

Novel Aza-Substituted Benzothiazol and 1,2,4-Triazol Dyes: Synthesis, Characterization and Properties

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ABSTRACT

Series of novel dichromophoric dyes based on 2-aminobenzothiazoles and 3-amino-1,2,4 -triazole have been synthesized in high yields. All the dyes have been classified as disperse dyes. Besides their electronic spectroscopic properties, high dye-uptakes on polyester, excellent fastness properties, highly extinction coefficients, and broad solvatochromic effects have been observed in these novel disperse dyes. The derivatives of amino triazole were appropriate as pH indicator in the range of 11-13, as well. Prog. Color Colorants Coat. 6(2013), 37-49. © Institute for Color Science and Technology.

1. Introduction

Azo compounds constitute the largest class of compounds amongst all known families of dyes. They have been studied more than any other class of dyes due to their popular application as textile fiber dyestuffs. Disperse dyes based on benzothiazole have gained importance and constitute the first example of the successful textile commercial exploitation of heterocyclic amines in the production of red dyes [1-3]. Due to their low-cost, brightness, and dyeing performance, this type of dyes has become economically important, motivating a substantial research effort both in industry and academia. For example, C.I. Disperse Red 177 and C.I. Disperse Violet 52 are important disperse dyes, which prepared from 2-aminothiazoles and 2-aminobenzo

thiazoles. They also have a long history and a significant role in textile industry. Azo dyes for polyester are normally of the monoazo type although a number of disazo compounds have reached commercial status [5-13].

Aside from the continuous interest on benzothiazole disperse dyes for textiles dyeing, a diverse range of non-textile applications have also emerged. As an example, azothiazole and azobenzothiazole dyes have found application in liquid crystal technology, reprography, and non-linear optics (NLO). Recently, they have been investigated as potential sensitizers for photodynamic therapy (PDT) [14-19]. As a result, azobenzothiazoles have found a new use as functional dyes.

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Furthermore, azo dyes have received considerable attention in the field of solvatochromic studies and in the design of polarity scale. Nevertheless, the majority of the developments concerning azobenzothiazole dyes have tended to focus on series of compounds where the substitution pattern was varied and the color-structure relationship, as well as the effect of the solvent, temperature, and acidity in the visible spectrum was studied [20-23].

Consequently, in continuing of our recent investigations on novel hemicyanine dyes [24-26], and in considering mentioned various applications of 2-aminobenzothiazole and 3-amino-1,2,4-triazole azo dyes, in this report synthesis of some novel series of dichromophoric disperse dyes with extended conjugation systems based on 2-aminobenzothiazoles and 3-amino-1,2,4-triazole is reported.

2. Experimental

2.1. Materials and equipment

Chemicals were purchased from Merck and used without further purification. Melting points were measured on a Buchi melting-point B-545 apparatus. ^1H NMR spectra were measured at 500 MHz, using a Bruker 500-Avance Fourier transform (FT)-NMR instrument with dimethyl sulfoxide ($\text{DMSO}-d_6$) as solvent. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Perkin-Elmer Spectrum One BX FT-IR spectrometer. UV-Vis spectra were recorded using a UV-Vis spectrophotometer, Cecil CE 9200. The fluorescence spectra were taken on a Perkin Elmer Ls 55 Fluorescence Spectrometer.

2.2. General procedure for the preparation of compounds **2**

Aniline **2** (1.82 mL, 0.02 mol) was added dropwise to a stirred solution of Glyoxal **1** (0.46 mL, 0.01 mol) or in acetic acid 30% (20 mL) at 5°C . The reaction mixture was stirred for 1 hour, filtered, and crystallized in water to afford the pure title compounds.

2.3. General procedure for the preparation of compounds **3a-p**

The aminobenzothiazole derivatives or amino-1,2,4-

triazole (20 mmol) were dissolved in H_2SO_4 50% (25 mL). The mixture was cooled by means of an ice-water bath and an aqueous solution of NaNO_2 (20 mmol, 5 mL) was added dropwise within 15 min at $0-5^\circ\text{C}$. The resulting yellow to orange solution was stirred at $0-5^\circ\text{C}$ for 1 h. Then the suspension of compound **2** (10 mmol) in HCl (20 mL, 1%) at $0-5^\circ\text{C}$ was added dropwise to diazonium salt at $0-5^\circ\text{C}$. The reaction mixture was stirred at room temperature for 1 h and neutralized by adding NH_3 solution 10%. The precipitated dye was isolated by filtration, washed with excess water and crystallized in ethanol to afford the pure products.

2.4. Dyeing procedure

Polyester fabrics (1 g) were dyed in a laboratory-scaled HT dyeing machine at a liquor ratio of 50:1 with different amounts of dyes and dispersing agent (1%). After adjusting the acidity by acetic acid ($\text{pH}=4.5$), the polyester fibers (1.0 g) were immersed in the dye bath, and the temperature was raised from 30°C to 90°C at the rate of $2^\circ\text{C}/\text{min}$ and heated to 130°C gradually at the rate of $1^\circ\text{C}/\text{min}$. Dyeing was carried out at this temperature for 60 min. Subsequently, it was cooled down to 70°C at the rate of $3^\circ\text{C}/\text{min}$. The dyed samples were reduction cleared using sodium hydrosulfite (2 g/l), sodium hydroxide (1 g/l) and detergent (1 g/l) at liquor to goods ratio of 50:1.

