Synthesis, Characterization and Applications of High Fastness Reactive Dyes on Cotton Fibers

Ghulam Shabir[a], Aamer Saeed[a]*, Muhammad Arshad[a], Pervaiz Ali Channar[b]
a-Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan.
b- Chemistry Division, Directorate of Science, PINSTECH Nilore Islamabad 45320, Pakistan
aamersaeed@yahoo.com*

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Summary: Two new series of azo reactive dyes containing labile chlorine atoms have been synthesized. The synthetic methodology involved the diazotization of 4-nitro-2-aminophenol (**2**) and 4-aminobenzene sulfonic acid (**7**), followed by azo coupling in alkaline medium with 1-amino-8-naphthol-3,6-disulphonic acid (**3**) and 7-amino-1-hydroxy naphthalene-3-sulfonic acid **(8)** respectively. The latter on condensation of key intermediates **4** and **9** with 1,3,5-trichlorotriazine afforded the cyanurated dyes (**5, 10**). A number of separately synthesized novel bis aromatic diamines (**1a-i**) were coupled with (**5** and **10**) at room temperature to achieve the targeted dyes **6a-h** and **11a-h,** respectively. Structures of newly synthesized compounds were confirmed by the spectral and elemental analysis. The dyes were applied on cotton fibers to assess their application properties, and were shown to possess high values of light fastness, wash fastness and rubbing fastness.

Keywords: Azo dye; Coupling reaction; Diazotization; Dyeing; Spectral study; Elemental analysis.

Introduction

Reactive dyes are a well known class of azo dyes recognized for their ability to establish a covalent bond with the substrates [1,2]. Availability of 1,3,5-Tricholrotriazine and β-sulphatoethyl sulphone groups on the molecules of these dyes favors the covalent bond formation. In addition to triazinyl and vinyl sulphone systems, there are other hetero cyclic nitrogen ring systems with fluoro or chloro substituents at the carbon atom and ß-sulphatoethyl sulphone which causes an electron deficiency in the terminal carbon atom [3,4]. Some other groups having a similar effect to the terminal carbon atom have also been exploited to confer the dye substantivity with cellulose. Thus, depending on the nature of reactive group/s they constitute a triazinyl ring or vinyl sulphone group, which react with the hydroxyl group of cellulose undergoing nucleophilic substitution reactions.

High brilliancy, variety of hues, high wet fastness, convenient handling and high applicability have contributed a lot in providing commercial status to reactive dyes [5, 6]. The nature and number of reactive groups effect the exhaustion and fixation of dyes on fibers [7]. Dyes with two reactive groups have a more fixation efficiency than dyes with one reactive group. Bifunctional dyes with the two reactive groups in the dye molecule exhibit high affinity with fibers. Moreover, using suitable reactive systems the higher fixation levels are possible due to presence of both nucleophilic substitution (triazinyl) and addition (vinyl sulphone) bonds, which improve the fastness characteristic and resistance toward acid, alkali and peroxide [8, 9].

Keeping in view the aforementioned facts, the objective of the current endeavour was to synthesize and evaluate tinctorially strong reactive dyes, which could be applied to cotton by exhaust dyeing using low salt (0-30g/l) quantities. To this end two series of novel monochloro-triazinyl (MCT) disazo reactive dyes (**6a-h** and **11a-h**) were synthesized by coupling a series of diazotized bisanilines intermediates with 1-Hydroxy -8-aminonaphthalene-3, 6-Disulphonic acid [H-acid] and 7-Amino-1-hydoxy naphphalene 3- sulphonic acid [γ-acid], respectively.

Experimental

Materials and Methods

All commercial products were procured from Sigma-Aldrich. Solvents used were of analytical grade and when necessary, were purified and dried by the standard methods. Melting points were determined in open capillary tubes on a Stuart melting point apparatus. The IR spectra were run on the single beam Nicolet IR 100 (Fourier-Transform); while UV of all the samples were run in water using UV-Genesys spectrophotometer. Mass spectral data were obtained from Waters GCT premier spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in D_2O using NMR Bruker DPX 300 spectrophotometer operating at 300 MHz. TMS was

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[*] To whom all correspondence should be addressed.

used as internal standard with the deuterium signal of the solvent as the lock and chemical shifts δ were recorded in ppm. The elemental analysis (C, H, N, S) of the compounds were conducted using Flash EA 1112 elemental analyzer while the pH was monitored using Portable pH Meter Model PHB4. Compounds were routinely checked by TLC on silica gel G plates and paper chromatography using different eluting solvents. All crude products were isolated as solids and purified by a combination of column chromatography and recrystallization. Fastness to light was assessed in accordance with BS 1006-1978 [10]. Rubbing fastness was checked with an Atlas Crock meter in accordance with AATCC TM 8-1961 [11] and the wash fastness was determined according to ISO: 765-1979 [12].

(a) General Procedure for the Synthesis of H-acid Based Reactive Azo Compounds;

i) Diazotization of 4-Nitro-2-aminophenol (4-NAP) and Coupling with H-acid:

4-NAP **(2)** (3.08 g, 0.02 mol) was suspended in H_2O(40 mL) containg concentrated hydrochloric acid (3mL). The mixture was gradually heated up to 70°C till clear solution obtained. The solution was cooled to 0-5 °C in an ice bath. A solution of sodium nitrite (1.4g, 0.020 mol) in H_2O (5 mL) previously cooled to 0°C was then added over a period of 5 minutes with stirring. The stirring was continued for 1h maintaining the same temperature with positive test for nitrous acid. Excess of nitrous acid was killed by adding a pinch of sulphamic acid. The clear diazo solution at 0-5 °C was used for subsequent coupling reaction.

To the well-stirred solution of H-acid **(3)** (6.38 g, 0.02 mol) previously prepared solution of diazonium salt was added drop wise over a period of 10-15 minutes. The pH of the reaction mixture was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v). During coupling the violet color was formed. Stirring was further continued for 3-4 hours maintaining the temperature below 5°C. At the completion of the reaction, the reaction mixture was heated up to 60°C and sodium chloride (25 g) added until the desired product was precipitated. It was stirred for 1h more, then filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90°C till constant weight obtained.

ii) Cyanuration

Cyanuric chloride (3.69 g, 0.02 mole) in acetone (50 mL) was stirred along with addition of neutral solution of **4** (9.68 g, 0.02 mol) in small portions at a temperature below 5°C for a period of 1h. The reaction mass was stirred at 0-5°C for further 4h at neutral pH till a clear solution was obtained. The cyanurated dye thus formed was salted out from 10% sodium chloride followed by filtration, washing and drying at 50°C (**5**). Cyanurated dye was used for subsequent condensation with different bis anilines.

iii) Condensation of Cyanurated Intermediates with Bis Anilines:

To the vigorously stirred aqueous solution of cyanurated intermediates **5** (0.631g, 0.001 mol) at room temperature, was added a solution of 5,5'-Methylenebis(2-Aminobenzoic acid), (0.143g 0.0005 mol) in 15 ml water in acidic medium of HCl. The pH of the reaction mixture was kept 4.0 and continued the stirring for 4h until completion of reaction was observed by paper chromatogram. The dye was salted out from 15% solution of sodium chloride, filtered and dried in oven at 70°C keeping overnight. In this way prepared all the compounds **6a-h** by changing the bis anilines and keeping the same conditions (See supporting informations Table S1). Physical and spectroscopic characterization data of synthesized dyes are as follows;

[$C_{51}Cl_6H_{30}N_{16}O_{20}S_4$] *6a*

Reddish violet crystal, (66%) λ_{max} (nm) (log ε): 564, 305. FT-IR (KBr, cm^{-1}) ν_{max}: 3465 br (OH, NH), 3043 (C=C-H), 2955 (CH_2), 1665, 1585, 1510 (C=C aromatic), 1465 (CH_2), 1070 (S=O), 760 (Ar-H), 720 (C-Cl), 690 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.99 (2H, s), 7.17 (2H, s), 7.30 (2H, d, *J*=7.55Hz), 7.59 (2H, s), 7.56 (2H, s), 7.67(2H, s), 7.75 (2H, d, *J*=7.55 Hz), 7.78 (2H, s), 7.89 (2H, d, *J*=7.4 Hz), 8.10 (2H, d *J*=7.4 Hz), 8.36 (N-H, s), 8.42 (N-H, s), 8.79 (O-H, s), 9.49 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 170.0, 167.3, 158.2, 142.4, 140.4, 138.2, 137.5, 135.5, 134.5, 129.1, 128.3, 126.1, 124.4, 120.9, 120.5, 120.2, 118.6, 117.6, 115.6, 108.3, 41.1. Anal. Calcd. For $C_{51}Cl_6H_{30}N_{16}O_{20}S_4$, C: 40.09, H: 1.98, N: 14.67, S: 8.97; Found: C: 40.05, H: 1.95, N: 14.60, S: 9.02.

