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# Synthesis, spectroscopic, thermal and electrochemical studies on

# thiazolyl azo based disperse dyes bearing coumarin

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#### Abstract

In this study, seven novel thiazolyl azo disperse dyes (**6a-g**) were synthesized and fully characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectral techniques. The electronic absorption spectra of the dyes in solvents of different polarities cover a  $\lambda_{max}$  range of 404-512 nm. The absorption properties of the dyes changed drastically upon acidification. This was due to the protonation of the nitrogen in the thiazole ring, which in turn increased the donor-acceptor interplay of the  $\pi$  system in the dyes, and therefore increased the absorption properties of the prepared dyes. Thermal analysis showed that these dyes are thermal stable up to 269 °C. Additionally, the electrochemical behavior of the dyes (**6a-g**) were investigated using cyclic voltammetric and chronoamperometric techniques, in the presence of 0.10 M tetrabutylammonium tetrafluoroborate, in dimethylsulfoxide, at a glassy carbon electrode. The number of transferred electrons, and the diffusion coefficient were determined by electrochemical methods. The results showed that, for all the dyes, one oxidation peak and two reduction peaks were observed.

*Keywords*: Azo dyes, Coumarin, 2-aminothiazole, Acidochromism, Spectroscopy, Electrochemistry.

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#### 1. Introduction

Nitrogen-containing heterocyclic compounds constitute an important class of aromatic heterocyclic structures due to their exceptional pharmacological properties [1]. These compounds have a variety of functional groups and form the backbone of bioactive compounds [2-6]. Thiazole ring plays an important role in the chemistry of heterocyclic compounds and exists in the structure of a number of biologically active molecules [7,8]. It is found in the structure of some natural products such as Vitamin B1 (thiamine), penicillin and carboxylase. Furthermore, 2-aminothiazole which is an important derivative of thiazole, is a leading precursor in the development of drug design [9]. 2-aminothiazole based compounds, which are derived by attaching different substituents at different positions on the ring, show some important pharmacological and biological activities [11,12]. Apart from the pharmacologically important field of use, 2-aminothiazole and its derivatives are widely used as coupling and diazo components in dye industry [13]. The increase in fiber production in the textile industry requires the development and synthesis of new disperse dyes. Disperse azo dyes have attracted considerable attention in having good fastness properties, and due to their cheap production in recent years. Color, light, and wash fastness of heteroarylazo disperse dyes obtained by coupling with the diazo component of another heteroaryl component are better than the carbocyclic analogs, since both the diazo and the coupling components are heterocyclic compounds [14-16]. Therefore, in recent years, a number of azo dyes, which were obtained by using 2-aminothiazole as the coupling component and its derivatives as the diazo components, and their properties were investigated [17-20]. The synthesis of these new derivatives of 2-aminothiazo will particularly contribute to diversification, and will also lead to increase in color range.

Coumarin has a high fluorescence in visible light, a high quantum yield, and superior photostability [21-24]. Moreover, the absorption and emission characteristics, according to the characteristics of the solvent used, can be adjusted easily in coumarin derivatives, especially when having electron accepting or donating substituents at the 3- and 7-positions [25,26]. Coumarin derivatives obtained in these forms are potential materials for a wide field of applications such as optical brighteners, laser dyes, nonlinear optical chromophores (NLO), solar collectors, monitoring systems in medicine and biology, electroluminescence (EL) materials, fluorescent labels and chemosensors [27-36]. Furthermore, coumarin ring is readily available and functionalized. Therefore, we proposed that the integration of coumarin unit into thiazolyl azo disperse dye based structures, leads to novel dye structures with promising properties that may be considered for the development of functional dyes. Therefore, in this study, we report the syntheses of azo dyes bearing coumarin unit as the main structure. Due to its good photophysical properties we think that the synthesized azo dyes (6a-g) can exhibit better photophysical activity. Firstly, here we determined the photophysical properties of a series of newly synthesized thiazolyl azo disperse dyes in different solvents and then examined the azo-hydrazone tautomeric equilibria in the same solvents. The reductionoxidation and thermal behavior of the azo dyes play an important role in biomedical research, dyeing textile fibers, liquid crystal displays, electro-optical devices, laser-inkjet printers, and treatment of azo dyes waste [37]. The electrochemical properties of the synthesized azo dyes were evaluated. The thermal properties of the synthesized azo dyes were also investigated by using thermogravimetric analysis.

#### 2. Experimental

#### 2.1. Materials and Methods

All the chemicals used in this study were purchased from Sigma-Aldrich, and were used as without any further purification. Thin-layer chromatography was carried out using precoated aluminium-backed plates (Merck Silica Gel 60 F254) and visualised under UV light ( $\lambda$ =254-362 nm). FT-IR (ATR) Spectra were recorded on a Perkin Elmer 100 FT-IR spectrometer (v are in cm<sup>-1</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz spectrometer in DMSO- $d_6$ . Coupling constant (J) are given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; doublet-doublet, dd; triplet, t; multiplet, m. Chemical shifts ( $\delta$ ) are given in parts permillion (ppm) using the residue solvent peaks as reference relative to TMS. 'J' values are given in Hertz (Hz). Mass analysis was obtained by using Waters 2695 Alliance ZQ Micromass LCMS working with ESI apparatus; in m/z (rel. %) (Department of Pharmacological Sciences, Ankara University Laboratories). The melting points were measured using Schmelzpunktbestimmer SMP II apparatus and are uncorrected. Thermal analyses (TG/DTA) were performed with a Perkin Elmer Diamond TG/DTA Thermal Analyzer at a heating rate of 10 °C min<sup>-1</sup> in a static atmosphere, at the temperature of 30–900 °C. Voltametric measurements were carried out using CHI 760d Electrochemical Workstation. Glassy carbon electrode (BAS MF-2012) and 11 µm-ultramicro carbon electrode (BAS MF-2007) were used as the working electrodes. The electrodes were polished with 1 µm and 0.05 µm alumina slurries made from dry Buehler alumina and ultra pure water, on polishing microcloth, before each use. A platinum wire was used as the auxiliary electrode (BAS MW-1032). The reference electrode was a silver wire in contact with 0.01 M AgNO<sub>3</sub> (BAS MF-2052). All the solutions were deaerated for 15 min. with pure nitrogen. All

measurements were taken at room temperature,  $21 \pm 1$  °C. In all the voltammetric measurements, the background currents were automatically subtracted from the original currents obtained. The number of transferred electrons, and the diffusion coefficients were determined by ultramicro electrode CV technique of Baranski method [38].

