

Design of Novel Reactive Dyes Containing Cationic Groups: Mechanism and Application for Environmentally Friendly Cotton Dyeing

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Abstract: In this work, four novel, high fixation reactive dyes containing cationic groups were synthesized using *m*-aminophenyltrimethylammonium salt or 4-(ethylsulfurate sulfonyl) aniline as the diazo component, 3-(*N,N*-diethylamino) acetanilide or 3'-aminoacetanilide as the coupling component and *m*-aminophenyltrimethylammonium salt or *N*-(2-aminoethyl) pyridinium chloride as the cationic group. The synthesized dyes containing multiple cationic groups were characterized by FT-IR and ¹H-NMR spectroscopy. The spectral properties were measured by UV-Vis absorption spectroscopy. Compared with conventional reactive dyes containing cationic groups, the synthesized dyes exhibited good water solubility upon introduction of a quaternary ammonium into the chromophore. The structural design of synthetic azo dyes allows enhanced the water solubility due to the introduction of a cationic group. The dyeing properties of the synthesized dyes to cotton fabric were explored at various temperatures and salt and alkaline concentrations. The results showed that the synthesized dyes possessed good dyeing properties with nearly 80% fixation and good color fastness on cotton (3-5) in the absence of salt. The success of the salt-free dyeing of cotton fabric with these dyes is an excellent example of environmentally friendly cotton dyeing. This study provides an important platform for the design of novel reactive dyes for cotton dyeing to reduce effluent pollution.

Keywords: Salt-free dyeing, Reactive dyes, Multiple cationic groups, Dye uptake, Cotton

Introduction

Reactive dyes have been used commercially for dyeing cotton fabric for over 60 years, and they have become a popular class of dyes owing to their wide spectrum of bright colors, brilliance, and high wet fastness [1-3]. However, when using reactive dyes, the cotton dyeing wastewater contains massive amounts of unfixed reactive dyes, inorganic salts, and chemical auxiliaries, which are serious environmental hazards [4,5]. In recent years, environmental issues due to low dye fixation have attracted enormous attention around the world [6,7]. To date, much work has focused on environmental protection, including pollutant treatment and toxicity evaluation [8,9]. The damage and toxicity caused by textile wastewater have been worrisome, as it can affect biological health and jeopardize ecological balance [10]. Therefore, developing high fixation reactive dyes and/or textile processing technology to reduce the consumption of chemical substances and increase dye utilization is of great importance [11-13].

Intense research has focused on the eco-friendly dyeing of cotton fabrics using reactive dyes [14-18]. In this process, cotton fabric is chemically modified to carry positive charges on its surface, increasing its interactions with generally negatively charged reactive dyes in dyebaths [19-21]. However, the lightfastness is decreased due to the presence of cationic groups on the modified cotton fabric [22]. On the other hand, new reactive dyes, such as multifunctional reactive

dyes, cationic reactive dyes, and neutral fixing dyes, have been designed and synthesized with improved dyeing properties including adhesion and reactivity [23,24]. When the reactive dyes for cotton dyeing contain cationic groups, the dye-fiber repulsion will be reduced or eliminated. Subsequently, covalent bonds can form between the reactive group (s) of dye molecules and the hydroxy groups of the cotton cellulose under alkaline conditions [25-27]. Therefore, to achieve environmentally friendly dyeing, reactive dyes containing cationic groups are employed for cotton dyeing in the absence of salt. Moreover, the dyeing properties on cotton are closely related to the functional groups (the different cationic and reactive groups) present in the structure of these reactive dyes [28,29].

Recently, several research groups have reported the synthesis of new reactive dyes containing cationic groups for the salt-free dyeing of cotton fabrics [30,31]. For example, cationic reactive dyes with monofluorotriazine as the reactive group have been synthesized, but the fluoride ions generated after dyeing negatively impacted marine organisms [32]. In addition, as reported, some anthraquinone reactive dyes containing cationic groups have been used for salt-free cotton dyeing, but their fixation efficiencies were unsatisfactory [33,34]. This is mainly because these dyes are not as water soluble as traditional reactive dyes, and the affinities of these reactive dyes for cotton fabrics was low. The introduction of only one quaternary amino group on halotriazine did not sufficiently increase the water solubility [35]. Researchers have also focused on developing a series of reactive dyes containing cationic groups with good water solubility [36,37].

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However, these dyes have not been applied to cotton dyeing. The factors influencing the water solubility of the cationic groups need to be further explored. There have been no reports on the introduction of two different cationic groups into a chromophore and halotriazine.

In view of this, a class of reactive dyes containing cationic groups with good dyeing performance was designed and synthesized for salt-free and low-alkali cotton dyeing. The synthesized dyes possess not only good water solubility but also high fixation. Their excellent color fastness is due to the nucleophilic substitution or nucleophilic addition reactions between the reactive group (s) of the dye and the hydroxy groups of the cellulose (Cell-OH) under alkaline conditions. In addition, the salt-free dyeing properties of the synthesized dyes and commercial reactive dyes were compared. In particular, the influence of the position of cationic groups on the water solubility and dyeing properties of the dyes is discussed in this work.