[$C_{51}H_{32}Cl_2N_{18}O_{26}S_4$] *6b*

Reddish violet crystal, (67%) λ_{max} (nm): 567, 310. FT-IR (KBr, cm^{-1}) ν_{max}: 3447 br (OH, NH), 3065 (C=C-H), 2950 (CH_2), 1662, 1586, 1507 (C=C aromatic), 1560 (NO_2), 1427 (CH_2), 1095 (S=O), 772 (Ar-H), 680 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.89 (2H, s), 7.15 (1H, s), 7.27 (2H, d, *J*=7.5Hz), 7.58 (2H, s), 7.56 (2H, s), 7.67 (2H, s), 7.75 (2H, d, *J*=7.5 Hz), 7.78 (2H, d, *J*=7.45 Hz), 7.89 (2H, d, *J*=7.45 Hz), 8.30 (N-H, s), 8.38 (N-H, s), 8.75 (O-H, s), 9.43 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 174.9, 158.8, 145.5, 141.8, 140.4, 138.3, 137.6, 136.5, 135.3, 131.2, 129.7, 128.7, 126.9, 120.9, 120.5, 120.2, 117.6, 117.1, 115.5, 108.6, 108.1, 44.9. Anal. Calcd. For $C_{51}H_{32}Cl_2N_{18}O_{26}S_{4,}$ C, 40.51; H, 2.13; N, 16.67; S, 8.48; Found: C, 40.43; H, 2.10; N, 16.53; S, 8.52.

[$C_{53}H_{34}Cl_2N_{16}O_{24}S_4$] 6c

Reddish violet crystal, (66%) λ_{max} (nm): 560, 310. FT-IR (KBr, cm^{-1}) ν_{max}: 3526-3200 (O-H, COOH, N-H), 3078 (C=C-H), 2953 (CH_2), 1735(C=O) 1627, 1587, 1523 (C=C aromatic), 1481 (CH_2), 1078 (S=O), 732 (Ar-H), 672 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.95 (2H, s), 7.15 (2H, s), 7.27 (2H, d, *J*=7.55 Hz), 7.38 (2H, d, *J*=7.55 Hz), 7.54 (2H, s), 7.71 (2H, d, *J*=7.60 Hz), 7.78 (2H, s), 7.88 (2H, d, *J*=7.60 Hz), 7.97(1H, s), 8.33 (N-H, s), 8.41 (N-H, s), 8.70 (O-H, s), 9.46 (O-H, s), 12.74 (O-H, COOH, br, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 169.0, 168.5, 158.6, 140.3, 138.6, 138.1, 137.7, 135.3, 130.6, 129.9, 128.7, 127.1, 126.5, 121.1, 120.9, 120.2, 117.6, 116.8, 115.7, 108.5, 45.9. Anal. Calcd. For $C_{53}H_{34}Cl_2N_{16}O_{24}S_{4,}$ C, 43.07; H, 2.32; N, 15.16; S, 8.68; Found: C, 43.02; H, 2.25; N, 15.09; S, 8.73.

[$C_{51}H_{32}Cl_2N_{18}O_{24}S_4$] 6d

Reddish violet crystal, (71%) λ_{max} (nm) : 557, 306. FT-IR (KBr, cm^{-1}) ν_{max}: 3480 (OH, NH), 3075 (C=C-H), 2830 (CH_2), 1645, 1587, 1505 (C=C aromatic), 1550 (NO_2), 1443 (CH_2), 1107 (S=O), 733 (Ar-H), 672 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 2.01 (2H, s), 7.15 (2H, s), 7.27 (2H, d, *J*=7.53 Hz), 7.50 (2H, s), 7.66 (2H, s), 7.74 (2H, d, *J*=7.53 Hz), 7.78 (2H, s), 7.84 (2H, d, *J*=7.6 Hz), 8.07 (2H, d, *J*=7.6 Hz), 8.33 (N-H, s), 8.41 (O-H, s), 8.65 (N-H, s), 9.38 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 168.8, 158.7, 144.4, 140.3, 138.7, 137.6, 136.6, 135.3, 133.8, 129.4, 128.6, 126.2, 120.9, 120.5, 120.2, 119.1, 117.6, 116.3, 115.5, 112.1, 108.8, 55.1, 45.2. Anal. Calcd. For $C_{51}H_{32}Cl_2N_{18}O_{24}S_{4,}$ C, 41.39; H, 2.18; N, 17.03; S, 8.66; Found: C, 41.33; H, 2.10; N, 17.00; S, 8.69.

[$C_{53}H_{38}Cl_2N_{16}O_{22}S_4$] 6e

Reddish violet crystal, (69%). λ_{max} (nm): 570, 310. FT-IR (KBr, cm^{-1}) ν_{max}: 3465 (NH), 3063 (C=C-H), 2943 (CH_2), 1663, 1595, 1512 (C=C aromatic), 1447 (CH_2), 1075 (S=O), 1055 (C-O), 770 (Ar-H), 673 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 4.07 (3H, s), 1.96 (2H, s), 6.75 (2H, d, *J*=7.15 Hz), 7.0 (2H, d, *J*=7.15 Hz), 7.15 (1H, s), 7.32 (1H, s), 7.50 (2H, s), 7.93(1H, s), 7.73 (2H, d, *J*=7.58 Hz), 7.86 (2H, d, *J*=7.58 Hz), 8.30 (N-H, s), 8.36 (O-H, s), 8.61 (N-H, s), 9.35 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 45.2, 55.1, 108.8, 112.1, 115.5, 116.3, 117.6, 119.1, 120.2, 120.5, 120.9, 126.2, 128.6, 129.4, 133.8, 135.3, 136.6, 137.6, 138.7, 140.3, 144.4, 158.7, 168.8. Anal. Calcd. For $C_{53}H_{38}Cl_2N_{16}O_{22}S$, C, 43.90; H, 2.64; N, 15.45; S, 8.84; Found: C, 43.81; H, 2.51; N, 15.40; S, 8.86.

[$C_{53}H_{34}Cl_2N_{16}O_{24}S_4$] 6f

Reddish violet crystal, (74%). λ_{max} (nm): 568, 309. FT-IR (KBr, cm^{-1}) ν_{max}: FT-IR (KBr, cm^{-1}) ν_{max}: 3555-3265 (O-H, COOH, N-H), 3060 (C=C-H), 2962 (CH_2), 1743 (C=O), 1629, 1587, 1540 (C=C aromatic), 1480 (CH_2), 744 (Ar-H), 678 (C-Cl). 3422 (OH, NH), 2929 (CH_2), 1660, 1590, 1502 (C=C aromatic), 1070, S=O, 723 (Ar-H), 672 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.79 (2H, s), 6.82 (2H, d, *J*=7.32 Hz), 7.29 (2H, d, *J*=7.32 Hz), 7.34 (2H, d), 7.45 (1H, s), 7.54 (2H, d, *J*=7.5 Hz), 7.69 (2H, d, *J*=7.5 Hz), 7.81 (2H, d, *J*=7.6 Hz), 8.08 (2H, d, *J*=7.6 Hz), 8.33 (N-H, s), 8.37(O-H, s), 8.38 (O-H, s), 9.38 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 180.32, 150.9, 149.2, 146.8, 139.4, 138.2, 136.4, 134.0, 131.7, 130.3, 129.2, 127.7, 126.3, 125.2, 123.4, 121.8, 119.0, 117.8, 116.1, 114.1, 118.1, 109.6, 38.15. Anal. Calcd. For $C_{53}H_{34}Cl_2N_{16}O_{24}S_{4,}$ C, 43.07; H, 2.32; N, 15.16; S, 8.68; Found: C, 43.01; H, 2.29; N, 15.10; S, 8.70.

