of solvent polarity on photo physical properties of azo disperse dyes 6a - e

A parallel series of azo disperse dyes **6'a**–**e** were made using 2naphthol in place of **3**. To evaluate the effect of solvent polarities on photo physical properties of azo disperse dyes, dyes **6a**–**e** synthesized from **3** as well as disperse dyes **6'a**–**e** synthesized from 2naphthol were analyzed in seven different solvents of differing polarity, dielectric constant, refractive indices. Effects of solvent polarity on absorption and emission of these dyes are summarized in Tables 1–5 (Figs. 5–9). It was observed that change in solvent polarity does not have significant influence on absorption maxima as well as emission maxima (Figs. 5–8) except for the dye **6e**, which contains a nitro group on the acceptor side of the azo dye. The dye **6e** absorbed at 506 nm in almost all solvents except in highly polar aprotic solvent, DMSO in which it showed red shift of 144 nm (Fig. 9).

Fluorescence emission of azo disperse dyes 6a-e were also insensitive to solvent polarity (Tables 1–5). The variation in emission intensity does not have any specific relation to the solvent polarity. Dyes **6a**, **6c** and **6d** showed highest emission intensity in non-polar solvent like chloroform (Figs. 5, 7 and 8), while compound **6b** showed high emission intensity in highly polar aprotic solvent, DMSO (Fig. 6). Dye **6e** showed least emission intensity in DMSO (Fig. 9). Intensities of fluorescence of all azo Step 1:



Fig. 2. Experimental scheme for azo disperse dyes.

disperse dyes **6a**–**e** were very low which may be ascribed to the presence of azo group [35–38]. Similar trend was observed in dyes (**6'a**–**e**) based on 2-naphthol except for the fact that they do not have any emission.

A comparison of dyes containing benzothiazolyl group (6a-e) with the parallel series of dyes (6'a-e) devoid of benzothiazolyl dyes revealed the following. The dyes 6a-e were red shifted



Fig. 3. UV visible absorption spectra of synthesized azo disperse dyes 6a-e in DMF.

compare to dyes **6**′**a**−**e** Figs. 5–10 (Tables 1–5) except for the dye **6e** and **6**′**e**; the dye **6**′**e** showed two absorptions.

3.2. Effect of pH on photo physical properties of azo disperse dyes 6a-e

pH sensitive dyes have applications as indicators and visible ratiometric sensors [47]. In order to understand the behavior of



Fig. 4. Fluorescence emission spectra of synthesized azo disperse dyes 6a-e in DMF.

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Table 1

Effect of solvents on photo physical properties of dyes **6a** and **6'a**.

Solvents	6a					6'a			λ _{emi} (nm) Emission			
	λ_{\max} (nm)	\mathcal{E} Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	$\lambda_{emi} (nm)$	Emission intensity	Δλ (nm)	λ_{\max} (nm)	E Molar absorptivity (dm³ mol ^{−1} cm ^{−1})	$\lambda_{emi} (nm)$	Emission intensity			
CHCl ₃ (a)	513	22,187	589	2.344	76	482	13,654	_	_			
EtOAc (b)	506	21,481	589	1.333	83	470	11,053	-	_			
1,4-Dioxane (c)	509	23,351	589	1.544	80	474	12,467	-	_			
Ethanol (d)	509	23,683	589	1.676	80	473	11,392	_	_			
ACN (e)	509	21,979	589	0.946	80	474	12,834	_	_			
DMF (f)	512	22,686	581	1.744	69	476	12,099	_	_			
DMSO (g)	515	21,107	587	1.239	72	476	12,947	-	-			

Table 2

Effect of solvents on photo physical properties of dyes 6b and 6'b.

Solvents	6b				6′b					
	λ_{\max} (nm)	\mathcal{E} Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	$\lambda_{\rm emi} ({\rm nm})$	Emission intensity	Δλ (nm)	λ_{max} (nm)	\mathcal{E} Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	$\lambda_{\rm emi} ({\rm nm})$	Emission intensity	
CHCl ₃ (a)	510	14,897	571	3.213	61	482	2579	_	_	
EtOAc (b)	506	12,877	586	0.913	80	473	2232	_	_	
1,4-Dioxane (c)	506	17,449	585	1.306	79	474	2058	_	_	
Ethanol (d)	506	11,277	585	1.010	79	477	2356	_	_	
ACN (e)	506	11,391	585	0.614	79	474	2802	_	_	
DMF (f)	509	14,020	589	0.959	80	474	2430	_	_	
DMSO (g)	512	12,115	567	3.738	55	480	2331	-	_	

dyes **6a–e** which carries an ESIPT unit, absorption and emission studies as a function of pH were undertaken in the pH range 2–12. Aqueous solutions containing DMF were prepared and pH (2,4,6,8,10,12) values were adjusted using 5% hydrochloric acid and 5% sodium hydroxide solutions.