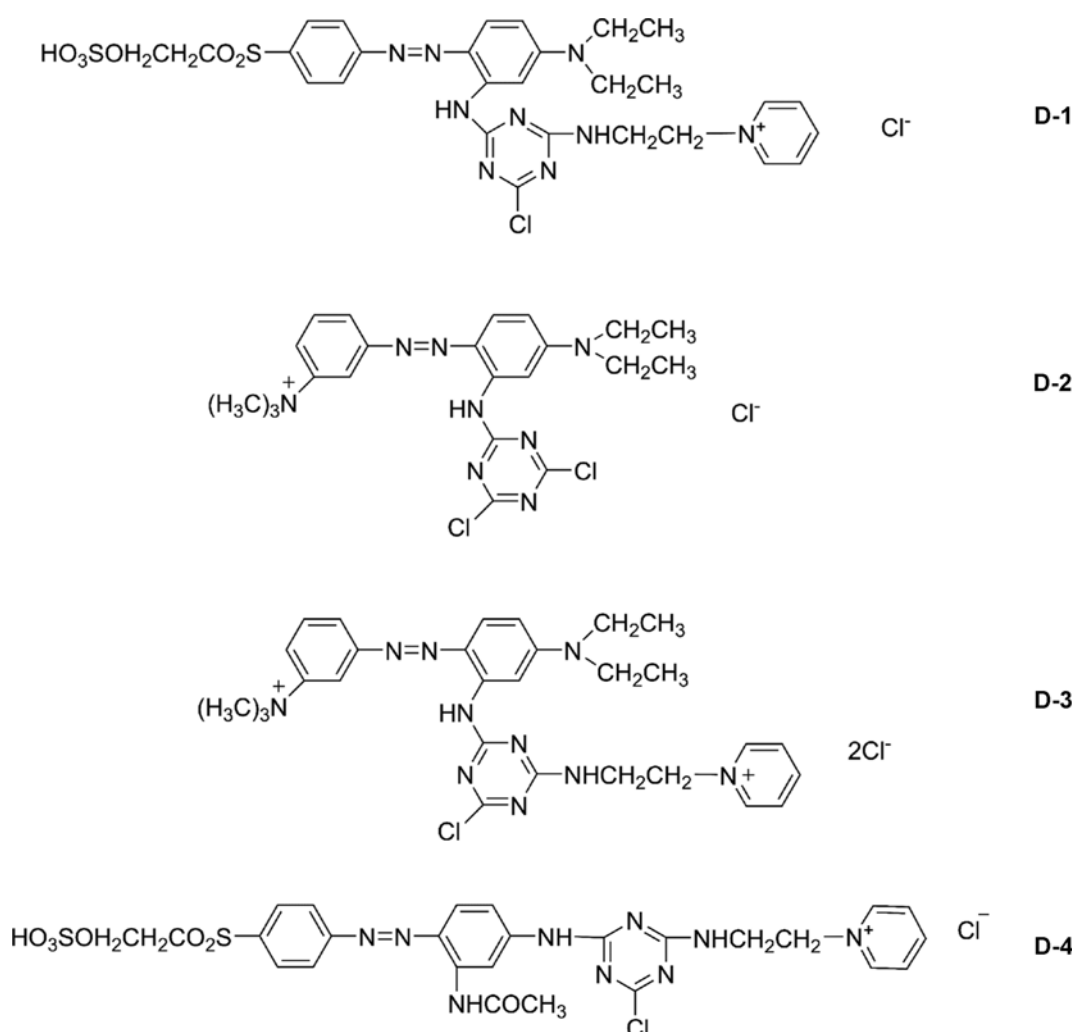
Experimental

Materials

All chemicals were analytically pure and were purchased from Shanghai Chemical Co., Shanghai, China. Cyanuric chloride, 2-chloroethylamine hydrochloride, and pyridine were supplied by Tokyo Chemical Industry Co., Ltd. (TCI), and 3'-aminoacetanilide was supplied by Merger (Shanghai) Chemical Technology Co., Ltd. 1-Aminobenzene-4- β -sulfatoethylsulfone and 3-(*N,N*-diethylamino) acetanilide were obtained from Wanfeng Chemical Engineering Company, Zhejiang, China. The commercial dyes 3RS, 3BS, and B were supplied by Hengda Company (Zhejiang, China) and used after desalting purification. Pretreated woven cotton fabrics (weight 200 g/m²) were obtained from Test Fabrics Inc, Shanghai, China.

Instrumentation

Fourier transform infrared (FT-IR) spectra were collected



Scheme 1. Chemical structures of the synthesized novel reactive dyes.

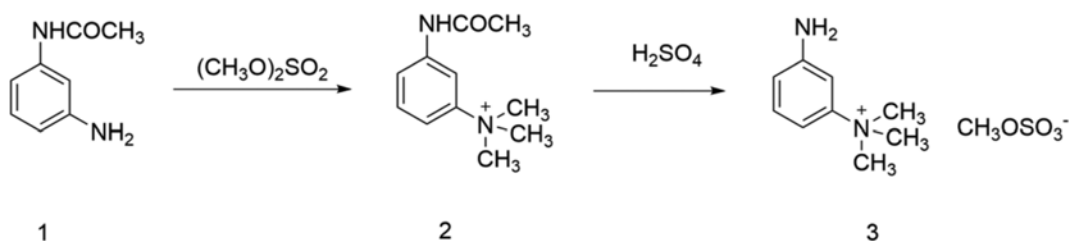
with a Nicolet FT-IR spectrophotometer (Nicolet Analytical Instruments, America). ^1H -nuclear magnetic resonance (NMR) spectra were measured on a Bruker (400 Hz) spectrometer (Bruker Corporation, Faellanden Switzerland) in DMSO-d_6 or D_2O . Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Lambda 35 spectrometer (PerkinElmer Corporation, America) at room temperature. Elemental analysis (EA) for carbon, hydrogen, and nitrogen were conducted with an Elmentar Vario EL III analyzer (Germany). Mass spectra (MS) data were acquired on a Varian LC-MS (America). Melting points (Mp values) were measured on a melting point apparatus (Mettler-Toledo, Switzerland). Cotton dyeing was carried out by using an infrared laboratory dyeing machine (Roaches International, England). The color strengths of the dyed cotton fabrics were determined by using an SF 600 PLUS spectrophotometer (Datacolor, Switzerland).

Synthesis of the Dyes

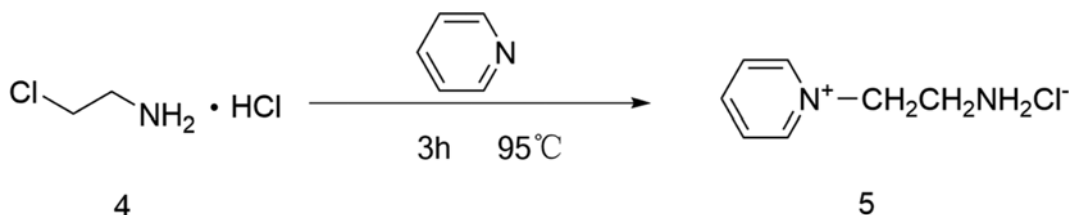
The synthesized reactive dyes containing cationic groups are shown in Scheme 1. *m*-Aminophenyltrimethylammonium salt and *N*-(2-aminoethyl) pyridinium chloride salt were prepared according to the literature [38,39]. The dyes and other intermediates were synthesized with the novel methods as described below.

Synthesis of *m*-Aminophenyltrimethylammonium Salt

3-Aminoacetanilide hydrochloride (1) (15 g, 0.1 mol), distilled water, and sodium bicarbonate were added to a 250 ml three-necked round-bottom flask and stirred to dissolve the solids. Dimethylsulfate (DMS) was slowly added to the reaction mixture containing 3-aminoacetanilide. The solution was heated to $65\text{ }^\circ\text{C}$ and maintained for 10 h to give 3-(acetylaminophenyl) trimethylammonium chloride (2). The reaction was monitored by thin-layer chromatography (TLC) (*n*-hexane: acetone, 1:1 v/v). The resulted mixture



Scheme 2. Synthesis of the *m*-aminophenyltrimethylammonium salt.



Scheme 3. Synthesis of *N*-(2-aminoethyl) pyridinium chloride.

was hydrolyzed by adding concentrated sulfuric acid (8 ml, 0.15 mol) and then stirred for 2 h at $95\text{ }^\circ\text{C}$. The reaction process was monitored by high-performance liquid chromatography (HPLC) using acetonitrile/water (80:20 by volume) as the eluent. After the reaction was complete, a solution of *m*-aminophenyltrimethylammonium salt ($t_R=1.05$ min) was obtained, and it was used in the next condensation reaction without isolation.