[$C_{51}H_{32}Cl_4N_{16}O_{20}S_4$] 6g

Reddish violet crystal, (74%). λ_{max} (nm): 560, 310. FT-IR (KBr, cm^{-1}) ν_{max}: 3462 (OH, NH), 3055 (C=C-H), 2965 (CH_2), 1633, 1586, 1522 (C=C aromatic), 1115 (S=O), 735 (Ar-H), 710 (C-Cl), 672 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.93 (2H, s), 7.02 (1H, s), 7.11 (2H, s), 7.30 (2H, s), 7.27 (2H, d, *J*=7.35 Hz), 7.50 (2H, s), 7.66 (2H, s), 7.69 (2H, d, *J*=7.35 Hz), 7.81 (2H, d, *J*=7.60 Hz), 8.08 (2H, d, *J*=7.6 Hz), 8.25 (N-H, s), 8.32 (O-H, s), 8.67(N-H, s), 9.36 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 169.9, 158.6, 144.3, 143.7, 140.1, 138.7, 137.4, 135.9, 135.3, 129.5, 128.2., 126.3, 120.9, 120.5, 120.2, 118.0, 117.6, 115.3, 114.0, 113.5, 109.6, 45.3. Anal. Calcd. For $C_{51}H_{32}Cl_4N_{16}O_{20}S_4$,C, 41.99; H, 2.21; N, 15.36; S, 8.79; Found: C, 41.80; H, 2.11; N, 15.32; S, 8.83.

[$C_{51}H_{34}Cl_2N_{16}O_{22}S_4$] 6h

Reddish violet crystal, (71%). λ_{max} (nm): 568, 309. FT-IR (KBr, cm^{-1}) ν_{max}: 3466 (OH, NH), 3058 (C=C-H), 2875 (CH_2), 1637, 1563, 1510 (C=C aromatic), 1120 (S=O), 737 (Ar-H), 672 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 2.10 (2H, s), 6.58 (2H, d, *J*=7.24Hz), 6.76 (2H, d, *J*=7.24 Hz), 7.10 (2H, s), 7.32 (2H, s), 7.50 (2H, s), 7.69 (2H, d, *J*=7.6Hz), 7.81 (2H, d, *J*=7.60 Hz), 8.33 (N-H, s), 8.45 (N-H, s), 8.78 (O-H, s), 9.42 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 168.7, 158.4, 141.9, 140.3, 138.6, 137.6, 135.3, 134.9, 134.3, 129.4, 128.3, 126.5, 121.9,120.8, 120.2, 119.6, 117.5, 116.6, 115.4, 114.3, 108.4, 47.3. Anal. Calcd. For $C_{51}H_{34}Cl_2N_{16}O_{22}S_4$, C, 43.08; H, 2.41; N, 15.76; S, 9.02; Found: C, 43.03; H, 2.35; N, 15.56; S, 9.10.

General Procedure for the Synthesis of γ-acid Based Reactive Azo Compounds

The procedure comprises the following three steps:

i) Diazotization of 4-Aminobenzene sulfonic Acid and Coupling with γ-acid:

4-Aminobenzene sulfonic Acid **(7)** (3.46 g, 0.02 mol) was dissolved in H_2O (40 mL) by heating and inceasing the pH of medium with sodium carbonate (2.20g, 0.02 mol). The solution was cooled to 0-5°C in an ice bath and was added hydrochloric acid (5.0 ml). A solution of sodium nitrite (1.4 g, 0.020 mol) in H_2O (5 mL) previously cooled to 0 °C, was then added at once. Stirring of reaction mixture was continued for 1h more maintaining the same temperature, with a positive test for nitrous acid on iodo paper. The clear diazo solution at 0-5°C was used for subsequent coupling reaction.

To the well-stirred solution of γ-acid **(8)** (4.78 g, 0.02 mol), a freshly prepared diazo solution was added drop wise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 with sodium carbonate solution (10% w/v). During coupling the yellow dye was formed. Stirring was further continued for 3-4 hours maintaining the temperature below 5°C. At the completion of reaction, the reaction mixture was heated up to 60°C and sodium chloride (20 g) added until the dye was salted out which was then filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90^{o}C.

ii) Cyanuration of Dye:

Cyanuration of dye was achieved by treating the neutral solution of intermediate **9** (8.46 g, 0.02 mol) with cyanuric chloride solution in acetone (3.69 g, 0.02 mole/ 50 mL) at a temperature below 5°C in 1h. Under neutral conditions reaction mixture was stirred at 0-5°C for further 4h until the completion of reaction was observed from paper chromatogram. The cyanurated dye thus formed was salted out from 10% sodium chloride, then filtered, washed and dried at 70^{o}C (**10**) in 90% yield. Cyanurated dye was used for subsequent condensation with different bis anilines.

iii) Condensation of Cyanurated Dye with Bis Anilines:

To the vigorously stirred aqueous solution of cyanurated dye **10** (0.570 g, 0.001 mol) at room temperature, was added a solution of 5,5'-Methylenebis(3-nitroaniline) (0.144 g 0.0005mol) in 15 ml water in acidic medium. The pH of the reaction mixture was kept at 4.0 until the completion of reaction was observed from paper chromatogram. The product was salted out from 15% solution of sodium chloride, filtered and dried in oven at 70^{o}C.. In this way prepared all compounds **(11a-h)** by changing the bis anilines under the previous conditions as in section 2.2 (For supporting informations consult Table S2). The physical and spectroscopic characterization data are as under;

[$C_{53}H_{36}Cl_2N_{14}O_{18}S_4$] 11a

Reddish yellow crystal, (65%) λ_{max} (nm): 502, 386, 293. FT-IR (KBr, cm^{-1}) ν_{max}: 3560-3350 (O-H, COOH, N-H), 3032 (C=C-H), 2915 (CH_2), 1755 (C=O), 1625, 1587, 1525, (C=C aromatic), 1540 (N=N), 1465 (CH_2), 1125 (S=O), 787 (Ar-H), 680 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 2.03 (2H, s), 6.83 (2H, s), 6.84 (4H, d, *J*=8.1Hz), 7.30 (2H, d, *J*=8.1Hz), 7.38 (2H, d, *J*=8.1Hz), 7.44 (1H, s), 7.56 (1H, s), 7.90 (4H, d, *J*=8.1Hz), 8.39 (N-H, s), 8.89 (N-H, s), 9.07(O-H, s), 9.48 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 168.5, 167.9, 166.0, 156.8, 156.5, 147.7, 144.3, 142.7, 135.3, 134.9, 131.3, 131.3, 128.8, 128.5, 126.7, 124.3, 123.8, 120.0, 118.4, 107.4, 45.5. Anal. Calcd. For $C_{53}H_{36}Cl_2N_{14}O_{18}S_4$, C, 46.94; H, 2.68; N, 14.46; S, 9.46; Found: C, 46.23; H, 2.54; N, 14.40; S, 9.50.

[$C_{51}H_{34}Cl_2N_{16}O_{18}S_4$] 11b

Reddish yellow crystal, (68%) λ_{max} (nm): 496, 389. FT-IR (KBr, cm^{-1}) ν_{max}: 3467 br (OH, NH), 3062 (C=C-H), 2920 (CH_2), 1647, 1572, 1520 (C=C aromatic), 1565 cm^{-1} 1462 (CH_2), 1123 (S=O), 772 (Ar-H), 682 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.95 (2H, s), 6.84 (4H, d, *J*=8.1Hz), 7.15 (2H, s), 7.66 (2H, s), 7.78 (2H, s), 7.44 (2H, s), 7.68 (4H, d, *J*=8.1Hz), 7.90 (2H, d), 7.97 (2H, d), 8.11 (N-H, s), 8.20 (N-H, s), 8.34 (O-H, s), 9.47 (O-H, s).

^{13}C-NMR (75 MHz, D_2O) δ (ppm): 169.0, 167.9, 156.5, 149.2, 147.7, 144.3, 143.8, 143.2, 142.7, 126.7, 131.9, 131.3, 128.8, 128.5, 124.3, 123.2, 121.6, 120.0, 117.4, 114.3, 107.4, 106.7, 42.3. Anal. Calcd. For $C_{51}H_{34}Cl_2N_{16}O_{18}S_4$, C, 45.11; H, 2.52; N, 16.50; S, 9.44; Found: C, 44.95; H, 2.30; N, 16.35; S, 9.51.