#### 2.2. Preparation of dyes (6a-g)

Diazotization of various heterocyclic amines was affected using  $H_2SO_4$  and NaNO<sub>2</sub>. A typical diazotization and coupling procedures are described below for 2-amino-4-(coumarin-3-yl)thiazole (**3**) and 1,2-dimethyl-1*H*-indole (**5a**), and all the other dyes were prepared in a similar manner. All the compounds obtained were purified by crystallization from ethanol, and then analyzed.

Preparation of (E)-3-(2-((1,2-dimethyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2H-chromen-2one (6a)

2-amino-4-(coumarin-3-yl)thiazole (3) (0.49 g, 2.0 mmol) was dissolved in glacial acetic acid-propionic acid mixture (2:1, 6.0 mL) and was rapidly cooled in a salt/ice bath to 0-5  $^{\circ}$ C. The solution was placed in an ice-salt bath to cool. After that, cold solution of NaNO<sub>2</sub> (0.15 g, 2 mmol) in water (3.0 mL) was added dropwise while stirring. The mixture was stirred for an additional 1 h at 0  $^{\circ}$ C. Excess nitrous acid was removed by the addition of urea. The resulting diazonium salt (4) was cooled in a salt/ice mixture. The 1,2-dimethyl-1*H*-indole (5a) (0.29 g, 2.0 mmol) was also dissolved in a mixture of glacial acetic acid- propionic acid solution (3:1, 8 mL) and cooled in an ice bath. Cold diazonium solution was added to this cooled solution in a dropwise manner while stirring. The solution was then stirred at 0-5  $^{\circ}$ C for 1 h. The pH of

the reaction mixture was maintained at 4-6 by the intermitent addition of saturated sodium carbonate solution. The mixture was further stirred for 1 h at room temperature. The resulting solid was filtered, washed with cold water, and then dried. Recrystallization of the resulting dried solid from ethanol gave an orange powder (MW: 400.45 g/mol, C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S yield: 0.649 g, 81%; m.p: 281-282 °C); FT-IR (ATR):  $v_{max}$ : 3077 (aromatic C-H), 1712 (C=O), 1484, 1475, 1451 (C=C), 1399 (N=N), 1360, 1315, 1251 (C-N), 1169 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.94 (s, 1H), 8.36 (m, 1H), 8.29 (s, 1H), 8.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.65 (m, 3H), 7.48 – 7.37 (m, 4H), 3.84 (s, 3H,-NCH<sub>3</sub>), 2.79 (s, 3H,-CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  179.3, 159.4, 153.0, 151.9, 147.2, 139.7, 138.4, 132.6, 132.6, 132.4, 129.6, 125.0, 124.6, 122.3, 120.7, 119.7, 119.2, 119.1, 118.5, 116.3, 111.7, 31.0, 10.6; LC-MS: (M+1)<sup>+</sup> (m/z): 401.24 (100%).

Preparation of (E)-3-(2-((1-methyl-2-phenyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2Hchromen-2-one (**6b**)

This dye was obtained by coupling diazotized amine (**4**) with 1-methyl-2-phenyl-1*H*-indole (**5b**), as a tile red powder (MW: 462.52 g/mol, C<sub>27</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>S, yield: 0.592 g, 64%; m.p: 261-262 °C). FT-IR (ATR):  $v_{max}$ : 3055 (aromatic C-H), 1720 (C=O), 1489, 1468(C=C), 1387 (N=N), 1323, 1252 (C-N), 1170 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.97 (s, 1H), 8.52 – 8.46 (m, 1H), 8.29 (s, 1H), 8.02 (dd, *J* = 7.7, 1.2; Hz, 1H), 7.85 – 7.76 (m, 3H), 7.70-7.60 (m, 4H), 7.55 – 7.39 (m, 5H), 3.91 (s, 3H,-NCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.4, 153.0, 139.8, 138.4, 132.4, 132.2, 130.4, 129.6, 128.6, 128.3, 125.8, 125.3, 125.2, 122.9, 120.6, 119.8, 119.7, 118.2, 116.3, 112.1, 32.7; LC-MS: (M+1)<sup>+</sup> (m/z): 463.39 (100%), 485.19 (M+Na).

Preparation of (E)-3-(2-((2-phenyl-1H-indol-3-yl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (6c)

This dye was obtained by coupling diazotized amine (**4**) with 2-phenyl-1*H*-indole (**5c**), as a red powder (MW: 448.50 g/mol, C<sub>26</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S, yield: 0.762 g, 85%; m.p: 272-273 °C) FT-IR (ATR):  $v_{max}$ : 3305 (N-H), 3130 (aromatic C-H), 1717 (C=O), , 1463, 1454 (C=C), 1393, 1349 (N=N), 1207 (C-N), 1168 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  13.00 (s, 1H,-NH), 8.98 (s, 1H), 8.50-8.42 (m, 1H), 8.38 (s, 1H), 8.16 – 8.09 (m, 2H), 8.02 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.71–7.52 (m, 5H), 7.51–7.35 (m, 5H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  179.3, 159.4, 153.0, 147.6, 146.8, 139.9, 137.0, 132.5, 130.7, 130.5, 129.7, 129.3, 126.0, 125.3, 124.7, 123.3, 120.6, 119.9, 119.7, 119.2, 116.3, 113.1; LC-MS: (M+1)<sup>+</sup> (m/z): 449.31 (100%).