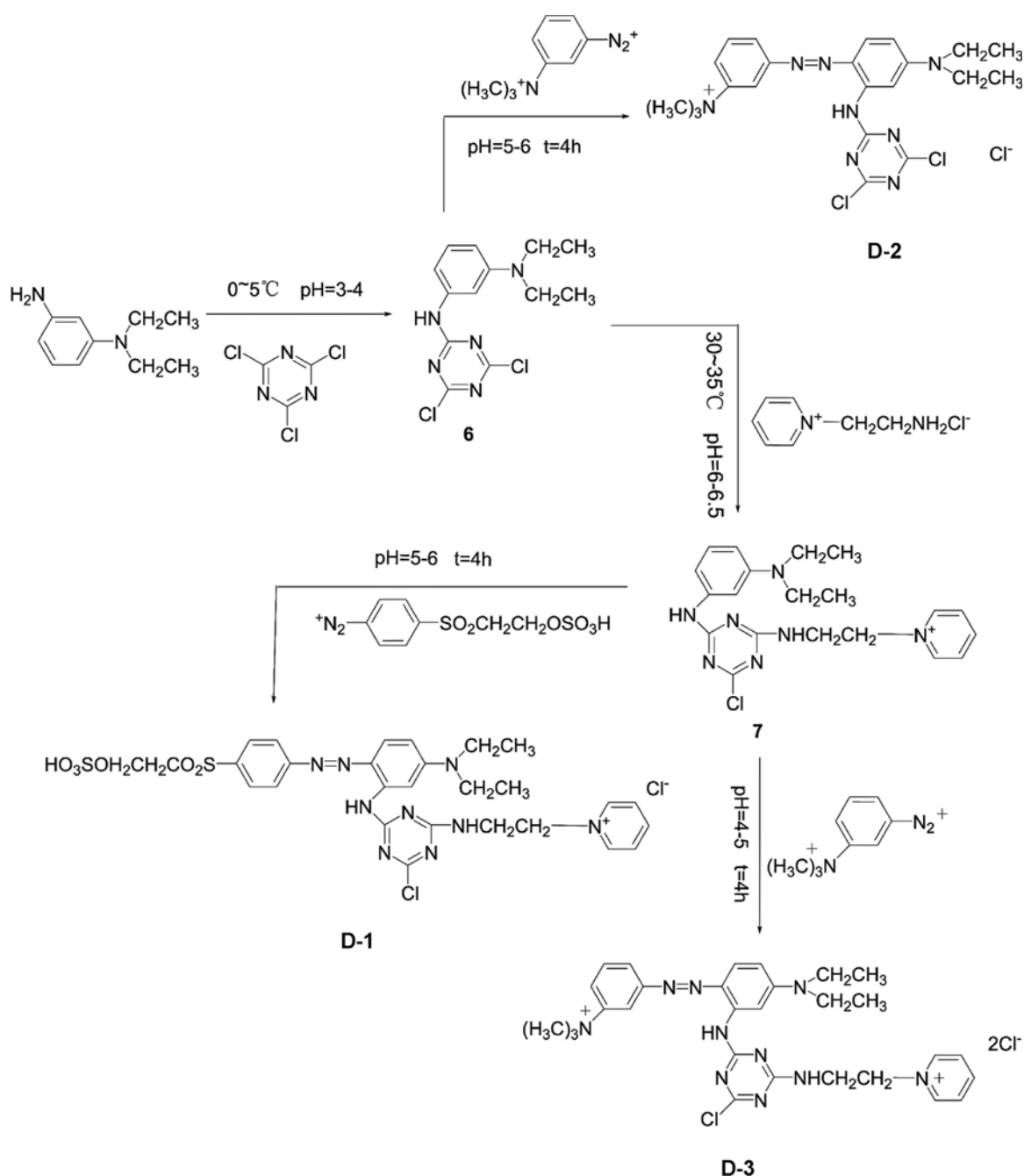
Synthesis of *N*-(2-Aminoethyl) Pyridinium Chloride Salt

Into a three-necked flask, 2-chloroethylamine hydrochloride (4) (11.6 g, 0.1 mol), distilled water (50 ml) and 3N pyridine were added and stirred under reflux for 3 h. Then, the resulting solution was extracted three times with toluene at room temperature. Concentrated hydrochloric acid was dropwise added to acidify the lower aqueous layer. A concentrated syrupy liquid was obtained using a rotary evaporator and then poured into propan-2-ol with stirring. The white product, *N*-(2-aminoethyl) pyridinium chloride (5), was obtained by filtration and drying. (Scheme 3).

The yield was 94 % (18.3 g). FT-IR (ν , cm^{-1}): 3371, 3117, 3080, 3042, 2987, 2967, 1631, 1606, 1484, 1115; ^1H -NMR (D_2O , δ_{H} , ppm): 8.88 (d, 2H, Ar-H), 8.58 (t, H, Ar-H), 8.10 (t, 2H, Ar-H), 4.95 (m, 2H, N-CH_2 -), 3.66 (t, 2H, $\text{N}^+\text{-CH}_2$ -).

Synthesis of the Reactive Dyes (D-1 to D-3)

Cyanuric chloride (22.3 g, 0.12 mol) and crushed ice (100 g) were added into a three-necked flask and stirred at $0\text{-}5\text{ }^\circ\text{C}$. After 1 h, the solution was reacted with *N,N*-diethyl-1,3-benzenediamine (16.4 g, 0.1 mol), which was synthesized according to a published protocol [40]. The reaction mixture was stirred for 3 h at $0\text{-}5\text{ }^\circ\text{C}$ and was monitored by TLC (methanol: dichloromethane, 1:3, v/v) for the formation of compound 6. To the above suspension of 6 was dropwise added a solution of *N*-(2-aminoethyl) pyridinium (19.5 g,



Scheme 4. Syntheses of D-1, D-2 and D-3.

0.1 mol) dissolved in distilled water (400 ml). Then, the mixture was maintained at 35–40 °C and pH 6–6.5 with monitoring by TLC (methanol: *n*-propanol: *n*-butanol: ethyl acetate: water: triethylamine, 0.5:4:2:1:3:1, v/v) to give component **7** as the coupling product. Concentrated hydrochloric acid (30 ml, 36 %, w/v) was added to a solution of 4-(ethylsulfate sulfonyl) aniline (28.1 g, 0.1 mol) or *m*-aminophenyltrimethylammonium salt (250 ml, 0.1 mol). The diazotization reaction was conducted at 0–5 °C for

1 h by adding a solution of sodium nitrite (8.3 g, 0.12 mol). The coupling reactions were completed within 4 h at 0–5 °C with monitoring by TLC (methanol: *n*-propanol: *n*-butanol: ethyl acetate: water: triethylamine, 0.5:4:2:1:3:1, v/v). The resulting red product was separated by filtration, washed and dried to give **D-1**. The orange products were precipitated by slowly adding potassium chloride (KCl, 20 % w/v) and separated by vacuum filtration to give **D-2** and **D-3** (Scheme 4).

Synthesis of the Reactive Dye (D-4)