[$C_{51}H_{34}Cl_4N_{14}O_{16}S_4$] 11c

Reddish yellow crystal, (67%). λ_{max} (nm) : 496, 394, 292. FT-IR (KBr, cm^{-1}) ν_{max}: 3435 br (OH, NH), 3043 (C=C-H), 2908 (CH_2), 1627, 1577, 1523 (C=C aromatic), 1440 (CH_2), 1070 (S=O), 767 (Ar-H), 680 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.78 (2H, s), 6.79 (2H, s), 6.84 (4H, d, *J*=8.1Hz), 7.34 (2H, s), 7.58 (2H, s), 7.68 (4H, d, *J*=8.1Hz), 7.729 (1H, s), 8.02 (N-H, s), 8.11 (N-H, s), 8.32 (O-H, s), 9.41 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 170.4, 158.8, 154.9, 152.3, 143.3, 142.2, 133.9, 132.0, 130.4, 126.6, 123.8, 119.2, 116.2, 103.75, 101.4, 95.5, 39.01. Anal. Calcd. For $C_{51}H_{34}Cl_4N_{14}O_{16}S_4$, C, 44.75; H, 2.50; N, 14.32; S, 9.37; Found: C, 44.20; H, 2.32; N, 14.15; S, 9.40.

[$C_{53}H_{40}Cl_2N_{14}O_{16}S_4$] 11d

Reddish yellow crystal, (70 %) λ_{max} (nm): 492, 390, 283. FT-IR (KBr, cm^{-1}) ν_{max}: 3437 (OH, NH), 3072 (C=C-H), 2838 (CH_2), 1653, 1574, 1525 (C=C aromatic), 1437 (CH_2), 1070 (S=O), 755 (Ar-H), 683 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 4.05 (3H, s), 2.01 (2H, s), 6.75 (4H, d, *J*=8.1Hz), 7.00 (2H, d, *J*=8.15Hz), 7.15 (1H, s), 7.44 (1H, s), 7.77 (2H, d, *J*=8.15Hz), 7.90 (4H, d, *J*=8.1Hz), 7.27 (2H, s), 8.40 (N-H, s), 8.89 (N-H, s), 8.95 (O-H, s), 9.43 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 170.5, 167.8, 156.5, 147.7, 144.9, 144.3, 142.7, 134.6, 134.6, 133.6, 131.8, 131.3, 128.8, 128.5, 126.7, 124.3, 123.2, 121.7, 119.2, 118.4, 116.2, 112.6, 107.4, 55.8, 41.7. Anal. Calcd. For $C_{53}H_{40}Cl_2N_{14}O_{16}S_4$, C, 47.93; H, 3.04; N, 14.77; S, 9.66; Found: C, 47.11; H, 2.99; N, 14.50; S, 9.71.

[$C_{51}H_{34}Cl_4N_{14}O_{14}S_4$] 11e

Reddish yellow crystal, (69%). λ_{max} (nm): 498, 388, 292. FT-IR (KBr, cm^{-1}) ν_{max}: 3455 (OH, NH), 3045 (C=C-H), 2890 (CH_2), 1645, 1572, 1522 (C=C aromatic), 1433 (CH_2), 1095 (S=O), 753 (Ar-H), 679 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 3.87 (3H, s), 2.05 (2H, s), 6.75 (4H, d, *J*=8.1Hz), 7.09 (2H, d, *J*=8.2Hz), 7.18 (1H, s), 7.27 (2H, s), 7.44 (1H, s), 7.77 (2H, d, *J*=8.20 Hz), 7.89 (4H, d), 7.98 (2H, d, *J*=8.1Hz), 8.32 (N-H, s), 8.92 (N-H, s), 9.10 (O-H, s), 9.33(O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 173.5, 168.6, 156.5, 147.7, 144.3, 143.7, 142.7, 135.6, 131.6, 131.2, 128.8, 128.5, 126.7, 124.3, 123.2, 120.5, 118.4, 114.2, 113.3, 107.4, 43.5. Anal. Calcd. For $C_{51}H_{34}Cl_4N_{14}O_{14}S_4$, C, 45.82; H, 2.56; N, 14.67; S, 9.59; Found: C, 45.35; H, 2.16; N, 14.45; S, 9.09.

[$C_{51}H_{32}Cl_6N_{14}O_{14}S_4$] 11f

Reddish yellow crystal, (74%). λ_{max} (nm) (log ε): 492, 389, 289. FT-IR (KBr, cm^{-1}) ν_{max}: 3453 (OH, NH), 3053 (C=C-H), 2929 (CH_2), 1637, 1586, 1512 (C=C aromatic), 1447 (CH_2), 1122 (S=O), 750 (Ar-H), 680 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.94 (2H, s), 6.85 (4H, d, *J*=8.1Hz) 7.02 (2H, s), 7.15 (2H, s), 7.44 (1H, s), 7.77(2H, d, *J*=7.8Hz), 7.90 (4H, d, *J*=8.1Hz), 7.30 (2H, s), 8.02 (2H, d, *J*=7.8Hz), 8.34 (N-H, s), 8.83 (N-H, s), 8.97(O-H, s), 9.41 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 168.5, 167.9, 147.7, 156.5, 144.3, 142.7, 142.2, 139.3, 134.3, 131.9, 131.5, 130.1, 128.8, 128.5, 127.2, 126.7, 124.3, 123.2, 121.1, 120.0, 118.4, 107.4, 44.3. Anal. Calcd. For $C_{51}H_{32}Cl_6N_{14}O_{14}S_4$, C, 43.57; H, 2.29; N, 13.95; S, 9.12; Found: C, 43.10; H, 2.23; N, 13.34; S, 9.20.

[$C_{51}H_{32}Cl_6N_{14}O_{14}S_4$] 11g

Reddish yellow crystal, (75%). λ_{max} (nm) (log ε): 495, 392, 289. FT-IR (KBr, cm^{-1}) ν_{max}: 3435 (OH, NH), 3043 (C=C-H), 2923 (CH_2), 1633, 1589, 1517 (C=C aromatic), 1453 (CH_2), 1097 (S=O), 772 (Ar-H), 685 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 1.99 (2H, s), 6.86 (4H, d, *J*=8.1Hz), 7.17 (2H, s), 7.2 (2H, s), 7.44 (2H, s), 7.56 (2H, s), 7.77(2H, d, *J*=7.9Hz), 7.93 (4H, d, *J*=8.1Hz), 8.02 (2H, d, *J*=7.9Hz), 8.31 (N-H, s), 8.83 (N-H, s), 9.05 (O-H, s), 9.37 (O-H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 170.5, 167.9, 156.5, 147.7, 144.3, 142.7, 142.3, 137.1, 134.9, 131.6, 130.5, 128.8, 128.5, 126.7, 125.1, 124.3, 124.1, 123.2, 119.5, 118.4, 107.7, 42.1. Anal. Calcd. For $C_{51}H_{32}Cl_6N_{14}O_{14}S_4$, C, 43.57; H, 2.29; N, 13.95; S, 9.12; Found: C, 43.17; H, 2.20; N, 13.35; S, 9.25.

[$C_{51}H_{36}Cl_2N_{14}O_{16}S_4$] 11h

Reddish yellow crystal, (70%). λ_{max} (nm) (log ε): 499, 389, 289. FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (OH, NH), 3064 (C=C-H), 2963 (CH_2), 1639, 1568, 1526 (C=C aromatic), 1448 (CH_2), 1152 (S=O), 755 (Ar-H), 682 (C-Cl). ^{1}H-NMR (300 MHz, D_2O) δ (ppm): 2.04 (2H, s), 7.15 (1H, s), 7.10 (1H, s), 6.58 (2H, d, *J*=8.1Hz), 6.78 (4H, d, *J*=8.15Hz), 7.44 (2H, s), 7.77 (2H, d, *J*=8.15 Hz), 7.87 (4H, d, *J*=8.1Hz), 8.41 (N-H, s), 8.83 (N-H, s), 9.06 (O-H, s), 9.45 (O-

H, s). ^{13}C-NMR (75 MHz, D_2O) δ (ppm): 171.2, 167.9, 156.5, 147.7, 144.3, 142.7, 141.9, 134.9, 131.3, 131.2, 128.8, 128.5, 126.7, 124.3, 123.2, 121.3, 119.6, 118.4, 116.6, 144.3, 107.8, 44.2. Anal. Calcd. For $C_{51}H_{36}Cl_2N_{14}O_{16}S_4$, C, 47.12; H, 2.79; N, 15.08; S, 9.86; Found: C, 47.05; H, 2.74; N, 14.95; S, 9.95.