3. Result and discussion

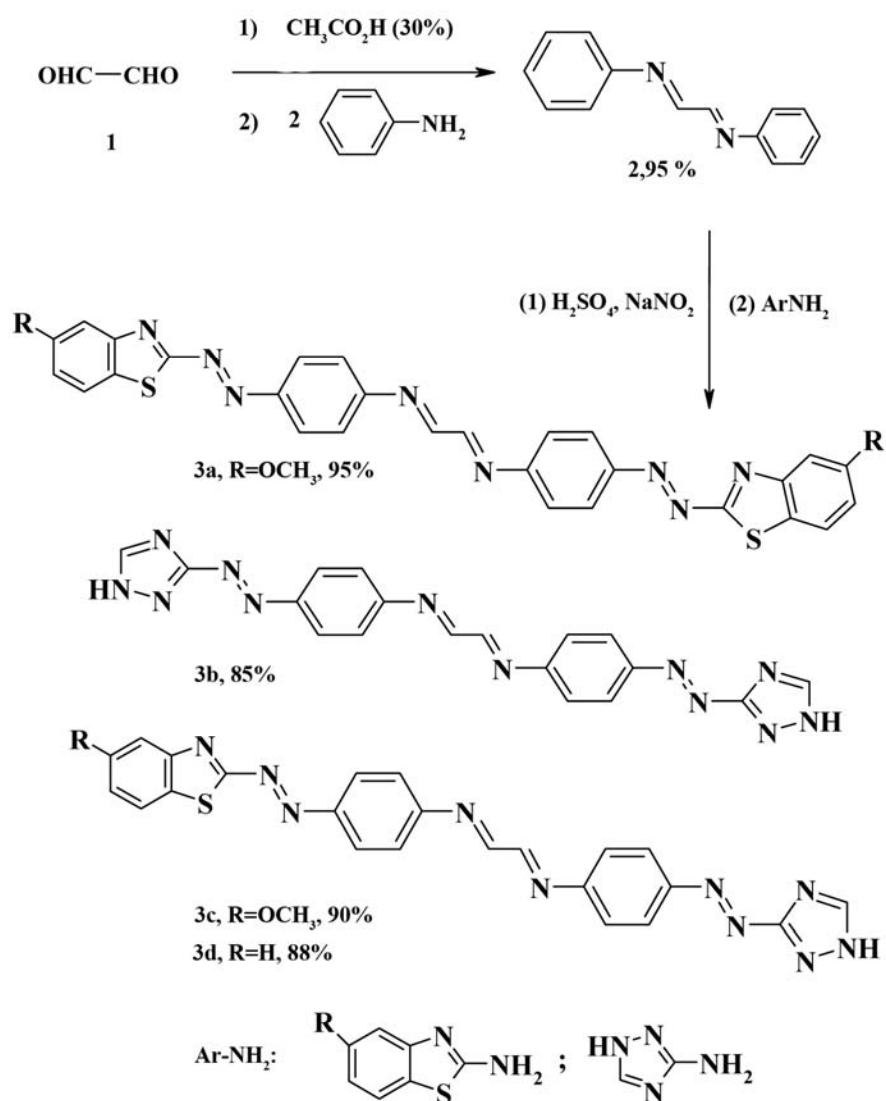
3.1. Synthesis and characterization

The reaction of Glyoxal **1** with two equivalents of aniline in acidic conditions within 1 h at $0-5^\circ\text{C}$ leads to the corresponding Schiff base (or azomethine) **2** in extremely high yield (95%) (Scheme 1). The structures of compounds **2** were deduced from their IR, ^1H -NMR and spectroscopic data.

The coupling of Schiff base **2** with two equivalents identical 6-substituted-2-azobenothiazole and 2-azo-1,2,4-triazole affords symmetrical and unsymmetrical products **3a-d** in high yields (85 - 95%) (Scheme 1).

The structures of the compounds **3a-d** were deduced from their IR, ^1H -NMR spectroscopic and CHN analysis data.

The dyes with electron-rich structures are in red color (λ_{max} : 398-494 nm in ethanol) (Table 1) with high molar absorption coefficients ($3.0-4.5 \times 10^4 \text{ .M}^{-1}.\text{cm}^{-1}$).



Scheme 1: Synthesis of dichromophoric benzothiazole and 1,2,4-triazole based disperse dyes **3a-d**.

Table 1: Summarized spectroscopic data for **3a-d** compounds.

Compound	λ_{max} (nm)	ε ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	Color
3a	494	3.8×10^4	Red
3b	398	4.5×10^4	Yellow
3c	414	3.3×10^4	Orange
3d	398	3.0×10^4	Yellow

λ_{max} : maximum absorption wavelengths; ε : corresponding molar absorption coefficient. Spectroscopic data and colors are reported in ethanol.

3.2. Physical properties of dyes (3a-d)

Fastness properties of these dyes are good to excellent (Table 2). The fastness properties were measured using 1.0% dye solution. Color fastness was determined according to the international standards: fastness to washing (ISO 105-C01), fastness to perspiration (ISO 105-E04), fastness to rubbing (ISO 105-X12), and fastness to light (ISO 105-B02). Change in shade and staining of adjacent multifiber (Multifiber DW, adjacent fabric, BS EN ISO 105-F10) were assessed using grey scales.

The K/S for the synthesized dyes **3a-d** is shown in Figure 1. Dye-uptakes for **3a-d** have been studied. In this series, the best dyeabilities were obtained for **3a**, **3c** and the least referred to **3d**.

3.3. pH effect

Many dyes have been used as pH indicators by the reversible action of acid and base, and this behavior led to the concept of acid-base indicators, although there are not many indicators in the pH range of 10-14 [22-24]. In this work, three derivatives of 3-azo-1,2,4-triazoles are used as pH indicators in the pH range of 11-13. For these compounds, color change in the pH range of 11-13 was extremely sharp and clear. **3b-d** dyes exhibited quite acceptable properties in terms of transition ranges and color changes to be used as indicators.