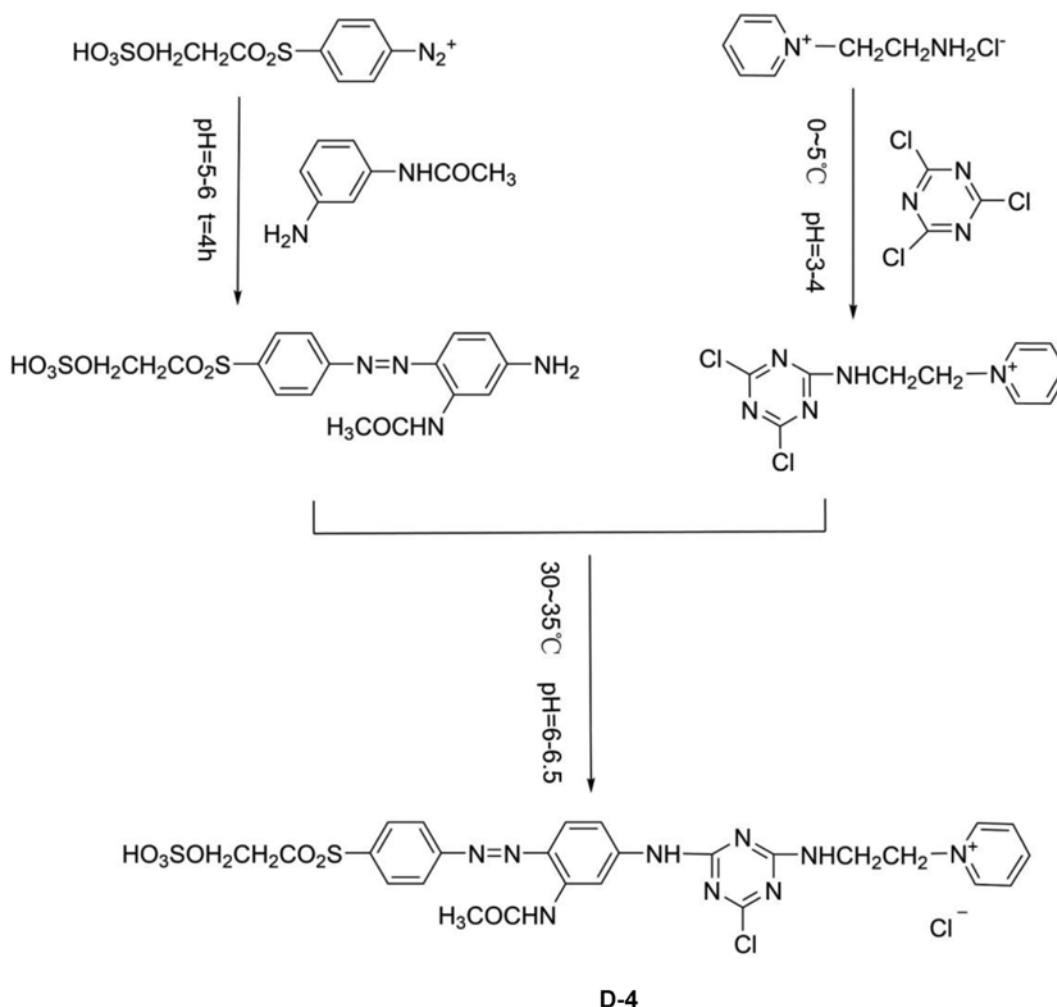
3'-Aminoacetanilide (15 g, 0.1 mol) dissolved in water (300 mL) was reacted with the 4-(ethylsulfate sulfonyl) aniline diazonium salts in an ice bath between pH 5-6. At the same time, a solution of cyanuric chloride (22.3 g, 0.12 mol) and crushed ice (100 g) was added into a three-necked flask and stirred for 1 h at 0-5 °C, and then, a solution of *N*-(2-aminoethyl) pyridinium chloride salt (19.5 g, 0.1 mol) was added dropwise to the suspension. The mixture was stirred for 3 h at 0-5 °C at pH 3-4 with monitoring by TLC (methanol: dichloromethane, 3:1, v/v). The ice bath was removed. The above solution of condensation products was added dropwise into the suspension containing the reactive ethylsulfate sulfonyl derivative. The mixture was stirred for 5 h at pH 6-6.5 and 35 °C with monitoring by TLC (methanol: *n*-propanol: *n*-butanol: ethyl acetate: water: triethylamine, 0.5:4:2:1:3:1, v/v) to give a solution of D-4. The yellow products were separated by filtration (Scheme 5).

These dyes were named D-1, D-2, D-3, and D-4. The obtained products were purified by column chromatography

on silica gel using methanol and dichloromethane (1:3, v/v) as the eluent and characterized by FT-IR and ¹H-NMR spectroscopy, elemental analysis and MS.

D-1, the yield was 64.55 %. *Mp*: >300 °C. FT-IR (ν, cm⁻¹): 3204, 3052, 2965, 2831, 2886, 2779, 1693, 1613, 1458, 1413, 1395, 1181, 846, 790; ¹H-NMR (DMSO-d₆, δ_H, ppm): 9.51 (s, H, O-H), 8.22 (d, 2H, Ar-H), 8.12 (t, 2H, Ar-H), 8.02 (d, 2H, Ar-H), 7.96 (d, 2H, Ar-H), 7.65 (t, H, Ar-H), 7.79 (d, H, Ar-H), 6.64 (d, H, Ar-H), 6.42 (d, H, Ar-H), 3.96 (t, 2H, O-CH₂-), 3.69 (q, 2H, NH-CH₂-), 3.51 (d, 4H, N-CH₂-CH₃), 2.25 (s, 3H, -CO-CH₃), 1.31 (t, 2H, -N⁺-CH₂-), 1.21 (t, 6H, -CH₂-CH₃), 1.11 (t, 2H, S-CH₂-). MS, *m/z*=690 (M-Cl). Anal. Calcd. for C₂₈H₃₃Cl₂N₉O₆S₂: C 46.28, H 4.58, N 17.35; found: C 46.19, H 4.62, N 17.29.

D-2, the yield was 69.76 %. *Mp*: 171-173 °C. FT-IR (ν, cm⁻¹): 3341, 2966, 2917, 2844, 1611, 1534, 1464, 1394, 1352, 1250, 1159, 1012, 844, 792, 683; ¹H-NMR (DMSO-d₆, δ_H, ppm): 8.31 (s, H, Ar-H), 8.02 (d, H, Ar-H), 7.90 (t, H, Ar-H), 7.74 (d, 2H, Ar-H), 7.45 (s, H, Ar-H), 6.68 (d, H, Ar-H), 3.77 (s, 2H, -NH), 3.37 (q, 4H, -N-CH₂-), 1.20 (t, 6H,



Scheme 5. Synthesis of D-4.

-CH₃), 1.06 (s, 9H, N⁺-CH₃). MS, $m/z=473$ (M-Cl). Anal. Calcd. for C₂₂H₂₇Cl₃N₈: C 51.83, H 5.34, N 21.98; found: C 51.74, H 5.51, N 21.83.

D-3, the yield was 73.15 %. *Mp*: 187-189 °C. FT-IR (ν , cm⁻¹): 3352, 2966, 2924, 2847, 2774, 2697, 1688, 1611, 1559, 1541, 1482, 1461, 1377, 967, 949, 823, 795, 774; ¹H-NMR (DMSO-d₆, δ_{H} , ppm): 8.36 (t, H, Ar-H), 8.04 (d, H, Ar-H), 8.02 (d, H, Ar-H), 7.96 (s, H, Ar-H), 7.94 (s, H, Ar-H), 7.78 (s, H, Ar-H), 7.76 (d, 2H, Ar-H), 7.26 (d, 2H, Ar-H), 6.77 (d, H, Ar-H), 6.74 (d, H, Ar-H), 3.97 (s, H, -NH), 3.61 (m, 6H, -NH-CH₂-, -CH₂-CH₃), 3.45 (q, H, -NH-CH₂), 1.21 (m, 17H, -N⁺-CH₂-, N⁺-CH₃-, -CH₂-CH₃). MS, $m/z=560$ (M-2Cl). Anal. Calcd. for C₂₉H₃₇Cl₃N₁₀: C 55.11, H 5.90, N 22.16; found: C 55.12, H 5.83, N 22.23.

D-4, the yield was 66.80 %. *Mp*: >300 °C. FT-IR (ν , cm⁻¹): 3359, 2959, 2914, 2847, 1611, 1478, 1401, 1321, 1289, 1135, 991, 890, 851, 792, 701; ¹H-NMR (DMSO-d₆, δ_{H} , ppm): 8.75 (d, H, Ar-H), 8.21 (t, H, Ar-H), 8.19 (d, 2H, Ar-H), 8.12 (d, 2H, Ar-H), 8.09 (t, 2H, Ar-H), 7.99 (d, H, Ar-H), 7.83 (d, H, Ar-H), 7.58 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 6.85 (d, 2H, Ar-H), 3.98 (t, 2H, O-CH₂-), 3.74 (q, 2H, NH-CH₂-), 2.25 (s, 3H, -CO-CH₃), 1.24 (t, 4H, S-CH₂-, -N⁺-CH₂-). MS, $m/z=676$ (M-Cl). Anal. Calcd. for C₂₆H₂₇Cl₂N₉O₇S₂: C 43.82, H 3.82, N 17.69; found: C 43.85, H 3.77, N 17.64.

Dyeing Application Procedure

Dyeing on cotton fabric (1 g) was carried out at a liquor ratio of 40:1 with a dye content of 1%-5% (o.w.f.) and different weights of electrolyte (Na₂SO₄) and alkali (Na₂CO₃). The dyeing procedure is shown in Figure 1. At the beginning of the dyeing process, the dyes and fabrics were mixed at 40 °C for 30 min, during which time salt was added into the dyebath in two portions. Then, the dyeing temperature was gradually raised to 70 °C, then alkali was added for fixation, and the fixation temperature was maintained for 60 min. After that, all the dyed cotton fabrics were rinsed in cold tap water and soaped in a soap solution (2 g/l soap flakes, 10 min, 95 °C). Then, the fabrics were rinsed with water and air dried.