Dyeing Method

A laboratory model glycerin-bath high-temperature beaker dyeing machine was employed. A paste of finely powdered dye (25 mg) was prepared with the dispersing agent EDTA (1ml, 10% W/V), in a ball mill for 10 min. To this paste, water (15 ml) was added under stirring and the pH was adjusted to 8.5-9.0, using Na_2CO_3 (1ml, 10% W/V). This dye suspension (100 ml) was added to a beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a wetted pattern of nylon fiber was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin-bath, the temperature of which was raised to 70°C at the rate of 2ºC/min. The dyeing was continued for 1h under pressure. After cooling for 1h, the beaker was removed from the bath and washed with water. The pattern was thoroughly washed with hot water at 50°C and then with cold water and finally dried at room temperature [13].

Results and Discussion

Synthetic Route for Azo Reactive Compounds

The reaction sequences employed for the synthesis of the targeted compounds **6a-h** are illustrated in scheme-1. Accordingly, 4-Nitro-2-aminophenol (4-NAP) (**2**) was diazotized by treating with sodium nitrite in the presence of HCl at low temperature 0-5^{o}C. Temperature and pH coditions were maintained to obtain dyes in maximum yields with high purity. The reaction of 4-NAP diazo with H-acid (**3**) in alkaline medium resulted in the coupling at *ortho* to the hydroxyl group of H-acid. The dyes were salted out by the addition of 10% sodium chloride solution to reaction mixture.

Cyanuration of intermediate **4** was achieved by treating it with cyanuric chloride solution in ice bath at pH 2.0-2.5 in 1:1 molar ratio. Cyanurated intermediate was filtered, separated and dried in the oven at 50^{o}C. The separately synthesized bis anilines (**1a-i,** Fig. 1) were added to solution of compound **5** at pH 4-5 at room temperature in molar ratio 1:2 to furnish **6a-h** compounds. The diverse bis anilines used as bridging component for compounds, did not affect the λ_{max} but increased the substantivity of dye with fiber (scheme-1).

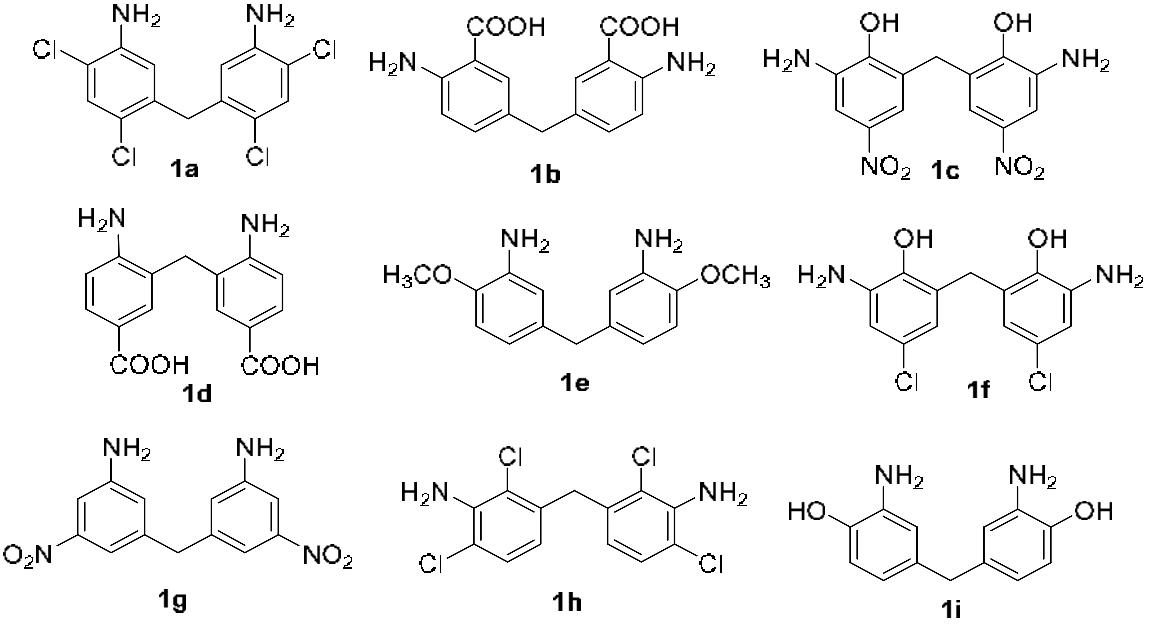
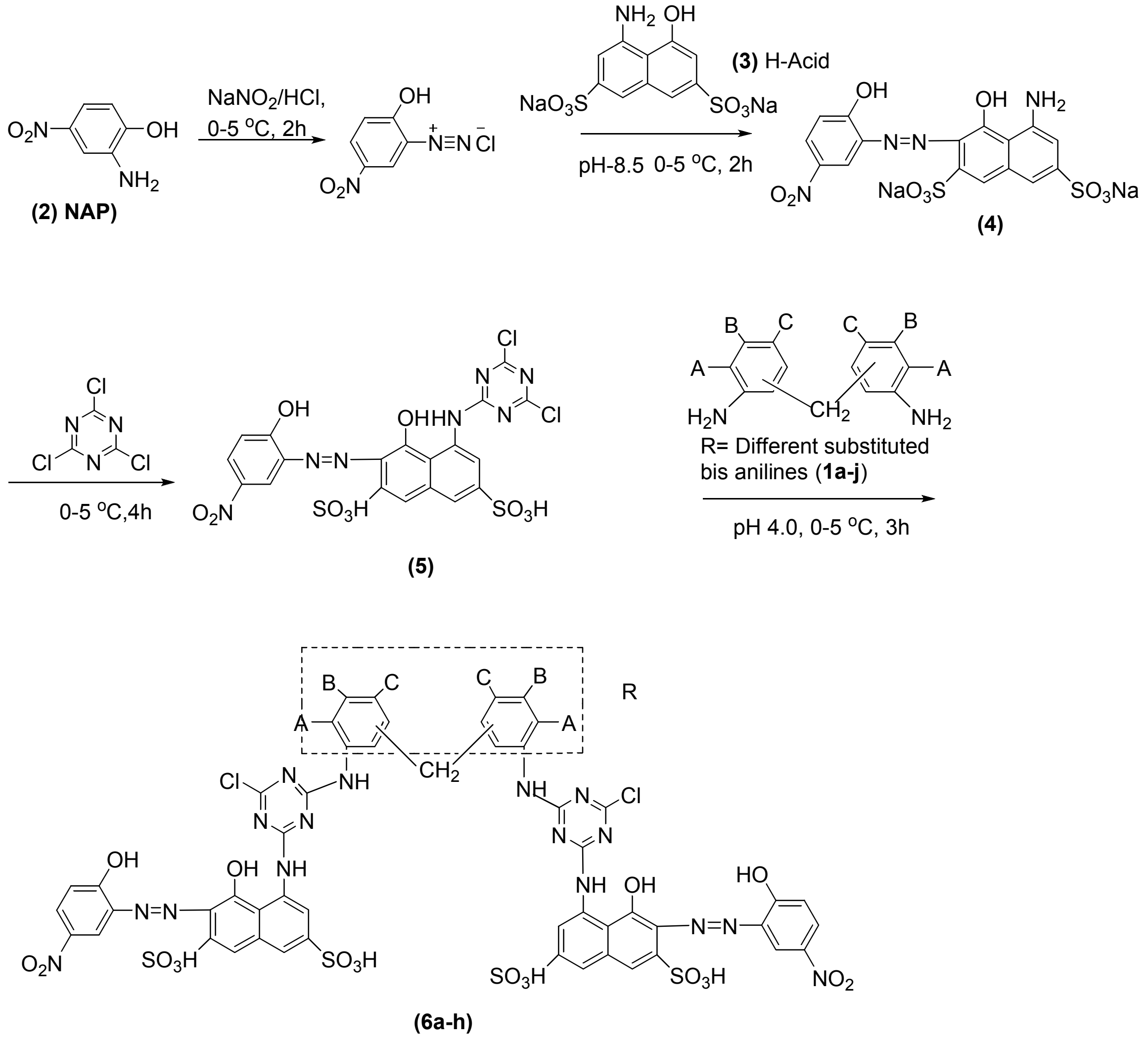


Fig. 1: Structures of methylene bisanilines **(1a-i)** used a linker.