To determine the transition range for color change of the indicators, the measurement of absorption was carried out at 398 nm, 414 nm, and 398 nm for the compounds **3b**, **3c**, **3d**, respectively, during the addition of dilute alkali solution (NaOH).

Table 2: Fastness properties of disperse dyes **3a-d** on polyester fibers.

Compound	Light	Washing		Rubbing	
		Staining	Change	Wet	Dry
3a	4-5	4-5	5	5	4-5
3b	2-3	4-5	4-5	5	4
3c	2-3	5	4-5	4-5	4
3d	3	5	5	3	3-4

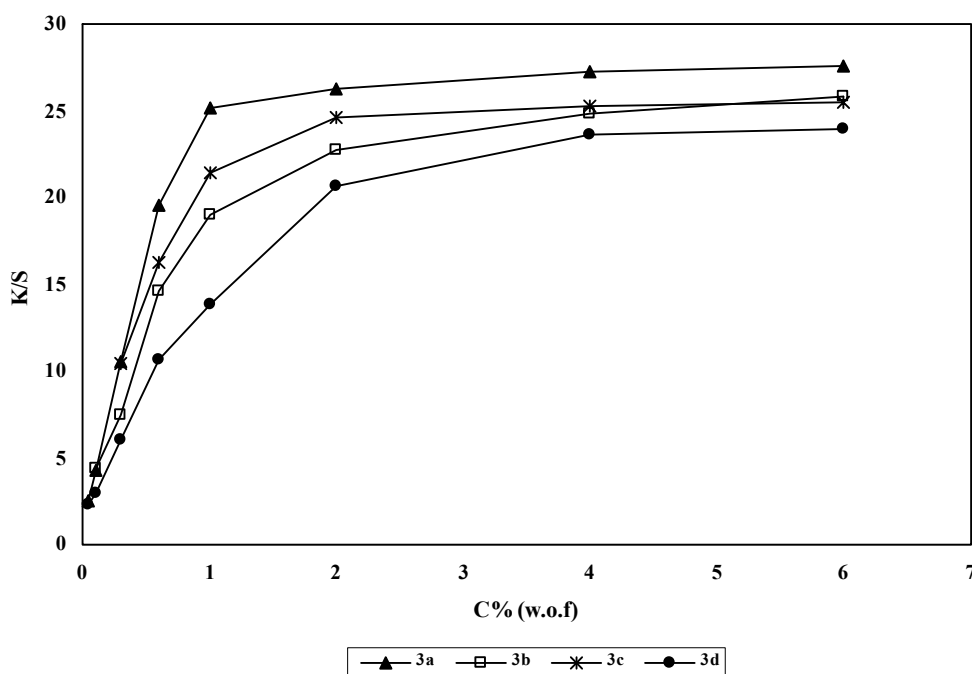


Figure1: K/S of bichromophoric dyes **3a-d**.

The distinct maximum of its absorption spectrum is shifted both bathochromically with any increase of the pH value (Figures 2-4).

From the UV-Vis absorption spectra based on the

varying basicity, **3b** showed yellow at $\lambda_{\text{max}}=398$ nm but with alkali addition this indicator showed strong red at $\lambda_{\text{max}}=498$ nm with high extinction coefficient in the pH range of 12-13.

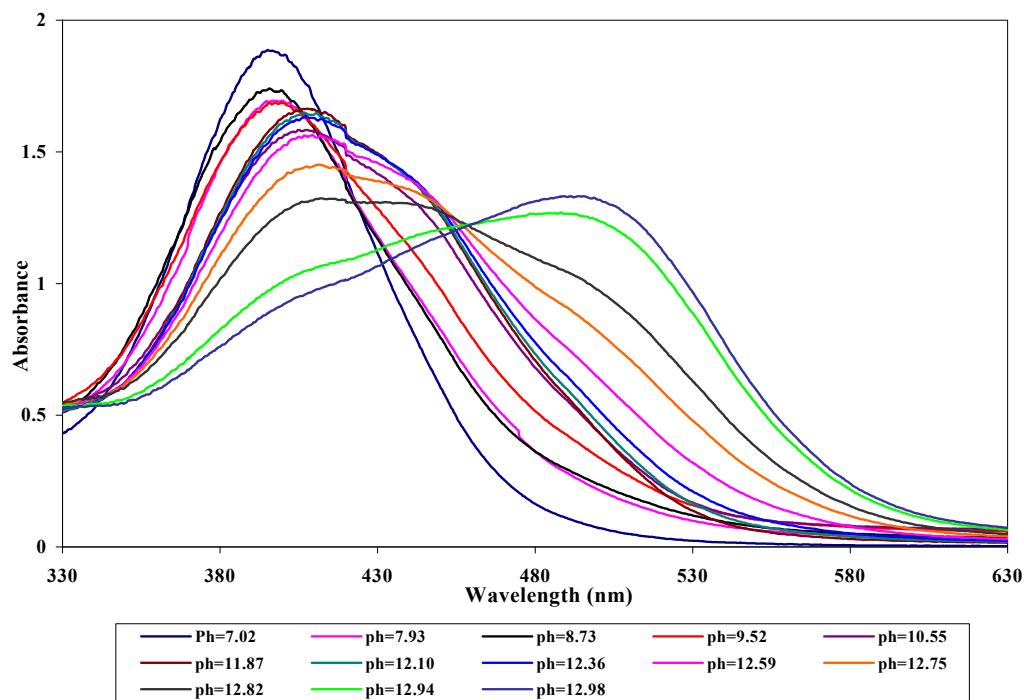


Figure 2: UV-Vis spectra of dye **3b** at different pH values ($C = 2 \times 10^{-4}$ mol/l).