Colors of dyes **6a**, **6b** and **6d** in all pH solutions remained same, but dyes **6c** and **6e** showed visible color change from acidic media to highly alkaline media. Dye **6c** showed orange color from pH 2 to pH 8 and turn into wine red beyond pH 10. Similarly, color of dye **6e** was orange in color and turned into dark reddish brown color in highly alkaline media. The absorption values are summarized in Table 6. Also dyes **6c** and **6e** showed dual absorption maxima at highly alkaline pH. Longer absorption band was observed at around 635 nm.

Emission maxima of all the dyes **6a**–**e** remained same at all pH. However the emission intensity changed with the change in pH, although not uniformly. The dye **6c** however showed a gradual increase in the emission intensity with decrease in pH. Dyes **6c** and **6e** with a nitro group on the acceptor side of the azo dye showed less emission intensities in highly alkaline media. The results are summarized in Table 6, Figs. 11–15.

3.3. Dyeing and fastness properties of the dyes **6a**–**e** on polyester fabric

Most of the azo disperse dyes are insoluble in water. These dyes are used to apply on polyester fabric from aqueous dispersion rather than from solution to avoid loss of dye [21]. Synthesized azo disperse dyes were insoluble in water and were prepared for application on polyester fiber by dispersing in water. These readily dispersible dyes 6a-e were dyed hydrophobic fibers (polyester fabrics) at 2% shade by using high temperature pressure technique. These dyes generally give red shade on polyester fabrics with excellent uniformity. Dyed fabrics were evaluated in terms of their fastness properties. Various fastness properties such as light, wash and sublimation of the dyed polyester fabrics were studied and the values are given in Table 7.

3.3.1. Fastness to washing

Wash fastness property depends upon the solubility of dye in water, type of linkage present in dye molecule and fiber, size of dye molecules and charge present on the dye. All synthesized azo disperse dyes **6a**–**e** show excellent wash fastness properties according to the international geometric gray scale. This result is attributed may be due to the less solubility of the dyes in water. Staining against polyester and cotton gives excellent ratings, as both fabrics remain undyed.

3.3.2. Fastness to sublimation

Fastness to sublimation is the most important requirement of dyed polyester fabrics, as migration of dye molecules and wet fastness of azo disperse dyes on polyester fabrics are totally

Table 3	
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Effect of solvents on photo physical properties of dyes 6c and 6'c.

Solvents	6c					6′c					
	λ_{\max} (nm)	\mathcal{E} Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	$\lambda_{emi} (nm)$	Emission intensity	Δλ (nm)	λ_{\max} (nm)	€ Molar absorptivity (dm³ mol ^{−1} cm ^{−1})	λ _{emi} (nm)	Emission intensity		
CHCl ₃ (a)	507	20,788	600	3.437	93	492	17,638	_	_		
EtOAc (b)	504	26,113	596	1.55	92	482	14,943	_	_		
1,4-Dioxane (c)	506	19,084	600	1.757	94	486	15,001	_	_		
Ethanol (d)	506	17,892	598	1.426	92	483	13,800	_	_		
ACN (e)	503	22,109	592	0.972	89	483	15,792	_	_		
DMF (f)	509	16,443	586	1.065	77	489	15,060	_	_		
DMSO (g)	516	17,295	592	1.032	76	498, 612	13,390, 4863	-	-		

Table 4

Effect of solvents on photo physical properties of dyes **6d** and **6'd**.

Solvents	6d					6′d			
	λ_{\max} (nm)	\mathcal{E} Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	λ _{emi} (nm)	Emission intensity	Δλ (nm)	λ_{\max} (nm)	E Molar absorptivity (dm ³ mol ⁻¹ cm ⁻¹)	λ _{emi} (nm)	Emission intensity
CHCl ₃ (a)	507	13,645	601	5.961	94	419	8479	_	_
EtOAc (b)	504	12,330	603	2.069	99	416	10,147	-	_
1,4-Dioxane (c)	504	9864	601	1.757	97	417	9618	_	_
Ethanol (d)	507	12,288	605	2.887	98	417	8868	_	_
ACN (e)	504	12,535	607	1.547	103	417	9368	_	_
DMF (f)	510	12,576	611	2.135	101	420	9785	_	_
DMSO (g)	513	12,165	617	2.010	104	420	9424	-	-

Table 5

Effect of solvents on photo physical properties of dyes **6e** and **6'e**.