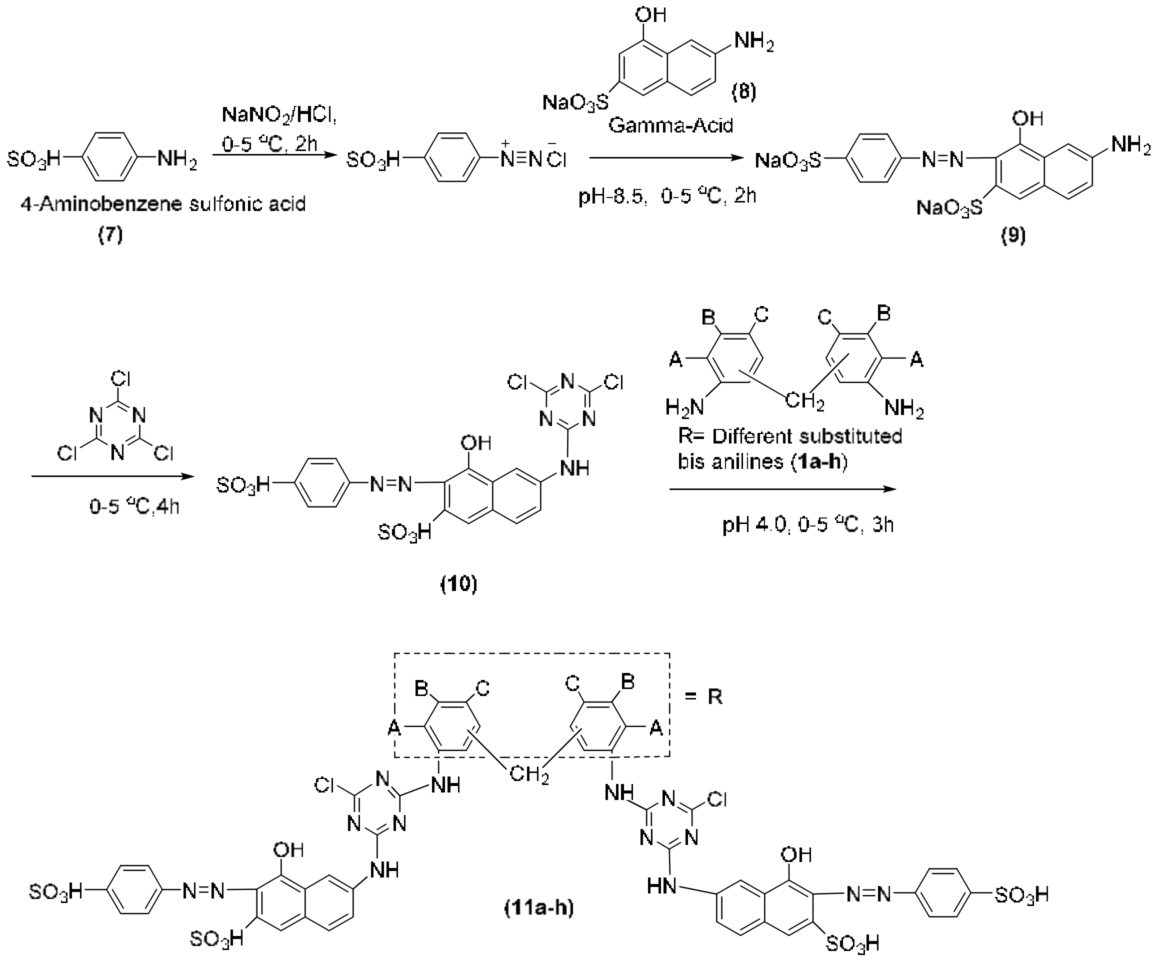


Scheme-1: Synthetic route to monoazo bis MCT reactive dyes **(6a-j)**

The synthesis of bisazo monochloro triazine (MCT) reactive dyes **11a-h** was conducted in accordance with scheme-2. Here reactive dyes were synthesized using 7-Amino-1-naphthol-3-sulphonic acid (γ-acid) coupler and 4-Aminobenesulfonic (sulfanilic acid) as monoazo component.

Accordingly, sulfanilic acid (**7**) was diazotized by treating it with Sodium nitrite and HCl at low temperature 0-5^{o}C. Conditions were kept same as discussed above during diazotization. Coupling of sulfanilic acid diazo with γ-acid **8** was achieved to afford **9** in alkaline medium at 0-5^{o}C. The addition of diazo was to well stirred solution of γ-acid was made at pH 8.5-9.0, which was adjusted with mild base like Na_2CO_3. The coupling was completed in 3-4 h as determined from TLC and paper chromatography. The dye was salted out by the addition of 8% sodium chloride to dye solution at room temperature.

Cyanuration of dye **9** was done by addition of dye to cyanuric chloride solution in an ice bath at pH 2.0-2.5 in 1:1 molar ratio [14]. Cyanurated dye was filtered, separated and then dried in oven at 60-65^{o}C. Bis aniline (**1a-i**) was added to solution of dye at pH 4-5 at room temperature in molar ratio 1:2 to furnish **11a-h** dyes. Different bis anilines were used as bridging component for dyes to enhance the adherence of dye with fiber (scheme-2) without affecting too much on dye shades and hues. The synthesized compounds were analyzed for elemental composition and the percentages of C, H, N and S in these derivatives ensured their exact compositions (Table-1 and 2).



Scheme-2: Synthetic route to monoazo bis MCT reactive dyes **(11a-h).**

Table-1: Characterization data of monoazo bis MCT reactive azo dyes **(6a-h)**

Dye	Molecular Formula	Mol. Wt	yield%	C% Cal/Found	H% Cal/Found	N% Cal/Found	S% Cal/Found	R_f^* Value
6a	$C_{51}Cl_6H_{30}N_{16}O_{20}S_4$	1523	76.78	40.09/40.05	1.98/1.95	14.67/14.60	8.97/9.02	0.52
6b	$C_{51}H_{32}Cl_2N_{18}O_{26}S_4$	1476	77.31	40.51/40.43	2.13/2.10	16.67/16.53	8.48/8.52	0.56
6c	$C_{53}H_{34}Cl_2N_{16}O_{24}S_4$	1510	76.35	43.07/43.02	2.32/2.25	15.16/15.09	8.68/8.73	0.48
6d	$C_{51}H_{32}Cl_2N_{18}O_{24}S_4$	1478	81.57	41.39/41.33	2.18/2.10	17.03/17.00	8.66/8.69	0.46
6e	$C_{53}H_{38}Cl_2N_{16}O_{22}S_4$	1420	79.78	43.90/43.81	2.64/2.51	15.45/15.40	8.84/8.86	0.50
6f	$C_{53}H_{34}Cl_2N_{16}O_{24}S_4$	1476	84.32	43.07/43.01	2.32/2.29	15.16/15.10	8.68/8.70	0.43
6g	$C_{51}H_{32}Cl_4N_{16}O_{20}S_4$	1478	84.31	41.99/41.80	2.21/2.11	15.36/15.32	8.79/8.83.	0.45
6h	$C_{51}H_{34}Cl_2N_{16}O_{22}S_4$	1487	81.65	43.08/43.03	2.41/2.35	15.76/15.56	9.02/9.10	0.44

*Ethanol: Ethyl acetate (5:5 v/v), Silica gel-G F254 TLC plate.