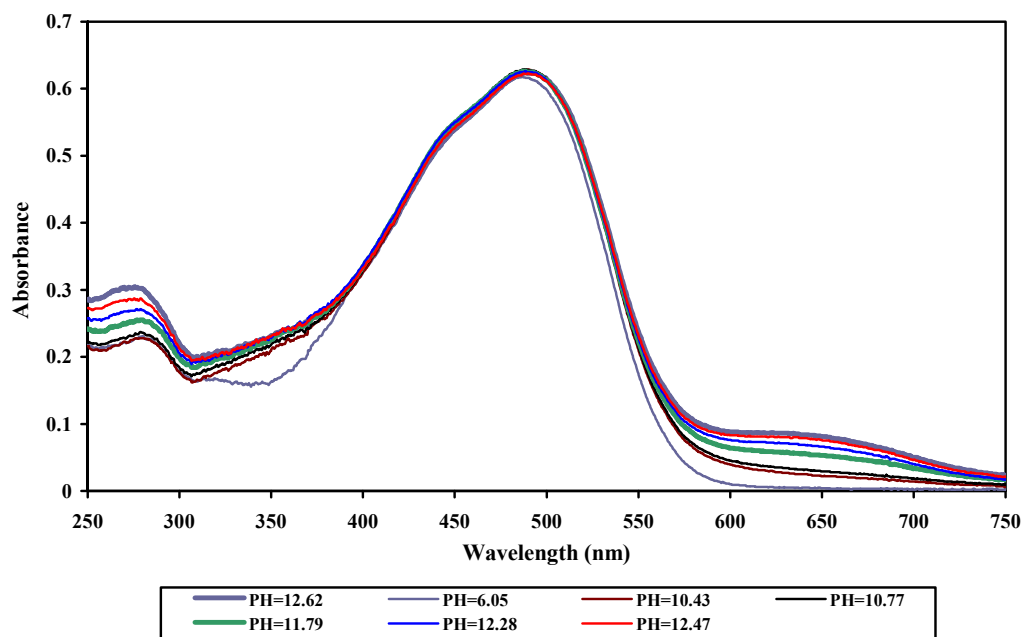


Figure 3: UV-Vis spectra of dye **3c** at different pH values ($C = 2 \times 10^{-4}$ mol/l).

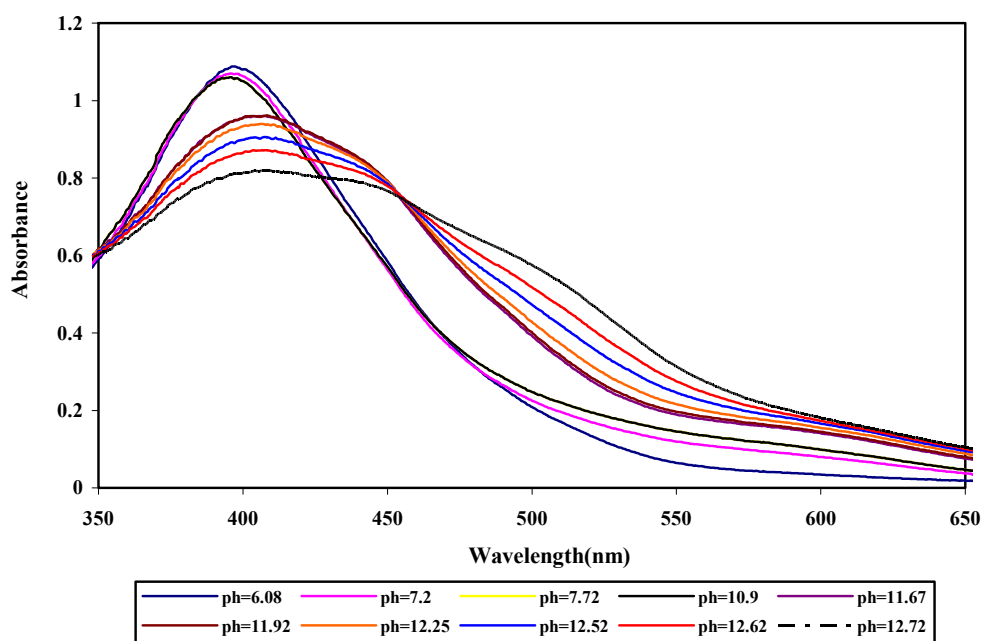


Figure 4: UV-Vis spectra of dye **3d** at different pH values ($C = 2 \times 10^{-4}$ mol/l).

Compound **3c** is orange at $\lambda_{\max}=414$ nm and during alkali addition. This indicator showed strong brown due to the creation of a new peak at 650 nm with high extinction coefficient in the pH range of 10.4-12.4. Also **3d** showed yellow at $\lambda_{\max}=398$ nm and strong orange at $\lambda_{\max}=419$ nm with high extinction coefficient in the pH range of 11.9-12.7 (Figures 2-4). Color changes are reversible and the compounds **3b-c** are stable in acidic and alkaline conditions. These compounds have excellent indicator properties within the alkaline-pH range.

3. 4. Solvatochromic effect

Solvatochromic effects of nine solvents have been studied on these dyes. The results are shown in Table 3 and Figures 5-8. According to Table 3, the most solvatochromic shift (i.e. 172 nm) was observed for **3a** (bathochromic shift). The results have been revealed that **3a** could significantly used as an indicator for these nine different solvents (Figure 5).