Preparation of (E)-3-(2-((4-(diethylamino)phenyl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (6d)

This dye was obtained by coupling diazotized amine (4) with *N*,*N*-diethylaniline (5d), as a claret red powder (MW: 404.48 g/mol,  $C_{22}H_{20}N_4O_2S$  yield: 0.421 g, 52%; m.p: 290-291 °C). FT-IR (ATR):  $v_{max}$ : 3148 (aromatic C-H), 1717 (C=O), 1484 (C=C), 1360 (N=N), 1349, 1235 (C-N), 1150 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.95 (s, 1H), 8.38 (s, 1H), 8.00 (d, *J* = 6.5 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 2H), 7.71-7,60 (m, 1H), 7.51 – 7.37 (m, 4H), 6.91 (d, *J* = 7.0 Hz, 3H), 3.15 (s, 6H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): a good spectrum was not obtained; LC-MS: (M +2)<sup>+</sup> (m/z): 406.62 (100%), 363.09 (6.1%, M-44).

Preparation of (E)-3-(2-((4-(phenylamino)phenyl)diazenyl)thiazol-4-yl)-2H-chromen-2-one (6e)

This dye was obtained, by coupling diazotized amine (**4**) with *N*,*N*-diphenylamine (**5e**), as a claret red powder (MW: 424.47 g/mol, C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S, yield: 0.636 g, 75%; m.p: 275-276 °C). FT-IR (ATR):  $v_{max}$ : 3349 (N-H), 3028 (aromatic C-H), 1708 (C=O), 1496, 1481 (C=C), 1387 (N=N) 1252, 1200 (C-N), 1142 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.36 (s, 1H,-NH), 8.92 (s, 1H), 8.39 (s, 1H), 7.96 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.67 – 7.61 (dt, *J* =8.5 Hz, 1.4 1H), 7.46 – 7.34 (m, 5H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* =9.1 Hz, 2H), 7.10 (d, *J* =7.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): a good spectrum was not obtained; LC-MS: (M+1)<sup>+</sup> (m/z): 425.57 (100%).

Preparationof(E)-1,3-dimethyl-5-((4-(2-oxo-2H-chromen-3-yl)thiazol-2-yl)diazenyl)pyrimidine-2,4,6(1H,3H,5H)-trione (**6f**)

This dye was obtained, by coupling diazotized amine (4) with 1,3-dimethylbarbituric acid (5f), as a dark caramel powder (MW: 411.39 g/mol,  $C_{18}H_{13}N_5O_5S$ , yield: 0.197 g, 24%; m.p: 324 °C). FT-IR (ATR):  $v_{max}$ : 3146 (aromatic C-H), 1723 (C=O), 1434 (C=C), 1347 (N=N) 1231 (C-N), 1090 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  14.50 (b, tautomeric hydrazone -NH), 8.81 (s, 1H), 8.16 (s, 1H), 7.93 (d, *J* = 7.0 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.37 (m, 3H), 3.23 (s, 6H,-NCH<sub>3</sub>);<sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): a good spectrum was not obtained; LC-MS: (M+1)<sup>+</sup> (m/z): 412.38 (32%), 434.13 (100%).

Preparation of (E)-6-amino-1,3-dimethyl-5-((4-(2-oxo-2H-chromen-3-yl)thiazol-2yl)diazenyl)pyrimidine-2,4(1H,3H)-dione (**6g**)

This dye was obtained, by coupling diazotized amine (**4**) with 6-amino-1,3-dimethyluracil (**5g**), as a light brown powder (MW: 410.41 g/mol,  $C_{18}H_{14}N_6O_4S$  yield: 0.263 g, 32%; m.p: 308 °C). FT-IR (ATR):  $v_{max}$ : 3222-3168 (N-H), 3028 (aromatic C-H), 1713 (C=O), 1447 (C=C), 1328 (N=N) 1252, 1202 (C-N), 1168 (C-O-C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.50 (b, tautomeric hydrazone -NH), 9.40 (s, 1H,-NH), 8.88 (s, 1H), 8.25 (s, 1H), 7.99 (d, *J* = 6.7 Hz, 1H), 7.70-7,60 (m, 1H), 7.51 – 7.39 (m, 3H), 3.41 (s, 3H,-NCH<sub>3</sub>), 3.25 (s, 3H, - NCH<sub>3</sub>). <sup>13</sup>C- NMR (75 MHz, DMSO-*d*<sub>6</sub>): a good spectrum was not obtained; LC-MS: (M+1)<sup>+</sup> (m/z): 411.26 (100%).

#### 3. Result and Discussion

3.1. The synthetic procedures and characterizations of thiazolyl azo disperse dyes (6a-g)

The azo disperse dyes (**6a-g**) were preapared by coupling; 1,2-methylindole (**5a**), 1-methyl-2phenylindole (**5b**), 2-phenylindole (**5c**), *N*,*N*-diethylaniline (**5d**), *N*,*N*-diphenylamine (**5e**), 1,3dimethylbarbituric acid (**5f**), and 6-amino-1,3-dimethyluracil (**5g**), with diazotized 2-amino-(4-coumarinyl)thiazole (**4**), (**Scheme 1**). In the synthetic pathway, 2-hydroxybenzaldehyde was condensed with ethylacetoacetate in ethanol using catalytic amounts of piperidine to afford 3-acetylcoumarin (**1**) in excellent yield. The 3-acetylcoumarin (**1**) was subjected to  $\alpha$ -bromination reaction to obtain 3-(2-bromoacetyl)coumarin (**2**). The condensation of (**2**) with an active thiourea compound under Hantzsch reactions followed by an intramolecular cyclization, gave 2-amino-4-(coumarin-3-yl)thiazole (**3**). Compound (**3**) was diazotized in