Table-2: Characterization data of monoazo bis MCT reactive azo dyes (**11a-h**)

Dye	Molecular Formula	Mol. Wt	Yield%	C% Cal/Found	H% Cal/Found	N% Cal/Found	S% Cal/Found	R_f^* Value
11a	$C_{53}H_{36}Cl_2N_{14}O_{18}S_4$	1401	73.43	46.94/46.23	2.68/2.54	14.46/14.40	9.46/9.50	0.41
11b	$C_{51}H_{34}Cl_2N_{16}O_{18}S_4$	1401	76.11	45.11/44.95	2.52/2.30	16.50/16.35	9.44/9.51	0.53
11c	$C_{51}H_{34}Cl_4N_{14}O_{16}S_4$	1388	77.19	44.75/44.20	2.50/2.32	14.32/14.15	9.37/9.40	0.52
11d	$C_{53}H_{40}Cl_2N_{14}O_{16}S_4$	1358	80.35	47.93/47.11	3.04/2.99	14.77/14.50	9.66/9.71	0.45
11f	$C_{51}H_{34}Cl_4N_{14}O_{14}S_4$	1378	79.63	45.82/45.35	2.56/2.16	14.67/14.45	9.59/9.64	0.48
11g	$C_{51}H_{32}Cl_6N_{14}O_{14}S_4$	1326	84.27	43.57/43.10	2.29/2.23	13.95/13.34	9.12/9.20	0.44
11h	$C_{51}H_{32}Cl_6N_{14}O_{14}S_4$	1354	85.71	43.57/43.17	2.29/2.20	13.95/13.35	9.12/9.25	0.45
11i	$C_{51}H_{36}Cl_2N_{14}O_{16}S_4$	1365	80.43	47.12/47.05	2.79/2.74	15.08/14.95	9.86/9.95	0.56

*Ethanol: Ethyl acetate (5:5 v/v), Silica gel-G F254 TLC plate.

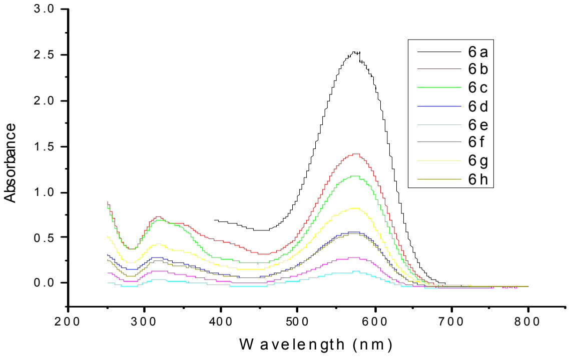


Fig. 2: Combined UV visible spectrum of monoazo bis MCT reactive azo dyes (**6a-h**).

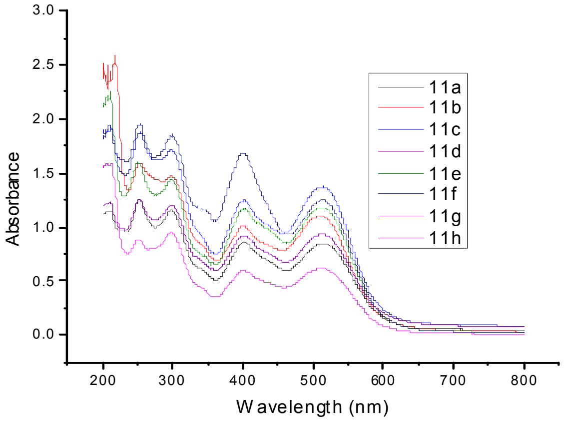


Fig. 3: Combined UV visible spectrum of `monoazo bis MCT reactive azo dyes (**11a-h**).

Spectral properties of compounds

The absorption maxima (λ_{max}) of the reactive dyes **6a-h** and **11a-h** were obtained in water ($1x10^{-7}$M) and are presented in Table 3 and 4, respectively. The λ_{max} values are directly related to the nature, electronic power and position of the substituents on the naphthyl ring of the coupler moiety as well as in the bridging anilines [15]. The compounds **6a** and **6h** exhibited two absorption maxima, one in the UV range due to π-π* transition of the C=C present in the aromatic moiety of dyes and others in the visible rang 557 to 570 nm common in all dyes. The absorption band that lies in the visible region is due to π-π* transition of azo linkage N=N of dyes was responsible for the reddish violet color **6a-h** compounds (Fig. 2). All dyes have same chromophoric functionalities, but the difference arises in the form of bis-anilines used as bridging groups. These bridging groups affect the λ_{max} of compounds vary but the effect is not too high as these are not directly attached to chromophoric groups of compounds and these group effects cannot be explained in regular way due to a diverse variety of groups in the bis anilines. Similarly, the dyes **11a-h** showed three absorption maxima in the mid UV, far UV and in the visible region of electromagnetic radiation spectrum (Fig. 3) due to different chromophoric systems in molecules. The values of log ε (molar extinction coefficient) are summarized in Table-3 and 4 for dyes 6a-h and **11a-h**. Both series of dyes have high values of molar extinction coefficient (log ε) which lie in the range 5.7-6.4, which presents the high absorption intensity of dyes.

The infrared spectra of the synthesized monoazo MCT reactive dyes based on H- acid showed bands due to O-H, N-H, Ar-H, C-H, C=O, C=C, C=N, NO_2 , SO_3H, N=N and C-Cl moieties stretching and bending vibrations at 3422-3526, 3048-3078, 2843-2965, 1735, 1622-1663, 1565-1590, 1539-1505, 1427-1481, 1120-1070, 770-723 and 670-690 cm^{-1}, respectively d [16,17]. Specifically speaking, using FT-IR spectrum of **6c** and **6f**, a broad band observed in the range 3200-3526 cm^{-1} which is due to H-bonding of OH and COOH groups present in the bridging groups. This broad band masked the peaks of N-H functionality. A peak observed in the range 1735-1750 cm^{-1} is due to the C=O functionality of compounds. The absorption bands at 1622-1663, 1565-1590, 1539-1505 and 770-723 cm^{-1} depicted the presence of C=C stretching and bending vibrations of aromatic moieties, respectively. C-Cl peak is observed in all compounds at 672-690 cm^{-1} which confirms the triazine ring in these compounds. Azo linkage is indicated by the peaks in the range 1540-1510 cm^{-1}. The dyes **6b** and **6h** have bridging aniline containing OH groups at *o*- and *p*-position to N-H group of diamines, provided a broad peak at 3422-3526 cm^{-1} due to OH and N-H stretching vibrations. Similarly, dye **6e** showed a peak at 3465 cm^{-1} due to N-H stretching vibrations. This molecule also exhibited a prominent peak at 1055 cm^{-1} due to C-O-C stretching vibrations. Dyes **6b** and **6d** possess NO_2 groups at meta position to NH group, so a peak at 1550-1560 cm^{-1} is present in their IR spectra. Dyes **6a** and **6g** have bridging anilines containing chloro groups at *o, p* and *m*-position to NH group, so C-Cl peak was observed at 710-720 cm^{-1} in addition to C-Cl absorption of the triazine ring system. Peak for C-Cl in triazine ring system is at lower wave number than Cl attached to benzene ring due to the fact that in the latter case bond is stronger than previous one. A band at 2843-2965 cm^{-1} is common in all these compounds due to a methylene group stretching vibrations present in all dyes.

The infrared spectra of the synthesized reactive dyes based on γ- acid, sulfanilic acid and cyanuric chloride showed absorption peaks owing to O-H, N-H, Ar-H, CH_2, C=O, C=C, C=N, NO_2, SO_3H, N=N and C-Cl stretching and bending vibrations at 3435-3467, 3032-3072, 2838-2963, 1755, 1625-1653, 1568-1589, 1512-1526, 1433-1465, 1125-1070, 750-787 and 680-689cm^{-1}, respectively. Particularly, using FT-IR spectrum of **11a**, a broad band in the range 3560-3350 cm^{-1} was due to H-bonding of OH, N-H and COOH groups present in the bridging groups. Due to broadness of this peak N-H functionality has been masked. A peak was present at 1755 cm^{-1} due to C=O functionality of COOH. The absorption bands at 1625-1653, 1568-1589, 1512-1526 and 750-787 cm^{-1} evidenced the presence of C=C stretching and bending vibrations of aromatic nuclei, respectively. A vibrational band at 680-689 cm^{-1} present in FT-IR spectra of all dyes confirmed the presence of the triazine ring. Azo linkage was inveterated by the peaks in the range 1540-1510 cm^{-1}.