Solvents	6e					6′e						
	λ _{max} (nm)	E Molar absorptivity (dm³ mol ^{−1} cm ^{−1})	λ _{emi} (nm)	Emission intensity	$\Delta\lambda$ (nm)	λ_{\max} (nm)	€ Molar absorptivity (dm ³ mol ^{−1} cm ^{−1})	$\lambda_{emi} (nm)$	Emission intensity			
CHCl ₃ (a)	495	24,089	594	3.618	99	506	9053	_	_			
EtOAc (b)	494	8840	572	3.302	78	488	11,772	_	_			
1,4-Dioxane (c)	500	24,707	588	3.876	88	399, 612	7817, 9609	_	_			
Ethanol (d)	524	3005	598	5.127	74	402, 546	6705, 11,031	_	_			
ACN (e)	503	3580	562	4.347	59	429, 573	8219, 13,039	-	_			
DMF (f)	506	16,000	590	3.862	84	438, 582	9331, 15,511	-	_			
DMSO (g)	644	8132	709	0.174	65	438, 582	9331, 15,511	-	-			





Fig. 5. Effect of solvent polarity on photo physical properties of azo disperse dyes 6a.



Where, a = chloroform, b = ethyl acetate, c = 1,4-dioxane, d = ethanol, e = acetonitrile, f = N,N-dimethylformamide, g = dimethylsulfoxide.

Fig. 6. Effect of solvent polarity on photo physical properties of azo disperse dyes 6b.



Where, a = chloroform, b = ethyl acetate, c = 1,4-dioxane, d = ethanol, e = acetonitrile, f = N,N-dimethylformamide, g = dimethylsulfoxide.

Fig. 7. Effect of solvent polarity on photo physical properties of azo disperse dyes 6c.



Where, a = chloroform, b = ethyl acetate, c = 1,4-dioxane, d = ethanol, e = acetonitrile, f = N,N-dimethylformamide, g = dimethylsulfoxide.

Fig. 8. Effect of solvent polarity on photo physical properties of azo disperse dyes 6d.



Where, a = chloroform, b = ethyl acetate, c = 1,4-dioxane, d = ethanol, e = acetonitrile, f = N,N-dimethylformamide, g = dimethylsulfoxide.

Fig. 9. Effect of solvent polarity on photo physical properties of azo disperse dyes 6e.



Where, a = chloroform, b = ethyl acetate, c = 1,4-dioxane, d = ethanol, e = acetonitrile, f = N,N-dimethylformamide, g = dimethylsulfoxide.

Fig. 10. Effect of solvent polarity on UV-visible absorption spectra of dyes 6'a-e.

Table 6 UV–Vis absorption and fluorescence maxima of dyes 6a-e at pH 2 to 12.

pН	он ба			6b			6c			6d			6e		
	λ _{abs} (intensity)	λ _{emi} (intensity)	Δλ	λ _{abs} (intensity)	λ _{emi} (intensity)	Δλ									
2	495 (2.383)	592 (0.076)	97	490 (2.400)	602 (0.89)	112	495 (2.393)	596 (0.156)	101	500 (2.384), 575 (2.619)	614 (0.114)	114	495 (2.353)	586 (0.370)	91
4	495 (2.395)	602 (0.027)	107	495 (2.391)	598 (0.054)	103	495 (2.394)	596 (0.098)	101	505 (2.342), 575 (2.524)	612 (0.168)	107	495 (2.364)	580 (0.372)	85
6	505 (2.314)	590 (0.16)	85	495 (2.395)	590 (0.181)	95	495 (2.411)	594 (0.098)	99	495 (2.407), 575 (2.647)	612 (0.112)	117	495 (2.344)	570 (0.798)	75
8	495 (2.397)	590 (0.120)	95	495 (2.388)	588 (0.368)	93	495 (2.415)	594 (0.076)	99	500 (2.367), 575 (2.554)	612 (0.161)	112	495 (2.169)	578 (0.670)	83
10	495 (2.368),	592 (0.107)	97	495 (2.381)	588 (0.178)	93	490 (2.459), 635 (1.261)	588 (0.021)	98	505 (2.317), 575 (2.457)	610 (0.168)	105	495 (2.458), 645 (2.437)	578 (0.017)	83
12	495 (2.346)	592 (0.128)	97	495 (2.365)	588 (0.217)	93	490 (2.454), 635 (1.171)	592 (0.016)	102	505 (2.31), 575 (2.429)	610 (0.186)	105	495 (2.488), 645 (2.377)	580 (0.012)	85



Fig. 11. UV visible absorption and emission spectra of dye 6a at various pH.