Visible Absorption Spectrophotometry

Solutions of the above reactive dyes at different concentrations in *N,N*-dimethylformamide (DMF) were used to prepare a dye standard curve. The wavelength of maximum

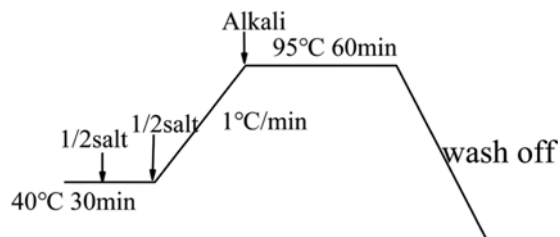


Figure 1. Dyeing profile of D-1 to D-4.

absorption (λ_{max}) and the molar extinction coefficient (ϵ) were measured by using a UV-Vis spectrophotometer.

Water Solubility Test

The water solubility of each of the four reactive dyes containing cationic groups was obtained indirectly by measuring the absorbance of the dyes in solution at the λ_{max} of the dye by using a UV-Vis spectrophotometer. In this study, 30 g of the reactive dye and 100 ml of distilled water were added to an Erlenmeyer flask and then stirred for 30 min at different temperatures. The supernatant was isolated by centrifugation for 10 min at a speed of 10000 r/min and analyzed on a UV-Vis spectrophotometer by diluting with 94% dimethylformamide solution or water [41].

Color Strength (K/S) Analysis

The color strengths (*K/S* values) of the dyed fabrics were measured using an SF 600 PLUS spectrophotometer. The measurement conditions were as follows: D65 illuminant, ultraviolet excluded, and 10° observer. The dyed fabrics were analyzed at four positions by rotating the fabric 90°, and an average color intensity result was obtained.

Dye Exhaustion and Fixation

The uptake rate of the reactive dyes on the cotton fabrics was determined by measuring the dyebath absorbance before and after the dyeing process and the soap bath at λ_{max} using a UV-Vis spectrophotometer. The percentage of dye bath exhaustion (%*E*) and fixation (%*F*) were calculated using equation (1) and equation (2), respectively.

$$\%E = (C_0 - C_1)/C_0 \times 100 \quad (1)$$

$$\%F = (C_0 - C_1 - C_2)/C_0 \times 100 \quad (2)$$

where C_0 and C_1 are the concentrations of the dyeing liquors at λ_{max} of the dyes before and after the dyeing, respectively. C_2 is the concentration of the soap liquor.

Color Fastness

The dyed samples were assessed in accordance with the relevant International Organization for Standardization (ISO) standards. Washing fastness was determined in accordance with ISO 105-C03 (2010); light fastness was determined based on ISO 105-B02(2013); and rubbing fastness was evaluated based on ISO 105-X12(2001).

Density Functional Theory Calculation

The optimized geometries, stable ground state conformers, and unit cell parameters of D-1 to D-4 were calculated by density functional theory at the B3LYP/6-31G (d) level. HOMO, LUMO, and energy information were calculated at the B3LYP/6-31G (d) level based on the optimized geometry.

Results and Discussion

Photophysical Properties

The UV-Vis spectroscopy results of D-1 to D-4 (2.4×10^{-2} g/l) measured in DMF are illustrated in Figure 2 and Table 1. The λ_{max} values of D-1, D-2, D-3, and D-4 were 495.0 nm, 480.0 nm, 482.5 nm, and 414.0 nm, respectively. D-1 was red; D-2 and D-3 were orange; and D-4 was yellow. All the dyes were synthesized based on a common chromophore or common substituent attached to the halotriazine. The absorption spectra (λ_{max} and ϵ value) are highly affected by the substituent and conjugation system [42-46]. D-1, with 4-(2-sulfatoethylsulphonyl) aniline as the chromophore, was more bathochromic than D-3, which is attributed to the introduction of electron-withdrawing groups on the diazonium group [47]. The slight hypsochromic shift is usually caused by the introduction of electron-withdrawing groups onto the halotriazine [38]. Figure 2 shows that D-2, with chloride as a substituent, was more hypsochromic than D-3, which has *N*-(2-aminoethyl) pyridinium chloride as substituent. Due to the strong electron push-pull in D-1, the molar extinction coefficient of D-1, with *N,N*-diethylbenzene-1,3-diamine as the coupling component, was much higher than that of D-4, which has 3'-aminoacetanilide as the coupling component [48].

According to quantum chemical theory, the dye shade is related to the excited-state transition energy, ΔE ($E_{HOMO-LUMO}$). The absorption of electromagnetic radiation with varying wavelengths may be closely related to the delocalized electron

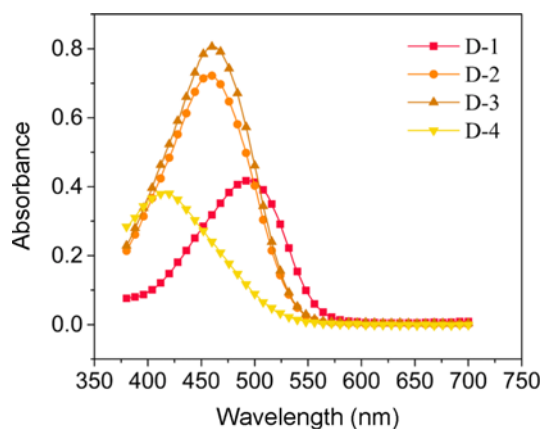


Figure 2. UV-vis spectra of D-1 to D-4 in DMF (2.4×10^{-2} g/l).

Table 1. Spectral data of D-1 to D-4

Dye	λ_{max} (nm)	ϵ ($l \cdot mol^{-1} \cdot cm^{-1}$)	Color
D-1	495.0	12415	Red
D-2	480.0	18793	Orange
D-3	482.5	24395	Orange
D-4	414.0	11411	Yellow

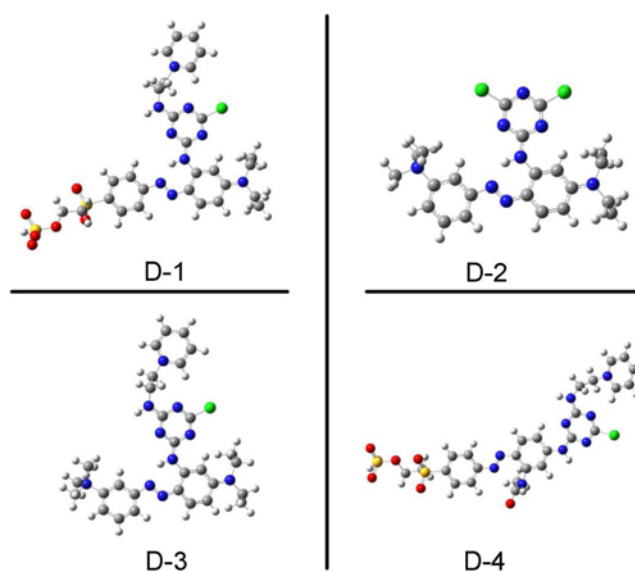


Figure 3. Optimized structures.

systems present in the structure and upon the energy of the electron clouds [49,50]. The synthesized reactive dye molecules were optimized by density functional theory at the B3LYP/6-31G (d) level. The optimized structures are shown in Figure 3. HOMO and LUMO diagrams of D-1 to D-4 are shown in Figure 4. The HOMO and LUMO electron cloud density distributions are concentrated owing to the -Cl substituent on D-2. As a result, compared with D-3, the transition state energy of D-2 was increased, resulting a hypsochromic shift, which is consistent with the experimental results. In addition, compared with D-4, the energy gap of D-1 was decreased due to the introduction of the electron-donating *N,N*-diethylbenzene-1,3-diamine group, which may be one reason for the poor light fastness.