Nonetheless, solvatochromic effects for **3a** and **3c** compounds were more obvious due to 172 nm and 37 nm bathochromic shift in DMF as solvent, respectively. The results have been revealed that the λ_{\max} of dyes **3b** and

3d didn't changed remarkably in these nine different solvents. (Figures 5-8).

3. 5. Fluorescence emission

All these dyes (**3a-d**) were excited at 279-355 nm and showed fluorescence emission at a broad range i.e., 428–573 nm with low and medium intensities. Figure 9 shows the excitation and fluorescence emission spectra of the 10^{-4} mol.L⁻¹ of the disperse dyes **3a-d** in DMF at 293 K. Two important characteristics for fluorescent compounds, i.e.

Stokes shift ($\nu_A-\nu_F$) and oscillator strength (f) have been studied for these dyes. The Stokes shift is a parameter that indicates the difference in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1 . The Stokes shifts (cm^{-1}) were calculated by Eq. (1).

$$(\nu_A-\nu_F) = (1/\lambda_A - 1/\lambda_F) \times 10^7 \quad (1)$$

Table 3: Physical properties and polarity parameters of the solvent used and the spectral data for **3a-p** samples at concentration of 2×10^{-4} mol.L⁻¹.

Dye	Solvent	ϵ	n	α	β	π^*	λ_{\max} (nm)
3a	THF	7.58	1.4072	0.00	0.55	0.55	496
	Aceton	21.01	1.3590	0.08	0.48	0.62	486
	DMF	38.25	1.4300	0.00	0.69	0.88	650
	DMSO	47.24	1.4790	0.00	0.76	1.00	500
	Acetonitril	35.94	1.3441	0.19	0.40	0.66	478
	Ethanol	24.30	1.3610	0.86	0.75	0.54	494
	Methanol	33.70	1.3290	0.98	0.66	0.60	485
	Ethylacetate	6.02	1.3720	0.00	0.45	0.55	466
	Chloroform	4.81	1.490	0.44	0.00	0.76	449
	THF	7.58	1.4072	0.00	0.55	0.55	386
3b	Aceton	21.01	1.3590	0.08	0.48	0.62	385
	DMF	38.25	1.4300	0.00	0.69	0.88	542
	DMSO	47.24	1.4790	0.00	0.76	1.00	399
	Ethanol	24.30	1.3610	0.86	0.75	0.54	396
	Methanol	33.70	1.3290	0.98	0.66	0.60	396
	THF	7.58	1.4072	0.00	0.55	0.55	450
	Aceton	21.01	1.3590	0.08	0.48	0.62	462
3c	DMF	38.25	1.4300	0.00	0.69	0.88	487
	DMSO	47.24	1.4790	0.00	0.76	1.00	496
	Acetonitril	35.94	1.3441	0.19	0.40	0.66	467
	Ethanol	24.30	1.3610	0.86	0.75	0.54	478
	Methanol	33.70	1.3290	0.98	0.66	0.60	478
	Ethylacetate	6.02	1.3720	0.00	0.45	0.55	444
	Chloroform	4.81	1.490	0.44	0.00	0.76	453
	THF	7.58	1.4072	0.00	0.55	0.55	389
3d	Aceton	21.01	1.3590	0.08	0.48	0.62	387
	DMF	38.25	1.4300	0.00	0.69	0.88	618
	DMSO	47.24	1.4790	0.00	0.76	1.00	399
	Ethanol	24.30	1.3610	0.86	0.75	0.54	395
	Methanol	33.70	1.3290	0.98	0.66	0.60	497

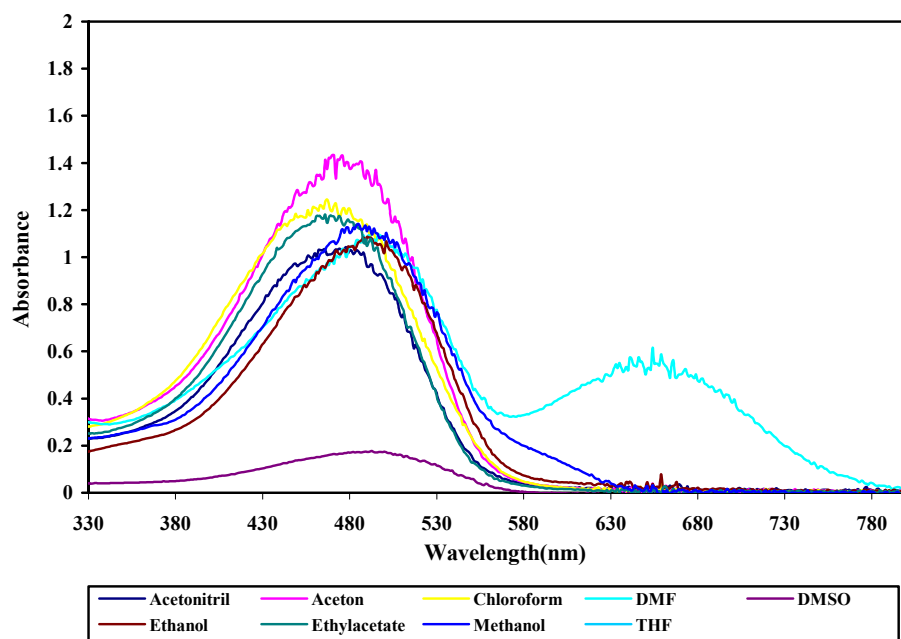


Figure 5: UV-Vis spectra of **3a** in different solvents at 293 K at concentration of 2×10^{-4} .