absolute ethanol, containing nitrosylsulphuric acid to afford the diazotized amine (4). The thiazolyl azo based disperse dyes (6a-g) were obtained from the diazotized amine (4) and relevant coupling components (5a-g). Dyes 6a and 6b were used as model compounds for dye **6c.** for evaluating its photophysical and tautomeric properties. Dyes **6a** and **6b** can exist only in azo tautomeric form. However, dye 6c exists in two possible tautomeric forms, namely the azo and the hydrazone forms. Dye 6d can be evaluated together with 6e because they were obtained from similar coupling components. Dye 6d can only exist in azo tautomeric form, but 6e may exist in both azo and hydrazone tautomeric forms, because of solvent-solute interactions. Dyes 6f and 6g can also exist in two possible tautomeric forms. Thus, in this study, the role of the azo-hydrazone tautomerism, in relation to the visible absorption spectra and solvatochromic behavior of the prepared dyes have been investigated deeply. The thiazolyl azo disperse dyes were obtained in good yields. All the compounds (6a-g) were characterized by spectroscopic methods (FT-IR, <sup>1</sup>H/<sup>13</sup>C NMR and LC-MS) (<sup>1</sup>H/<sup>13</sup>C NMR and LC-MS spectra can be seen in Figs. S1a-g, Figs. S2a-c and Figs. S3a-g in Supplementary materials). Physical and spectral data of the dyes prepared are given in Section 3.

#### Scheme 1 is here

The existence of typical lactone carbonyl groups in the synthesized dyes (**6a-g**), confirmed by the infrared spectra showed bands at 1723-1708 cm<sup>-1</sup> region. The spectra also showed the azo (-N=N-) group at 1399-1348 cm<sup>-1</sup> region. The <sup>1</sup>H-NMR spectra of the dyes have a signal at 8.94 ppm attributed to the signal of the hydrogen in the thiazole ring, and 8.29 ppm also attributed to the signal of the hydrogen in the coumarin ring. The azo dye **6c** showed a broad peak at 13.00 ppm for the indole –NH. The –NH peak from *N*,*N*-diphenylamine for dye **6e** 

appeared at 9.36 ppm. The results from NMR spectra for both dyes showed that the dyes may exist in azo tautomeric form in DMSO. In the <sup>1</sup>H-NMR spectra of dye **6f** in DMSO- $d_6$ , the signal at 14.50 ppm can be attributed to the –NH proton of the hydrazone. The tautomeric hydrazone (–NH) and the tautomeric imine (–NH), for dye **6g**, were recorded as broad singlets at 11.50 and 9.40 ppm in DMSO- $d_6$  respectively. It is expected that the hydrazone – NH proton resonance appears approximately between 13.0-16.0 ppm. Therefore, the peak which is at downfield is attributed to hydrazone –NH (**Scheme 2**). These results show that, dyes **6f** and **6g** may exist predominantly as the hydrazone-imine form in DMSO- $d_6$  solution.

### Scheme 2 is here

#### 3.2. Absorption Properties

The absorption maxima ( $\lambda_{max}$ ) values of dyes can be directly proportional to polarity of their solvents and the electronic effect of the substituents in the diazo and the coupling components [39-41]. Therefore, to investigate the influence of polarity on the absorption maxima of the dyes (**6a-g**), their absorption spectra were recorded in solvents of different polarities at 20  $\mu$ M concentration. The absorption maxima ( $\lambda_{max}$ ) of the synthesized dyes (**6a-g**) are presented in **Table 1**.

#### Table 1 is here

The absorption maxima of the synthesized dyes ranged from 404 to 512 nm. Within the synthesized thiazolyl azo disperse dyes (**6a-g**), we investigated the relationship between the shift observed in the absorption maxima, and the polar characteristics of the coupling components. All the dyes (**6a-g**) exhibited solvatochromic properties in all the solvents used,

i.e. a bathochromic shift of the absorption band was observed with increasing solvent polarity. It was observed that the  $\lambda_{max}$  values of the preapared dyes (**6a-g**), showed larger bathochchromic shifts in highly polar solvents, e.g. DMSO and DMF, than the rest solvents, e.g. acetonitrile, chloroform and toluene, as shown in **Table 1**. Interestingly, it was also observed that the  $\lambda_{max}$  values of all the preapared dyes showed larger bathochromic shifts in acetic acid than in polar aprotic solvents such as acetonitrile and THF. These larger bathochromic shifts, in a proton-donating solvent such as acetic acid were considered due to the intermolecular hydrogen bonding between the dyes and the acetic acid which are capable of stabilizing the ground state of the dyes leading to a consequential bathochromic shifts (for dye **6b**, 466 nm in acetic acid, 462 nm in acetonitrile, 458 nm in THF; for dye **6f**, 441 nm in acetic acid, 436 nm in acetonitrile, and 439 nm in THF).

A comparison between the  $\lambda_{max}$  values of dyes **6a** and **6b**, and their corresponding model compound **5c** which is only in azo form in all the solvents used reveals that the additional substitution of methyl group on the nitrogen atom of the indole ring brings about small hypsochromic shifts of the  $\lambda_{max}$  values (**Table 1**). Therefore, we assigned the structures of the dyes **6a** and **6b** to the azo form in all the solvents used. However, the  $\lambda_{max}$  values of dye **6c** in DMSO ( $\lambda_{max}$ =500 nm) and in DMF ( $\lambda_{max}$ =496 nm) differ significantly from the other solvents used. The absorption at longer wavelengths may be attributed to the anionic form. Also, dye **6c** ( $\lambda_{max}$ =500 nm in DMSO) absorbs at longer wavelengths than the corresponding model dyes; **6a** ( $\lambda_{max}$ =462 nm in DMSO) and **6b** ( $\lambda_{max}$ =471 nm in DMSO) (**Figs. 1a** and **1b**). This can also be attributed to the anionic form for dye **6c**.