Water Solubility Test

The water solubility of this type of dye is provided by the quaternary ammonium group, but the introduction of a quaternary amino group alone is insufficient to achieve sufficient water solubility [37,51]. Moreover, research has also shown that the position and number of cationic groups affect the solubility of dyes [52]. To demonstrate the relationship between the position of the quaternary ammonium moiety and the water solubility, reactive dyes with different patterns and numbers of cationic groups were synthesized. The changes in the solubility of D-1, D-2, D-3 and D-4 in water with temperature are shown in Figure 5. The results showed that D-1 and D-4 were very sparingly soluble in water. The water solubility of bifunctional reactive dyes containing sulfatoethylsulfone groups was poor. The solubility of ethylsulfurate sulfonyl derivatives in water was low as it did not form a salt under neutral or weakly acidic conditions, and the introduction of a quaternary ammonium

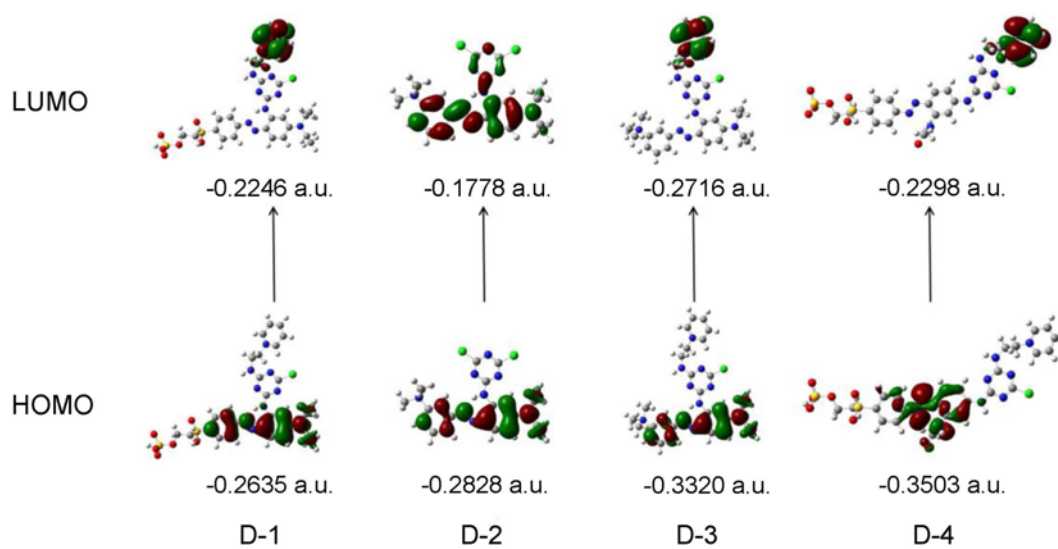


Figure 4. HOMO and LUMO maps for D-1 to D-4.

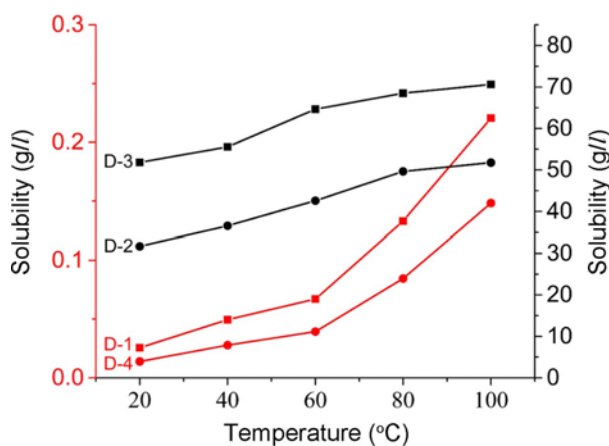


Figure 5. Solubilities of reactive dyes D-1, D-2, D-3, and D-4 in water.

group into halotriazine alone was not able to make the compound water soluble.

However, higher water solubility was obtained by the introduction of a quaternary ammonium salt into the chromophore. Compared with common reactive dyes containing cationic groups as the water-soluble groups, D-2 and D-3 had good water solubilities, reaching over 30 g/l at 20 °C. In addition, the solubility data in Figure 5 suggested that D-3, possessing two cationic groups, had a higher water solubility than D-2, which possessed one cationic group.

Dyeing Properties

Dyeing on cotton fabrics was carried out in an infrared laboratory dyeing machine (Roaches International, England) by using the conventional exhaustion method. The hue values and dyeing properties of the dyed fabrics are reported in terms of the CIELAB system colorimetric parameters, a^*

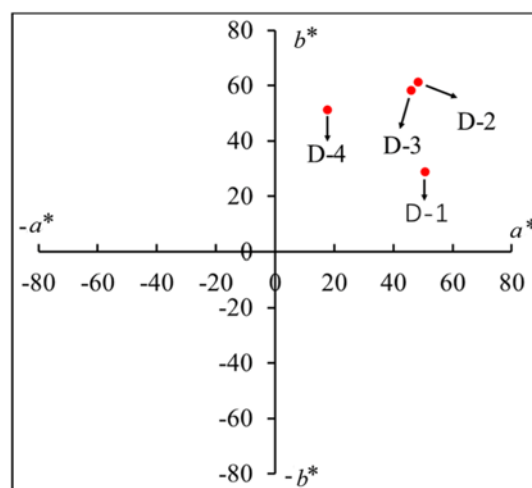


Figure 6. Hue values of the dyed fabrics.

and b^* values and are shown in Figure 6, and $0^\circ (+a^*)$, $180^\circ (-a^*)$, $90^\circ (+b^*)$, and $270^\circ (-b^*)$ represent redness, greenness, yellowness, and blueness, respectively [53]. The data in Figure 6 suggests that D-1 was yellowish red, D-2 and D-3 were reddish orange, and D-4 was reddish yellow. From Figure 6, the results showed that these dyes gave excellent shades and exhibited good affinity for the cotton fabrics.

The dye exhaustion, fixation and K/S values of dyes D-1 to D-4 at 2.0 % (o.w.f.) without salt dyeing were investigated and the data are listed in Table 2. The reactive group had an obvious effect on dye uptake. Dyes possessing two kinds of reactive groups have better dyeing properties than dyes possessing only one kind of reactive group [54]. The reactive dyes containing two reactive groups (sulfatoethylsulfone and monochlorotriazine), such as D-1 and D-4, had better dye uptake, which could reach over 80 % during low-salt dyeing.

Table 2. Exhaustion, fixation, and *K/S* values for D-1 to D-4

	D-1	D-2	D-3	D-4
% <i>E</i>	93.58	92.66	88.28	82.17
% <i>F</i>	87.09	82.62	83.87	72.46
<i>K/S</i>	10.52	14.58	17.17	4.87

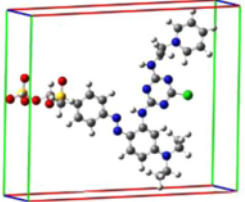
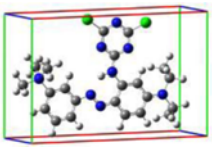
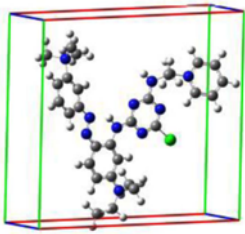
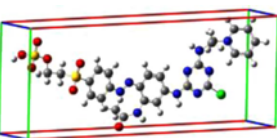
Compared with D-3, containing a monochlorotriazine group, D-2, containing a dichlorotriazine group, had higher reactivity, and the exhaustion of D-2 could reach over 90 % during salt-free dyeing.