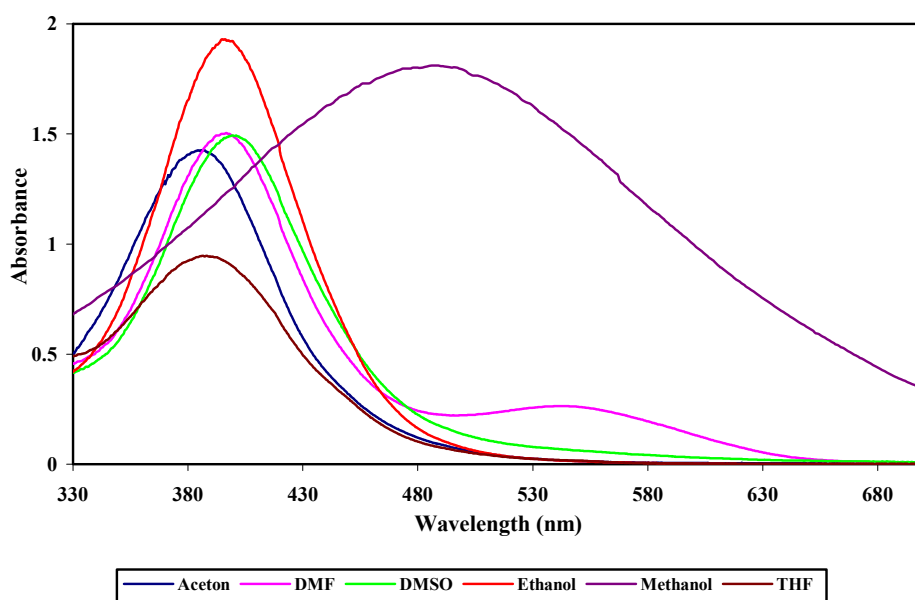


Figure 6: UV-Vis spectra of **3b** in different solvents at 293K at concentration of 2×10^{-4} mol.L⁻¹.

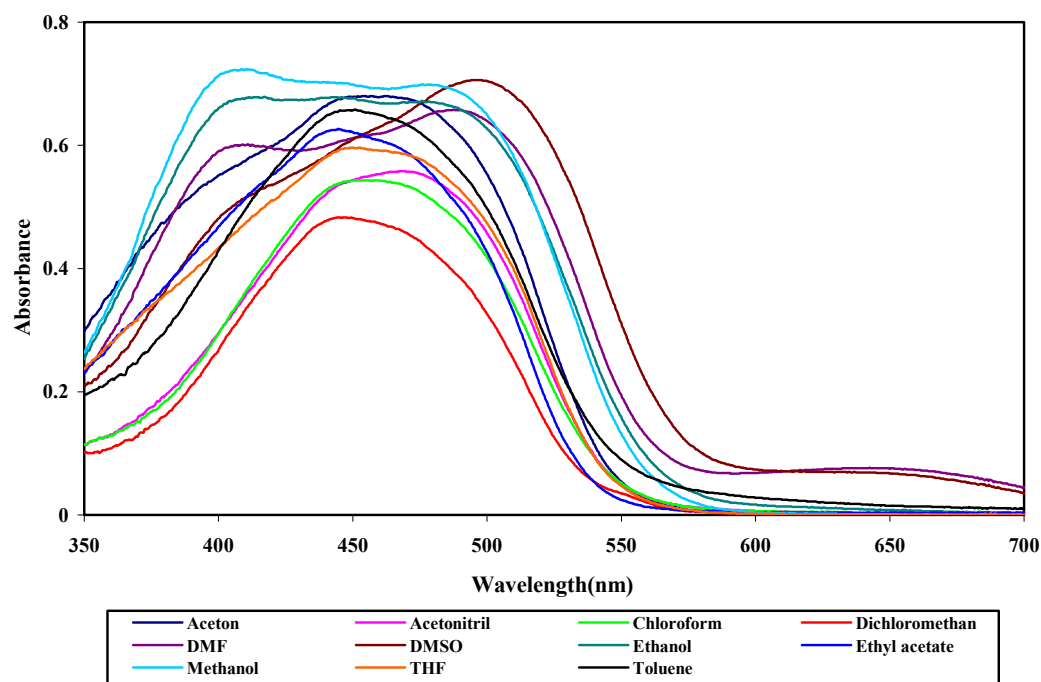


Figure 7: UV-Vis spectra of **3c** in different solvents at 293K at concentration of $2 \times 10^{-4} \text{ mol.L}^{-1}$.