#### Figure 1a is here

Figure 1b is here

As can be seen in **Table 1**,  $\lambda_{max}$  values for dyes **6d** and **6e** showed similar effects in solvents with different polarities, which is susceptible to positive salvotochromic effect in the solvents used. Therefore, the absorption at longer wavelengts may be attributed to the azo tautomer. Similar results were observed, in  $\Delta \lambda_{max}$  values, of dye **6d** when compared with dye **6e**. The introduction of the N,N-diphenylamine into the diazo component of dye 6e, increased the bathochromic shift significantly in DMSO ( $\lambda_{max}$ =500 nm) (Fig S4c in Supplementary materials). The electron donating N,N-diphenylamine moiety enhanced the electron delacolization from N,N-diphenylamine to the thiazole part, via the azo bridge in dye 6e. With regards to absorption, compunds 6f and 6g showed only weak solvatochromism properties. In contrast, hypsochromic effects were observed with solvent polarity, in these dyes (6f and 6g) (Figs S4d and S4e in Supplementary materials). The hypsochromic shift the most likely is as a result of the more pronounced donor-acceptor interplay between the donor functionalities and the electron-poor uracil ring. As can be seen in Scheme 2, the dyes 6f and 6g may be stabilized in the hydrazone forms because of the intramolecular N-H...N hydrogen bond. The stabilized hydrazone form for both dyes in <sup>1</sup>H NMR spectra in DMSO- $d_6$ , can be seen clearly (Figs. S1f and S1g in Supplementary materials), and they exhibited only one absorption band in the absorption spectra. These results suggest that the dyes 6f and 6g may exist predominantly in the hydrazone forms in all the solvents used. The results from spectroscopic techniques are compatible with our previous study [42,43]. Dye **6g** is insoluble in organic nonpolar solvents such as toluene therefore, we couldn't not show absorption of dye 6g in toluene.

#### 3.3. Acidochromic Effects

Application of a relevant dye in monitoring pH changes has attracted considerable attention in recent years. In our study, the presence of basic nitrogen atom in the thiazole ring, and an acidic hydrogen in the indole and N,N-diphenylamine rings prompted us to study the possibility of protonation and deprotonation of these dyes in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), by using trifluoroacetic acid (TFA) and piperidine respectively. The effects of the acid and base on the absorption maxima of the dye solutions were elucidated and the results are shown in **Table 2**.

#### Table 2 is here

The absorption maxima of the thiazolyl azo disperse dyes (**6a-e**) in  $CH_2Cl_2$  showed bathochromic shift due to protonation upon addition of TFA (10 mM) to the solutions of the dyes. Upon addition of the trifluoroacetic acid (TFA) to the solutions of the dyes (**6a-e**) in  $CH_2Cl_2$ , major color changes were observed with the growth of a new absorption band in the range 512-610 nm and a well-defined isosbestic points.

The azo dyes (**6a and 6b**) exhibited bathochromic shifts of 58 nm for **6a**, and 56 nm for **6b**, relative to the absorption maxima. This might be explained by the initial protonation of the thiazole ring (**Scheme 3**). However, dye **6c** showed bathochromic shift of 76 nm as compared with the model compounds **6a** and **6b**, for which the absorption maximum may be explained by the initial protonation of the thiazole ring, that led to the increased in donor-acceptor interplay between the 2-phenylindole nitrogen functionality and the protonated nitrogen on thiazole ring (**Figs. 2a- 2c**).

#### **Figures 2a-c are here**

#### Scheme 3 is here

Upon addition of TFA, the absorption properties of the dyes **6b**, **6c**, **6d**, and **6e** also changed significantly (**Table 2**). Interestingly, dye **6e** showed significant bathochromic shift (108 nm) relative to the absorption maxima as compared to the other dyes (**Fig. 2b**). Dye **6e** showed absorption maxima at 470 nm in CH<sub>2</sub>Cl<sub>2</sub>, and upon addition of TFA to the solution of **6e**, the wavelength ( $\lambda_{max}$ ) value shifted to 542 nm. For the protonated form of dye **6e**, the positive charge on the nitrogen atom in the thiazole moiety was completely delocalized leading to the experimentally observed bathochromic shift (108 nm) in comparison with the neutral form. The protonation of the azo group led to an increase in donor-acceptor interplay between the *N*,*N*-diphenylamino functionality and the protonated thiazole ring [44,45] (**Scheme 4**).

#### Scheme 4 is here

It was observed that, the thiazolyl azo disperse dyes (**6a-e**) showed color change in acidic media (**Fig. 3**) and these color differences can be observed easily with naked eye. For dyes **6a** and **6b** a color change from orange to rose was observed at 512 nm and 520 nm in acidic media respectively. For dye **6c**, a color change from yellow to pinky was observed at 542 nm in acidic media. Interesingly, for dye **6d** a color change was observed from red to blue and changed the  $\lambda_{max}$  values from 499 nm to 610 absorption in acidic media. Moreover, for this dye (**6d**) large bathochromic shift was observed as compared to the other dyes. Dye **6e** showed a color change from orange to brown and a change in  $\lambda_{max}$  value from 484 nm to 592 nm in acidic media.

#### Figure 3 is here

Dyes 6c and 6e have acidic proton, and their photophysical properties can be change in basic solution (Figs. 4a,b and Figs. 5a,b). Therefore, the behavior of dyes 6c and 6e, in basic solution have been investigated and the results are shown in **Table 2**. The  $\lambda_{max}$  values of dye 6c, especially in DMSO and DMF solutions were sensitive to the addition of piperidine and showed small bathochromic shifts were observed. When piperidine was addeded to DMSO and DMF solutions, the  $\lambda_{max}$  value of dye **6c** showed small bathochromic shift, but this effect was not observed in chloroform solution. As shown in Fig. 4a, the addition of piperidine to a solution of dye **6c** in DMF led to a shift of the  $\lambda_{max}$  value from 496 nm to 518 nm (**Fig. 4a**). Also, dye 6c showed a yellow color in DMF solution, but upon addition of piperidine, the color changed from yellow to rose (Fig. 4b). This result shows that, the dye 6c may exhibit partial deprotonation form in DMSO and DMF. On the other hand, there was no significant change for the  $\lambda_{max}$  value and color of dye **6e**, when piperidine was added to solutions of the dye in DMSO and DMF. This indicates that dye 6e exists either as in anionic form or tautomer-anion mixture, in DMSO and DMF, and more basic solutions of DMSO and DMF. These results are in aggrement with those obtained for hetraylazoindoles in our previous works [41]. A small bathochromic shift was observed, when piperidine was added to chloroform solution of dye 6e, which led to a shift from 486 nm to 504 nm (Fig. 5a), and the same color change was observed (Fig. 5b). The results show that the dye 6e exist in anionic form in basic chloroform solution.