Fig. 12. UV visible absorption and emission spectra of dye 6b at various pH.



Fig. 13. UV visible absorption and emission spectra of dye 6c at various pH.



Fig 14. UV visible absorption and emission spectra of dye 6d at various pH.



Fig. 15. UV visible absorption and emission spectra of dye 6e at various pH.

Table 7Fastness properties of azo disperse dyes 6a-e.

Dye no.	Light fastness (1–8)	Wash fastness (1-5)	Staining on fabric after washing (1-5)		Sublimation fastness (1–5)	Staining on fabri after sublimation (1–5)	
			Polyester	Cotton		Polyester	Cotton
6a	5	4	4-5	5	4-5	3-4	4
6b	4	4-5	4-5	5	4	4	4
6c	6	4-5	5	4	5	4-5	5
6d	4	5	4-5	4	4	3	4
6e	4	5	5	4	4	5	4

Table 8

Color values of azo disperse dyes 6a-e.

Dye No.	L*	<i>a</i> *	b^*	с*	ho	K/S
6a	49.29	54.25	30.99	62.48	29.74	1.335
6b	50.42	51.51	25.56	57.50	26.39	1.218
6c	51.66	50.88	26.88	57.55	27.85	1.248
6d	33.40	41.92	15.10	44.56	19.81	1.469
6e	56.52	29.13	8.50	30.34	16.27	0.812

depended on heat treatment. Sublimation properties of azo disperse dyes 6a-e also show good ratings according to the international geometric gray scale. The dyes 6a and 6d showed good to very good rating for sublimation fastness and staining on the undyed polyester as well as cotton fabrics.

3.3.3. Fastness to light

Light fastness is the degree to which a dye resists fading due to light exposure. All dyes have some susceptibility to light damage which fully depends on molecular structure. Dye **6c** shows good to very good light fastness and others show good light fastness according to the AATCC Test method.

3.4. Color assessment

The colorimetric parameters of dyed polyester fabrics using synthesized azo disperse dyes **6a**–**e** were recorded on a reflectance spectrophotometer CE-7000A Gretag-Macbeth. The color values of synthesized azo disperse dyes 6a-e on polyester fabrics were determined by using CIE 1976 Color Space method in terms of L^* , a^* and b^* and tabulated in Table 8. All dyes have good affinity toward the polyester fabrics at high temperature and gave red shades on polyester fabrics. The values of color coordinates suggested that the color hue of all dyes shifted toward the redder direction on the red-green axis as well as toward the yellowish direction on yellow-blue axis as positive values of a^* and b^* respectively. Dye **6a** is redder as well as yellower than other azo disperse dyes (a^* , b^* values from Table 8). Color strength of all dyes applied on polyester fabrics are expressed as K/S values which dependent on type of substituent present on aromatic ring. The K/S values are in the range of 0.81-1.47.

Table 9

Comparison between fastness properties of 2-naphthol azo disperse dyes and 2-naphthol benzothiazolyl azo disperse dyes.



Table 9 (continued)



3.5. Comparison study

Azo disperse dyes derived from the coupler 2-naphthol are known to have deficiency in their light fastness properties [27]. To overcome this deficiency we introduced heterocyclic benzothiazolyl ring ortho to hydroxyl group present on naphthalene moiety. This may enhance the fastness properties. Therefore dispersed azo dyes 6a-e from 3 were synthesized and compared with the dyes 6'a-e obtained from 2-naphthol in place of 3.

A comparative account of fastness rating data is compiled in Table 9. It is observed that the dyes from **3** have uniformly higher light fastness properties on polyester as compare to the dyes from 2-naphthol. The presence of benzothiazolyl ring adjacent to hydroxyl group has decisive role in enhancing the photo stability of these dye

6a—**e**. The occurrence of ESIPT as shown in Fig. 1 may be held responsible for the enhanced photo stability and hence light fastness.

4. Conclusion

We have successfully synthesized azo disperse dyes using 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol as a coupler. All these disperse dyes give red shades on polyester fabric. Comparison study proves that inclusion of heterocyclic benzothiazolyl ring enhance the fastness properties. Synthesized azo disperse dyes 6a-e show fluorescence with lower intensity in various pH solutions and in different organic solvents.

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