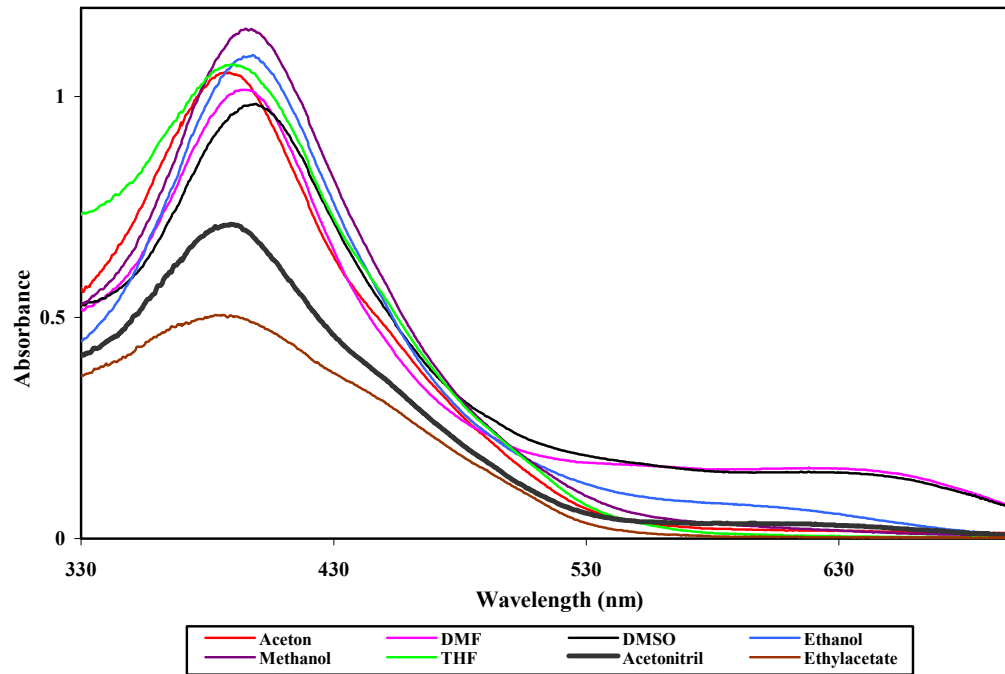


Figure 8: UV-Vis spectra of **3d** in different solvents at 293 K at concentration of $2 \times 10^{-4} \text{ mol.L}^{-1}$.

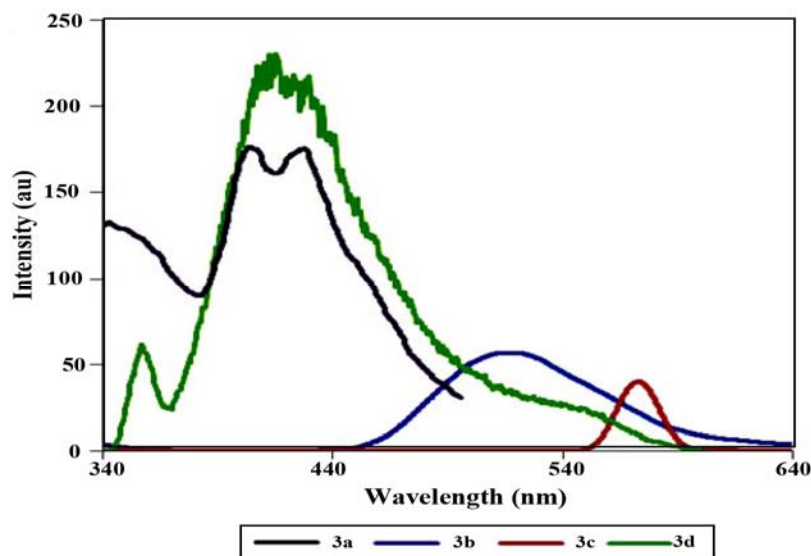


Figure 9: Fluorescence emission spectra of disperse dyes **3a-d** in DMF at 293 K. concentration: 1×10^{-4} mol.L $^{-1}$.

The Stokes shift values of the dyes under study were observed between 555 and 1972 cm $^{-1}$ (Table 4). The oscillator strength (f) shows the effective number of electrons whose transition is from ground to excited state. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the half-band width of the absorption band (cm $^{-1}$) at ϵ_{\max} [30].

$$f = 4.32 \times 10^{-9} \times \Delta\nu_{1/2} \times \epsilon_{\max} \quad (2)$$

The values of 0.17-0.98 were obtained for the oscillator strengths of the **3a-d** disperse dyes (Table 4)

The fluorescence quantum yield (Φ_F) is known as the ratio of the absorbed photons to the emitted photons through fluorescence[30]. As a result, the quantum yield gives the ability of molecules to emit the absorbed light energy. The quantum yield of **3a-d** was calculated according to Eq. (3) using 1,1,4,4-tetraphenyl-1,3-butadiene ($\Phi_{\text{ref}}=0.7$) as a reference:

$$\phi_F = \phi_{\text{ref}} \left(\frac{S_{\text{sample}}}{S_{\text{ref}}} \right) \left(\frac{A_{\text{ref}}}{A_{\text{sample}}} \right) \left(\frac{n_{\text{sample}}^2}{n_{\text{ref}}^2} \right) \quad (3)$$

A_{sample} , S_{sample} , n_{sample} and A_{ref} , S_{ref} , n_{ref} are absorbance at the excitation wavelength, the integrated emission band area and the refractive index of the sample and the reference, respectively.

The fluorescence quantum yield values of 0.09-0.48 were obtained for the **3a-d** disperse dyes (Table 4).

4. Experimental data

3a. *N, N'-ethane-1,2-diylidenebis {4-[(E)-5-methoxy 1,3-benzothiazol-2-yl]diazanyl}aniline*. Red powder; yield (95%); m.p. 172-174 °C. IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 2923 (CH=); 1610 (C=N); 1536 (C=C); 1285 (C-N). ^1H NMR (500 MHz, CDCl_3): δ_{H} 3.90 (6H, s, 2 OCH_3); 6.73 (2H, d, $^3J_{\text{HH}}$ 8.08 Hz, 2 CH); 7.07 (4H, d, $^3J_{\text{HH}}$ 7.36 Hz, 4 CH); 7.42 (4H, d, $^3J_{\text{HH}}$ 7.36 Hz, 4 CH); 7.90 (2H, d, $^3J_{\text{HH}}$ 8.25 Hz, 2 CH); 7.97 (2H, d, $^3J_{\text{HH}}$ 8.25 Hz, 2 CH); 8.04 (2H, s, 2 CH). ES $^+$ -MS: m/z (%) = 589 (M^+ , 2), 313 (6), 295(4), 284 (48), 180 (59), 165 (66), 106 (11), 92 (100). Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_8\text{O}_2\text{S}_2$ (590): C, 61.01; H, 3.73; N, 18.98%. Found C, 61.08; H, 3.69; N, 18.95%.