> Figures 4a and 4b are here Figures 5a and 5b are here

Dyes **6f** and **6g** are not included in the donor-acceptor system therefore no significant change in their color and absorption maximum were observed when TFA was added to  $CH_2Cl_2$ solutions of the dyes **6f** and **6g** (**Figs. S5c** and **S5d in Supplementary materials**).

#### 3.4. Electrochemical properties

The electrochemical behavior of the compounds in DMSO at glassy carbon electrode was investigated using cyclic voltammetric (CV) and chronoamperometric (CA) techniques. The CV of the compounds (**6a-g**), in DMSO, containing 0.1 M TBATFB, on glassy carbon electrode at 0.01, 0.05, 0.1, 0.5, 1 V s<sup>-1</sup> scan rates (vs. Ag/Ag<sup>+</sup>), are shown in **Fig. 6**. The reduction ( $E_{pc}$ ) and oxidation ( $E_{pa}$ ) potentials are presented in **Table 3**.

### Figure 6 is here

### Table 3 is here

To investigate the donor-acceptor electronic influence the electrochemical properties of the compounds were investigated by cyclic voltammetry and CA methods. These results are shown in **Table 4**. All the dyes showed similar cyclic voltammograms illustrated by the **Fig. 6**. The CV of all the dyes were recorded at five different scan rates (0.01, 0.05, 0.1, 0.5, 1 V.s<sup>-1</sup>).

#### Table 4 is here

For all the dyes, one oxidation peak was observed. In the anodic scan, the anodic peak, in the potential range of +0.60 to +1.2 V (vs. Ag/Ag<sup>+</sup>), was observed. The compounds displayed

oxidations at more positive potentials as a consequence of the destabilizing effect of the electron-withdrawing group [46,47]. Also, all the dyes displayed two reduction peaks, in the range of -0.5 to -2.0 V (vs Ag/Ag<sup>+</sup>). The first reduction peak appears to be associated with the formation of unstable amine products, which were reduced in the potential range of +0.45 to - 1.0 V. Moreover, the reversible reduction of azo groups, for all the compounds prepared, was confirmed from the shift of the reduction peak in the range of -1.76 to -2.0 V (vs Ag/Ag<sup>+</sup>), can be attributed to the reduction of the azo compounds to hydrazone derivatives [48].

The simplest way to understand whether the investigated compounds derivatives made a strong adsorption onto the electrode surface was the appearance of another peak at a more positive or negative potentials than the reduction peak. There were no such pre- or post- peaks observed for any of the compounds investigated, which indicated the absence of strong adsorption. Also, the fact that the slopes of log ( $ip_{c'}$  µA) vs. log (v/ V.s<sup>-1</sup>) were about 0.5 for both the first and second reduction peaks were a further verification of this situation [49-51]. Therefore, it can conveniently be claimed that the reactions investigated are not controlled by adsorption phenomenon. At the same time, the decrease of  $ip_{c'}v^{1/2}$  vs. scan rate graphs indicates that the reactions are diffusion controlled [52]. Since the current function decreases exponentially towards the higher scan rates, shows that the mechanism of electron transfer is followed by EC (electrochemical-chemical) type (**Fig. 6**) [53].

### 3.5. Determination of the Number of Transferred Electrons and the Diffusion Coefficients

The number of transferred electrons (n) during the reduction of the compounds and their diffusion coefficients (D) were determined using ultramicro electrode and chronoamperometry [38]. The n and D values were calculated as follows Eq. 1:

$$n = \frac{n_s S^2 i_s c_s}{S_s^2 i c} \qquad D = \frac{D_s S_s^2 i^2}{S_s^2 i_s^2} \tag{1}$$

where; i is the limiting steady-state current, S is the slope of the of the chronoamperometric i vs  $t^{-1/2}$  plot for compounds.

Diffusion coefficients of the compounds obtained from the Cottrell slopes, are in accordance with their molecular weights. These are the expected results because the increase in the carbon chain increases the molecular weight which is inversely related to the diffusion coefficient in the compounds (**6a-g**) (**Table 4**).

#### 3.6. Thermal stabilities

The thermal stabilites of the synthesized thiazolyl azo dyes were investigated by using thermogravimetric analysis (TGA). The overlay TGA analysis curves for the azo dyes (**6a-g**) under nitrogen atmosphere (**Fig. 7**) showed no weight loss up to 100-150 °C, indicating the absence of water molecules and any other adsorptive solvent molecules. The TGA curves indicate that the dyes are having good thermal stability except **6b**, and in the TGA curve of dye **6a**, two steep weight loss which was observed from 269 °C to 515°C is included. Dye **6f** bearing 1,3-dimethylbarbituric acid moiety as the coupling component is having good thermal stability from 305 °C to 511°C.

#### Figure 7 is here

#### 4. Conclusions

In summary, we have synthesized and characterized a novel series of thiazolyl azo dyes. These dyes were characterized by UV-vis, FT-IR,  ${}^{1}H/{}^{13}C$  NMR, and mass spectroscopic techniques. Additionally, the solvents effects on the visible absorption spectra of the dyes were evaluated. The synthesized dyes exhibited solvatochromism, namely the absorption band was red shifted with increasing solvent polarity. These azo dyes displayed significant changes in their absorption maxima, and upon addition of TFA, this induced the protonation of the nitrogen atom on the thiazole ring. Due to the wide range of  $\pi$  conjugation, the thiazolyl azo dyes showed acidochromic properties. It was observed that, the absorption curves of the dyes were significantly sensitive to acid. The electrochemical behavior of the dyes were investigated using CV and CA techniques. The results showed that, for all the dyes, one oxidation peak, and two reduction peaks were observed. Moreover, the TGA results show that the dyes possess a good thermal stability for applications.

### Acknowledgements

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### Supplementary material

Supplementary data (copies of <sup>1</sup>H NMR, <sup>13</sup>C NMR, and LC-MS spectra for compounds **Figs. S1–S14**) associated with this article can be found, in the online version, at....