The dye uptake was related to the molecular size and the dihedral angle parameters of D-1 to D-4. The unit cells of the optimized structures of D-1 to D-4 are shown in Table 3. The planarity of a dye can affect the interactions between the dye molecules and substrate, cotton fibers in this case. Dye molecules with higher planarity can be easily immobilized on the surface of fibers in a large area. It was observed that D-2 had a smaller volume and better planarity than the other dyes, resulting in its better dyeing performance.

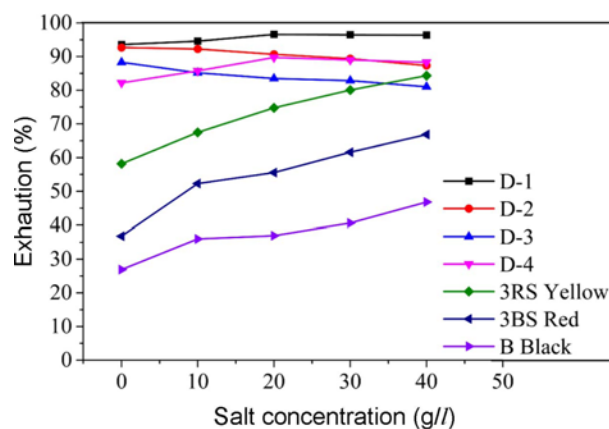
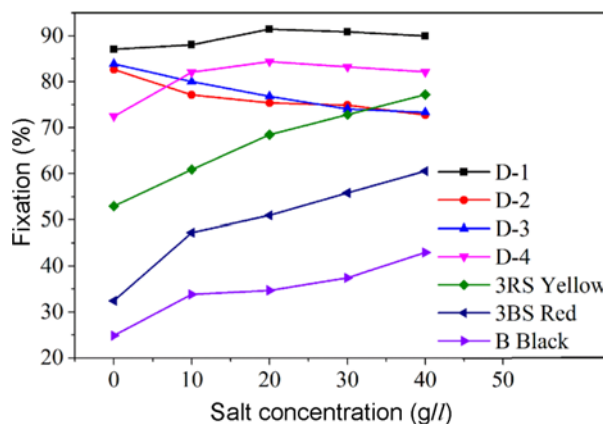
Effect of Salt on Exhaustion and Fixation

During conventional dyeing of cotton fabric with reactive dyes, a large amount of salt is used to increase the dye uptake [22] because the substantivity of dyes on fabric can

Table 3. Unit cells of the dye molecules

Dye	Unit cell	<i>a</i>	<i>b</i>	<i>c</i>
D-1		22.17 Å	17.61 Å	4.89 Å
D-2		15.92 Å	10.21 Å	5.22 Å
D-3		18.23 Å	16.10 Å	4.91 Å
D-4		28.09 Å	10.59 Å	5.30 Å

be improved and the repulsive force between the dye and cotton fabric could be decreased by the addition of a salt [16]. The dyeing process was carried out at different salt concentrations to determine the optimum concentration of salt. Figure 7 and Figure 8 clearly show that the dye uptake of the commercial reactive dyes 3RS Yellow, 3BS Red, and B black increased greatly as the concentration of salt increased. Overall, salt plays an important role in dyeing with conventional reactive dyes. However, as shown in Figure 7 and Figure 8, the dyeing properties of the synthesized dyes were better than those of conventional reactive dyes in salt-free dyeing processes. Moreover, the dye uptake of the synthesized dyes increased as the salt concentration increased from 10 g/l to 20 g/l, while it decreased when the salt concentration was further increased. On the one hand, electrostatic attraction between reactive dyes containing cationic groups and cotton fabric was generated, achieving salt-free dyeing or low-salt dyeing. On the other hand, the excess salt will reduce the solubility of the dye and cause aggregation of the dye, decreasing the dye uptake.

**Figure 7.** Effect of electrolytes (Na_2SO_4) on exhaustion.**Figure 8.** Effect of electrolytes (Na_2SO_4) on fixation.

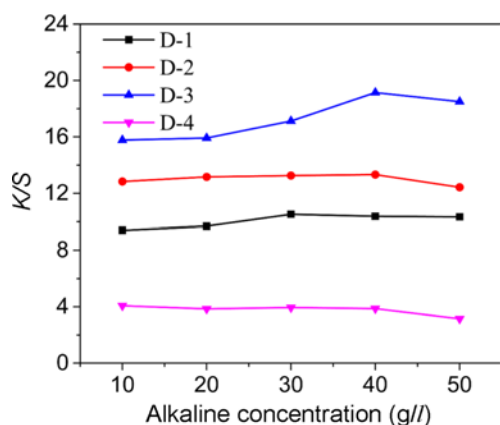


Figure 9. Effect of alkaline (Na_2CO_3) concentration on cotton dyeing.

Effect of Alkaline on Dyeing Performance

The reactive groups react with the hydroxy groups on the cotton fibers to form covalent bonds under alkaline conditions.

The effect of basicity on the K/S value is shown in Figure 9. As shown in Figure 9, the K/S value slightly increased as the concentration of base increased from 10 g/l to 30 g/l, while it decreased with further increases in the alkaline concentration. D-1 and D-4 had two reactive groups (sulfatoethylsulfone and monochlorotriazine), so they were more reactive, as described above. Such a system can undergo β -elimination during the alkaline fixation stage of dyeing to form vinylsulfone groups. A nucleophilic substitution and Michael addition between the reactive groups of the dyes and the hydroxy groups of the cellulose fibers (Cell-OH) occurred under alkaline conditions. Taking D-1 as an example, the reaction mechanism between the cellulose fabric and the dye is shown in Scheme 6 and Figure 10. However, the reactive groups in the dyes could be hydrolyzed due to the high basicity, decreasing the K/S value.

Effect of Temperature on Dyeing Performance

The dyeing temperatures were determined by the reactive groups in the dyes. The reactivity of sulfatoethylsulfone ranks