Table 4: Absorption and fluorescence characteristics of the disperse dyes **3a-d** in DMF at 293 K. concentration: 1×10^{-4} mol.l⁻¹.

Compound	λ_{ex}	λ_{em}	$\epsilon_{max} \times 10^4$	$\nu_A-\nu_F$	Intensity	f	Φ_F
3a	351	428	3.8	1953	176	0.98	0.38
3b	279	516	4.5	625	57	0.26	0.16
3c	279	573	3.3	555	40	0.17	0.09
3d	355	433	3.0	1972	211	0.44	0.46

Presented units: λ_{ex} and λ_{em} in nm; ϵ_{max} in M⁻¹.cm⁻¹, $\nu_A-\nu_F$ in cm⁻¹, and Intensity in au

3b. *N, N'-ethane-1,2- diylidenebis {4-[(E)-1,2,4-triazol-3-yl diazenyl]aniline}*. Yellow powder; yield (85%); m.p. 176-179 °C. IR (KBr) (ν_{max}/cm^{-1}): 3443 (NH); 2925 (CH=); 1597 (C=N); 1556 (C=C); 1261 (C-N). ¹H NMR (500 MHz, CDCl₃): δ_H : 5.82 (2H, d, ³J_{HH} 10.76 Hz, 2 CH); 6.86 (2H, d, ³J_{HH} 7.45 Hz, 2 CH); 6.99 (4H, d, ³J_{HH} 7.31 Hz, 4 CH); 7.75 (4H, d, ³J_{HH} 7.31 Hz, 4 CH); 9.20 (2H, d, ³J_{HH} 10.76 Hz, 2 NH). Anal. Calcd for C₁₈H₁₂N₁₂ (396): C, 54.54; H, 3.03; N, 42.42%. Found C, 54.51; H, 3.05; N, 42.45%.

3c. *4-[(E)-(5-methoxy-1,3-benzothiazol-2-yl) diazenyl, N-[2-({4-[(E)-1,2,4-triazol-2-yl) diazenyl] aniline}*. Orange powder; yield (90%); m.p. 153-156 °C. IR (KBr) (ν_{max}/cm^{-1}): 3444 (NH); 2927 (CH=); 1606 (C=N); 1544 (C=C); 1273 (C-N). ¹H NMR (500 MHz, CDCl₃): δ_H : 3.82 (3H, s, OCH₃); 5.83 (2H, d, ³J_{HH} 10.50 Hz, 2 CH); 6.73 (2H, d, ³J_{HH} 8.41 Hz, 2 CH); 7.07 (4H, d, ³J_{HH} 6.95 Hz, 4 CH); 7.31 (4H, d, ³J_{HH} 6.95 Hz, 4 CH); 7.91 (1H, d, ³J_{HH} 8.30 Hz, CH); 7.97 (1H, d, ³J_{HH} 8.30 Hz, CH); 8.05 (1H, s, CH); 9.08 (2H, d, ³J_{HH} 10.50 Hz, 2 NH). Anal. Calcd for C₂₄H₁₇N₁₀OS (493): C, 58.42; H, 3.45; N, 28.39%. Found C, 58.41; H, 3.47; N, 28.36%.

3d. *4-[(E)-(1,3-benzothiazol-2-yl) diazenyl, N-[2-({4-[(E)-1,2,4-triazol-2-yl) diazenyl] aniline}*. Orange powder; yield (88%); m.p. 159-163 °C. IR (KBr) (ν_{max}/cm^{-1}): 3445 (NH); 2922 (CH=); 1597 (C=N); 1549 (C=C); 1280 (C-N). ¹H NMR (500 MHz,

CDCl₃): δ_H : 5.80 (2H, d, ³J_{HH} 10.50 Hz, 2 CH); 6.77 (2H, d, ³J_{HH} 8.36 Hz, 2 CH); 7.12 (4H, d, ³J_{HH} 7.36 Hz, 4 CH); 7.44 (4H, d, ³J_{HH} 7.36 Hz, 4 CH); 7.90 (1H, d, ³J_{HH} 8.44 Hz, CH); 7.93 (1H, d, ³J_{HH} 8.44 Hz, CH); 8.09 (1H, s, CH); 9.12 (2H, d, ³J_{HH} 10.50 Hz, 2 NH). Anal. Calcd for C₂₃H₁₅N₁₀S (463): C, 59.61; H, 3.24; N, 30.24%. Found C, 59.63; H, 3.21; N, 30.25%.

4. Conclusions

Four novel dichromophoric bis-azo dyes with highly extended conjugation systems were synthesized in high yields. Their spectroscopic data showed high molecular extinction coefficients between $3.0 - 4.5 \times 10^4$ M⁻¹.cm⁻¹.

The dyes were red (λ_{max} : 398–494 nm) in ethanol. Furthermore, the solvatochromic effects of nine solvents were studied on these dyes. The most solvatochromic shift was 172 nm (bathochromic shift) for compound **3a**. These results demonstrate that the synthesized dyes **3a** and **3c** could be used as an indicator for these nine different solvents. Furthermore, the amino triazole dyes **3b-c** showed strong changes in λ_{max} from yellow to red and orange (**3b, 3d**). Dye **3c** showed color changes from yellow to brown due to creation of a new peak at 650 nm with high extinction coefficients in alkali pH=11-13. So, they are useful as pH indicator in the range of 11-13.

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