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### **Scheme Captions**

Scheme 1. Synthetic pathway and structure of dyes 6a-g.

Scheme 2. The azo-hydrazone tautomeric forms of 6f and 6g.

Scheme 3. Protonated azo form and its resonance stabilized structures of dye 6a.

Scheme 4. Azo-hydrazone tautomeric and cationic forms of dye 6e.

### **Figure Captions**

Fig 1a. Absorption spectra of dye 6a (20  $\mu$ M) in various solvents.

Fig 1b. Absorption spectra of dye 6c (20  $\mu$ M) in various solvents.

Fig 2a. Spectrophotometric titration of TFA to dye 6a (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

Fig 2b. Spectrophotometric titration of TFA to dye 6c (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

**Fig 2c.** Spectrophotometric titration of TFA to dye **6e** (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

Fig 3. Pictures of absorption color of 6a-g (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub> solutions in the absence (left) presence (right) of 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

Fig 4a. Absorption spectra of dye 6c (20  $\mu$ M) in DMF and in addition of piperidine (0.5-2 mL).

Fig 4b. Pictures of absorption color of 6c (20  $\mu$ M) in different solutions in the absence (left) presence (right) of piperidine.

Fig 5a. Absorption spectra of dye 6e (20  $\mu$ M) in chloroform and in addition of piperidine (0.5-2 mL).

Fig 5b. Pictures of absorption color of 6e (20  $\mu$ M) in different solutions in the absence (left) presence (right) of piperidine.

**Fig 6.** Cyclic voltamogram (CV) of compound **6a-g** in DMSO containing 0.1 M TBATFB on glassy carbon electrode at a scan rate of 0.01-1 Vs<sup>-1</sup>(vs. Ag/Ag<sup>+</sup>).

Fig 7. Thermal gravimetric analysis (TGA) curves of dyes 6a-g.

## **Tables Captions**

Table 1. Photophysical data of dyes 6a-g.

Table 2. pH-Dependent absorption properties of dyes 6a-g.

**Table 3.** Electrochemical data of compounds in DMSO.  $Ag/Ag^+$  in DMSO; scan rate = 0.1 V/s; TBATFB (0.1 mol.L<sup>-1</sup>)

**Table 4.** Transferred electron numbers (n), limit current (i), cottrell slope (s), diffusion

 coefficients of the compounds in DMSO.

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Dve	DMSO DMF		Acetonitrile	Acetic Acid	THF	Chloroform	Toluene	
- 5				$\lambda_{abs}(nm^{a})(log\epsilon^{b})$				
6a	462(4.56)	459(4.55)	453(4.53)	453(4.51)	451(4.50)	455(4.53)	452(4.45)	
6b	471(4.46)	467(4.38)	462(4.30)	466(4.31)	458(4.36)	465(4.37)	458(4.38)	
6c	500(4.46)	496(4.47)	466(4.41)	473(4.42)	467(4.41)	470(4.39)	461(4.28)	
6d	508(4.20)	508(3.95)	500(3.91)	499(4.47)	492(3.93)	486(4.05)	485 (3.94)	
6e	512(4.52)	506(4.48)	490(4.49)	492(4.50)	491(4.51)	486(4.48)	478 (4.32)	
6f	411(4.55)	417(4.76)	404(4.22)	412(4.43)	404(4.42)	422(4.18)	416 (4.42)	
6g	444(4.62)	443(4.52)	436(4.10)	441(4.25)	439(4.27)	448(4.17)	-	

Table 1. Photophysical data of dyes 6a-g.

<sup>a</sup>Long wavelength absorption maximum, in nm;  $c=(20 \ \mu M)$ ;  ${}^{b}\varepsilon = molar$  absorption coefficient,  $cm^{-1}M^{-1}$ .

Dyes	$\begin{array}{l} UV/vis~(CH_{2}Cl_{2})\\ \lambda_{max}~(nm)^{a}~(log\epsilon^{b}) \end{array}$	$\begin{array}{c} UV/vis~(TFA~in\\ DCM)~\lambda_{max}~(nm)^{a}\\ (log\epsilon^{b}) \end{array}$	$\begin{array}{l} UV/vis~(Pip.\\ in~DMSO)~\lambda_{max}\\ (nm)^a~(log\epsilon^b) \end{array}$	UV/vis (Pip. in DMF) $\lambda_{max} (nm)^{a} (log\epsilon^{b})$	UV/vis (Pip. in Chloroform) $\lambda_{max}$ (nm) <sup>a</sup> (loge <sup>b</sup> )
6a	454(4.40)	512(4.38)	-	-	
6b	464(4.11)	520(4.04)	-	-	<b>A</b> - <b>Y</b>
6c	466(4.50)	542(4.46)	519(4.21)	518(4.41)	479(4.18)
6d	499(4.35)	610(4.13)	-	-	<u> </u>
6e	484(4.44)	592 (4.32)	513(4.02)	509(4.13)	504(4.10)
6f	417(4.19)	418(4.15)	-	Ċ	-
6g	437(3.78)	450(4.28)	-	<u> </u>	-

Table 2. p	oH-Dep	endent	absor	ption	prop	erties	of	dyes	6a-g.	
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<sup>a</sup>Long wavelength absorption maximum, in nm;  $c=(20 \ \mu M)$ ;<sup>b</sup> $\epsilon$  = molar absorption coefficient, cm<sup>-1</sup>M<sup>-1</sup>.

**Table 3.** Electrochemical data of compounds in DMSO.  $Ag/Ag^+$  in DMSO; scan rate = 0.1 V/s; TBATFB (0.1 mol.L<sup>-1</sup>).