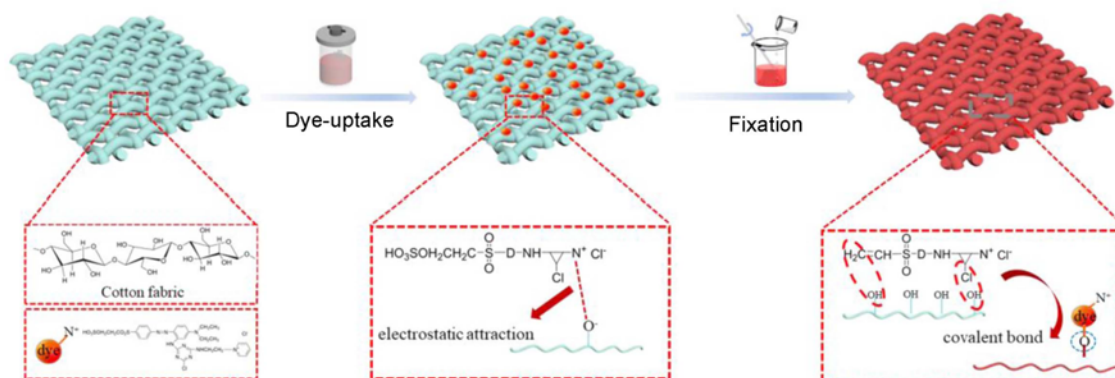
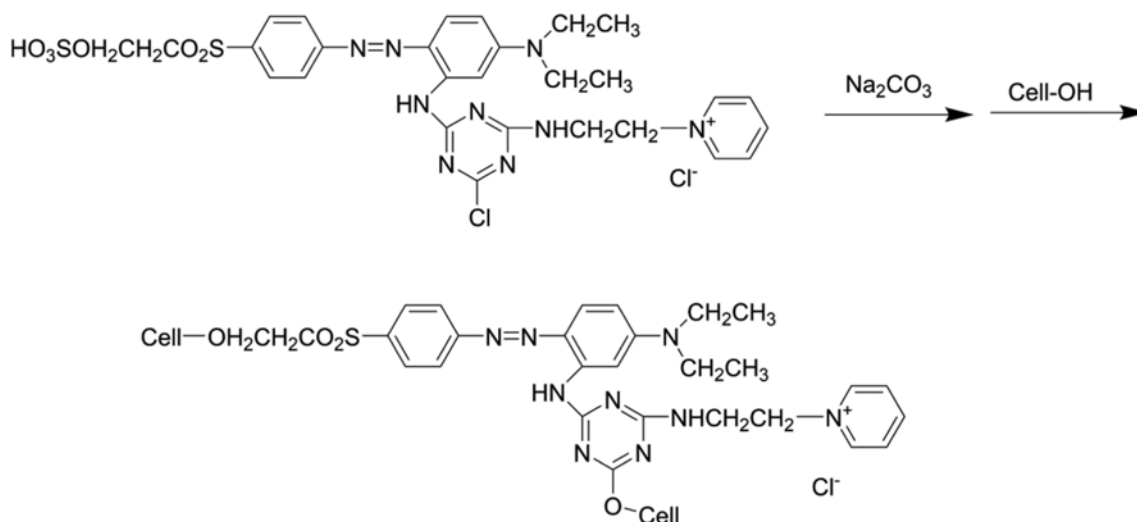


Figure 10. Mechanism of cotton dyeing with D-1.



Scheme 6. Reaction of D-1 with cellulose fabric.

between those of dichlorotriazine and monochlorotriazine. Generally, dyeing procedures with reactive dyes containing sulfatoethylsulfone as the reactive group are carried out in the range of 50-70 °C, reactive dyes containing dichlorotriazine as the reactive group are used at 40-50 °C, and reactive dyes containing monochlorotriazine as the reactive group are used at 60-80 °C. The effect of the dyeing temperature on the K/S value is shown in Figure 11. From the results given in Figure 11, When the temperature was increased from 50 to 70 °C, the K/S values of D-1, D-3, and D-4 significantly increased, and they decreased when the temperature was increased above 70 °C. This phenomenon is likely associated with the aggregation of dye molecules and inability of dyes to fix on the fibers at lower temperatures [55]. With increasing temperature, the water solubilities of the dyes increased, and the swelling of the cotton fabric intensified, favoring the diffusion of the dyes into the fabric. However, as shown in Figure 11, the K/S value of D-2 on cotton decreased as the dyeing temperature was increased from 50 °C to 90 °C. The results suggested that 50 °C was the optimum temperature for D-2. This can be explained by the fact that the hydrolysis reaction of the dyes was enhanced as the temperature increased, resulting in decreased dye uptake.

Build-Up Properties of the Dyes

Usually, build-up properties are used to evaluate the

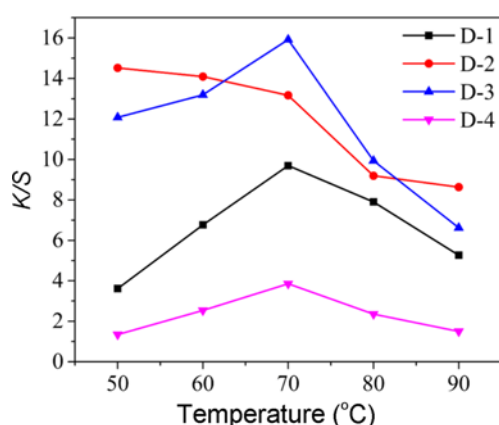


Figure 11. Effect of temperature on cotton dyeing.

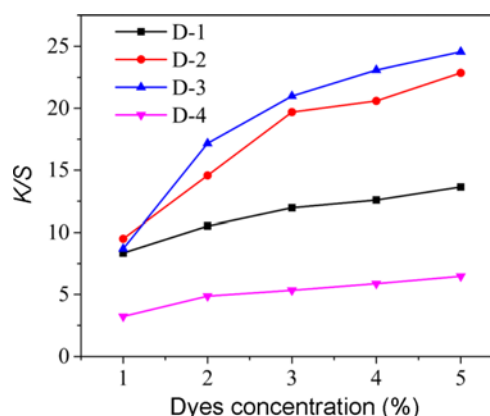


Figure 12. Build-up properties of the reactive dyes on cotton fabrics.

performance of the dyes, making them a crucial parameter [56]. The build-up properties of these dyes in the range of 1-5 % (o.w.f.) are shown in Figure 12. With increasing dye concentration, the color strength of the dye on the cotton fabrics increased significantly, while the K/S values increased slowly when the concentration of dye was higher than 3 %. D-3 exhibited better build-up properties than the other dyes on cotton fabrics, which can be attributed to its high molar absorption coefficient. By comparison, D-2 and D-3 had better build-up performances. This may be because they possess great solubility and high absorption coefficients due to the introduction of quaternary ammonium groups onto the chromophore.

Fastness Properties of the Dyed Cotton Fabrics

The fastness properties of the cotton fabrics dyed with these reactive dyes at 2 % color shade are listed in Table 4. The rubbing fastness of D-4 was better than those of the other dyes, which could reach over 4 grades. This was attributed to its planar structure. The washing fastnesses of all the samples were excellent due to the covalent bonds between the dye and the cotton fibers. However, their lightfastness levels were moderate, which can be explained by the azo bond in the chromophore being broken by photooxidation, reducing the light fastness of the dyed

Table 4. Fastness properties of the dyed cotton fabrics^a

Dye	Rubbing fastness		Washing fastness						Light-fastness
	Dry	Wet	SW	SA1	SP	SN	SC	SA2	
D-1	3	3	4	4-5	4	4	3-4	4-5	3
D-2	4	3	4-5	5	4-5	5	4-5	4-5	3-4
D-3	4-5	3	4-5	4-5	4-5	4-5	4	5	4
D-4	4-5	4	4-5	5	5	4-5	5	5	3-4

^aDye concentration 2 % (o.w.f.). SW: staining on wool, SA1: staining on acrylic, SP: staining on polyester, SN: staining on nylon, SC: staining on cotton, SA2: staining on acetate.

fabrics. Compared with D-4, the lightfastness levels of dyes with reactive groups containing *N,N*-diethylbenzene-1,3-diamine as the coupling component are lower, which was attributed to the increase in electron density on the chromophore, reducing the dye photostability.

Conclusion

Four novel, high fixation reactive dyes containing different patterns and numbers of cationic groups were synthesized for the salt-free dyeing of cotton. All the synthesized dyes were characterized by various techniques. The relationship between the water solubility and the cationic groups was investigated. These four dyes exhibited much better dyeing properties for cotton fabrics in the absence of salt compared with those of commercial reactive dyes, even some reported cationic reactive dyes. The optimized geometries, stable ground state conformers and unit cell parameters from DFT calculations were consistent with the experimental results of D-1 to D-4. The rubbing and lightfastness of D-4 dyed fabrics were better than those of the other dyes, and their washing fastness levels was similar. The success of the salt-free dyeing of cotton fabric with these dyes represents a great advance in environmentally friendly cotton dyeing. Furthermore, these dyes also show excellent dyeing properties for acrylic and wool fibers, making them suitable for one-bath union dyeing of wool/acrylic blended fabrics in the future.

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