6a         -0.79         -1.78         +0.95           6b         -0.82         -1.79         +1.09           6c         -0.79         -1.81         +0.89           6d         -0.64         -1.83         +1.05           6e         -0.62         -1.78         +0.82           6f         -0.72         -1.81         +0.82           6g         -0.70         -1.81         +1.02
6b       -0.82       -1.79       +1.09         6c       -0.79       -1.81       +0.89         6d       -0.64       -1.83       +1.05         6e       -0.62       -1.78       +0.82         6f       -0.72       -1.81       +0.82         6g       -0.70       -1.81       +1.02
6c -0.79 -1.81 +0.89 6d -0.64 -1.83 +1.05 6e -0.62 -1.78 +0.82 6f -0.72 -1.81 +0.82 6g -0.70 -1.81 +1.02
6d -0.64 -1.83 +1.05 6e -0.62 -1.78 +0.82 6f -0.72 -1.81 +0.82 6g -0.70 -1.81 +1.02
6e       -0.62       -1.78       +0.82         6f       -0.72       -1.81       +0.82         6g       -0.70       -1.81       +1.02
6f -0.72 -1.81 +0.82 6g -0.70 -1.81 +1.02
6g -0.70 -1.81 +1.02

	Cottrell Slope (S)x10 <sup>5</sup> of		Diffusion coefficient (D, cm <sup>2</sup> /s) x 10 <sup>7</sup> $D \pm ts/\sqrt{N}$		UN	ИE	Transferred electron		
Dyes					Limit current (i. A)x10 <sup>10</sup>		number(n) (Baranski method)		
	1. peak	2. peak	1. peak	2. peak	1. peak	2. peak	1. peak	2. peak	
6a	$1.71\pm0.02$	$2.17\pm0.03$	$7.98\pm0.05$	$9.88\pm0.04$	$1.15\pm0.04$	$3.18\pm0.01$	$0.91\pm0.03$	$0.94\pm0.01$	
6b	$5.95\pm0.12$	$4.66\pm0.12$	$2.68\pm0.05$	$1.75\pm0.01$	$9.83 \pm 0.03$	$8.90\pm0.04$	$0.98\pm0.01$	$1.08\pm0.02$	
6c	$4.83\pm0.02$	$3.41\pm0.02$	$3.72\pm0.03$	$2.65\pm0.06$	$7.63\pm0.02$	$6.65\pm0.03$	$0.86\pm0.02$	$0.90\pm0.03$	
6d	$1.82\pm0.03$	$2.35\pm0.01$	$6.71\pm0.01$	$8.24\pm0.05$	$2.22\pm0.06$	$3.66\pm0.02$	$0.92\pm0.03$	$0.91\pm0.05$	
6e	$3.16\pm0.01$	$3.19\pm0.05$	$4.95\pm0.02$	$3.82\pm0.04$	$5.47\pm0.01$	$5.29\pm0.06$	$1.01\pm0.05$	$0.98\pm0.01$	
6f	$2.27\pm0.11$	$2.89\pm0.03$	$5.42\pm0.05$	$4.91\pm0.02$	$3.87\pm0.03$	$4.24\pm0.02$	$0.96\pm0.01$	$1.06\pm0.01$	
6g	$2.09\pm0.01$	$2.67\pm0.06$	$5.62\pm0.04$	$4.66\pm0.01$	$3.12\pm0.02$	$4.02\pm0.03$	$0.95\pm0.02$	$0.88\pm0.04$	

**Table 4.** Transferred electron numbers (n), limit current (i), cottrell slope (s), diffusioncoefficients of the compounds in DMSO.

Results are average of three measurements and standard deviation.

**/** 



Fig. 1a. Absorption spectra of dye 6a (20  $\mu$ M) in various solvents.



Fig. 1b. Absorption spectra of dye 6c (20  $\mu$ M) in various solvents.



Fig. 2a. Spectrophotometric titration of TFA to dye 6a (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

![](_page_33_Figure_2.jpeg)

**Fig. 2b.** Spectrophotometric titration of TFA to dye **6c** (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

![](_page_34_Figure_1.jpeg)

**Fig. 2c.** Spectrophotometric titration of TFA to dye **6e** (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>. Arrows indicate the increase and decrease of absorbance intensity upon addition 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

![](_page_34_Picture_3.jpeg)

Fig. 3. Pictures of absorption color of 6a-g (20  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub> solutions in the absence (left) presence (right) of 10 mM TFA in CH<sub>2</sub>Cl<sub>2</sub>.

![](_page_35_Figure_1.jpeg)

Fig. 4a. Absorption spectra of dye 6c (20  $\mu$ M) in DMF and in addition of piperidine (0.5-2 mL).

![](_page_35_Picture_3.jpeg)

Fig. 4b. Pictures of absorption color of 6c (20  $\mu$ M) in different solutions in the absence (left) presence (right) of piperidine.

![](_page_36_Figure_1.jpeg)

Fig. 5a. Absorption spectra of dye 6e (20 µM) in chloroform and in addition of piperidine (0.5-2 mL).

![](_page_36_Figure_3.jpeg)

Fig. 5b. Pictures of absorption color of 6e (20  $\mu$ M) in different solutions in the absence (left) presence (right) of piperidine.

![](_page_37_Figure_1.jpeg)

**Fig. 6.** Cyclic voltamogram (CV) of compound **6a-g** in DMSO containing 0.1 M TBATFB on glassy carbon electrode at a scan rate of 0.01-1 Vs<sup>-1</sup>(vs. Ag/Ag<sup>+</sup>).

![](_page_38_Figure_1.jpeg)

Fig. 7. Thermal gravimetric analysis (TGA) curves of dyes 6a-g.

![](_page_39_Figure_1.jpeg)

![](_page_40_Figure_1.jpeg)

Scheme 2. The azo-hydrazone tautomeric forms of 6f and 6g.

![](_page_41_Figure_1.jpeg)

Scheme 3. Protonated azo form and its resonance stabilized structures of dye 6a.

![](_page_42_Figure_1.jpeg)

Scheme 4. Azo-hydrazone tautomeric and cationic forms of dye 6e.

# Highlights

- Seven novel thiazolylazo disperse dyes were synthesized and fully characterized.
- The solvatochromic behaviors and coupling component effects on absorption spectra in various solvents were evaluated.
- The absorption spectra of the dyes changed drastically upon acidification.
- The dyes showed good thermal stability for practical applications.