Dyes **11b-h**, showed a broad peak at 3435-3467 cm^{-1} due to OH and N-H stretching vibrations. All compounds have sulfonic groups which have been confirmed by the appearance of absorption bands at 1070-1123 cm^{-1}. The dye **11d** exhibited prominent peak at 1055 cm^{-1} due to C-O-C stretching vibrations, as it contains methoxy group at *o*-position to N-H. Dye **11b** has NO_2 group so a peak at 1565 cm^{-1} was present in its IR spectrum. An absorption band at 2843-2965 cm^{-1} is common in all compounds and is due to methylene group stretching vibrations.

^{1}H-NMR and ^{13}C-NMR spectra of the synthesized reactive dyes were taken to correlate the structres of synthesized dyes with their spectra. The ^{1}H-NMR spectrum of representative dye **6f** showed down field signal at 12.74 ppm due to COOH groups present in the bridging diamines and in the aromatic region of the TMS scale in between δ7.15-8.10 ppm due to eighteen aromatic protons. Broad singlets were observed at 9.40-9.46, 8.61-8.75 and 8.30-8.38 ppm, due to O-H and NH moities attached at naphthalene ring and benzene ring, and these peaks are common in all dyes. Sharp singlet at range 1.785-2.05 ppm was observed due to bridging CH_2 group present in bis-anilines. All these dyes **6a-h** are the compounds of a series where the difference occurred in case of bridging groups while chromophores, coupling component and reactive systems are same. Here peak positions and intensities were varied for O-H and bridging methylene protons. In case of compounds **6a, 6b, 6c** and **6d** which contained NO_2 and Cl at *o, m-* and *p*-position to NH group of bis-anilines, methylene as well as N-H peaks shifted downfield but for dyes **6e** and **6h** which had OCH_3 and OH groups at *o* position to N-H moiety, their signal shifted upfield and extra peak for 3H in **10e** was seen at 4.07 ppm. ^{13}C-NMR spectra of dyes **6a-h** showed signals for different aliphatic carbons at 40-50 and for aromatic carbons in the range 109-160 ppm which confirmed the structures of these compounds.

In case of ^{1}H-NMR spectra of dyes **11a-h**, the representative compound **11c** showed signals for aliphatic and aromatic protons at 1.78, 6.79, 6.84, 7.34, 7.58, 7.68 and 7.729 ppm, while signals for N-H and O-H protons are present at 8.02, 8.11, 8.32 and 9.41ppm attached at aromatic nuclei. In ^{13}C-NMR spectra of **11c** signals in the aliphatic as well as aromatic regions of the spectrum at positions 39.01, 95.51, 101.49, 103.75, 116.20, 119.29, 123.83, 126.65, 130.40, 132.02, 133.90, 142.20, 143.33, 152.38, 154.92, 158.89, 170.47 ppm are the apparent evidence for the formation of this compound. Similarly, other dyes of this series have been confirmed from their respective ^{1}H-NMR and ^{13}C-NMR spectra.

Dyeing properties of compounds

All the dyes **6a-h** and **11a-h** were applied at 2.0 % depth on cotton fibers according to the usual procedure in the dye bath containing materials to achieve dominant and gorgeous shades of targeted compounds (Table S3, for supporting information).

Exhaustion and fixation study:

Exhaustion and fixation study was accomplished by the application of compounds at 2% dyeing on cotton fibers. Exhaustion and fixation values are presented in table 3 and 4.

Table-3: Exhaustion and fixation data of monoazo bis MCT reactive azo dyes **(6a-h).**

Dyes	Shade on Fiber	λ_{max} nm in H_2O	Log ε	% Exhaustion	% Fixation
6a	Reddish violet	564	6.704	62.17	70.23
6b	Reddish violet	567	6.443	72.33	87.53
6c	Reddish violet	560	6.373	76.67	92.88
6d	Reddish violet	557	6.043	63.45	81.23
6e	Reddish violet	570	5.410	63.15	76.43
6f	Reddish violet	568	5.758	77.53	93.15
6g	Reddish violet	560	6.219	65.52	78.37
6h	Reddish violet	568	6.042	74.38	83.47

Table-4: Exhaustion and fixation data of monoazo bis MCT reactive azo dyes **(11a-h).**

Dye	Shade on Fiber	λ_{max} nm in H_2O	Log ε	% Exhaustion	% Fixation
11a	Reddish yellow	502	6.36	75.38	91.93
11b	Reddish yellow	496	6.394	66.31	78.24
11c	Reddish yellow	496	6.229	69.61	83.68
11d	Reddish yellow	492	6.344	68.86	80.19
11f	Reddish yellow	498	6.439	63.12	74.18
11g	Reddish yellow	492	6.093	62.44	77.75
11h	Reddish yellow	495	6.375	62.78	76.69
11i	Reddish yellow	499	6.397	74.16	84.29

Exhaustion deals with the degree of dye migration from dye bath to fiber and is usually articulated as percentage of the amount of dye initially placed in the dye bath. Fixation of dye is concerned with the amount of dye fixed with the textile fiber. For financial and ecological reasons a high degree of exhaustion and fixation is essential. These are two important factors which put in a lot in selection of compounds for dyeing fiber. Concentration of dye in two phases is the driving force for exhaustion and fixation of dyes on fiber. In order to acquire high degree of exhaustion, assisting chemicals like sodium chloride, Na_2SO_4 and EDTA are added in the dye bath to perk up exhaustion. Triazine ring develops a covalent bond with cotton fibers and enhances the fixation of compounds on fibers.

The percentage exhaustion and percentage fixation of 2% dyeing on cotton range from 62-77% and 70-93 % for **6a-h** series; 62-75 and 74-91% for **11a-h** series, are represented in Table-3 and 4. Good exhaustion and fixation values have been observed for all the dyes owing to the fast diffusion of the dye molecule within the fabric under dyeing condition and the physical as well as chemical interactions of polar groups present in disazo, coupler and bridging components. A reactive component establishes covalent linkages with fiber. Dyes **6c**, **6f** and **11c** expressed high exhaustion and fixation values in because of carboxylic groups present in the bridging anilines.

Fastness properties

Fastness study of compounds was made after application of 2% dye with respect to cotton fibers as represented in Table-5 and 6. Light fastness, wash fastness and rubbing fastness were examined which provided the real image regarding the quality of dye.

Table-5: Fastness properties data of monoazo bis MCT reactive azo dyes (**6a-h**).

Dye	Light Fastness	Wash Fastness	Rubbing Fastness	
			Dry	Wet
6a	5-6	4-5	4	3
6b	6-7	4-5	4	3
6c	6-7	4	5	4
6d	5-6	4-5	4-5	3-4
6e	5-6	4-5	4-5	3-4
6f	6-7	3-4	4-5	3-4
6g	5-6	4	4	3-4
6h	5-6	4	4-5	3-4

Table-6: Fastness properties data of monoazo bis MCT reactive azo dyes **(11a-h).**

Dye	Light Fastness	Wash Fastness	Rubbing Fastness	
			Dry	Wet
11a	6-7	4-5	4-5	3
11b	5-6	4-5	3-4	3
11c	5-6	4	3-4	3
11d	5-6	4-5	4	3-4
11f	5-6	4-5	4	3-4
11g	5	3-4	3-4	3-4
11h	5	3-4	3-4	3-4
11i	5-6	3-4	4	3-4

Light fastness is related to resistance offered by dye to fading on exposure to light. Different compounds exhibited different degrees of confrontation to fading by light. Light fastness of all compounds was high in the range 6-7. These dyes have little susceptibility to light damage, which is simply due to their strong colors indications that they absorb the wavelengths and don't reflect back. Light is absorbed by pigmented compounds may serve to degrade them.

Wash fastness is the resistance offered by dyed fibers to retain color when washed by soaps and detergents. In the test, change in color of the textile and also staining of color on the adjacent fabric are assessed. Wash fastness of compounds falls in the range 5-6.

Color fastness to rubbing is a main test which is always required for every colored fabric either it is printed or dyed [18]. Rubbing fastness was designed to determine the degree of color which may transfer from the surface of a colored fabric to a specified test cloth for rubbing. Rubbing fastness of all compounds was very high 4-5. Rubbing fastness is the indication of other improved properties like wash fastness, substantively and durability in use. It is obvious from rubbing fastness value that all these compounds have high washing fastness and fixation on the cotton fibers.

Conclusions

Two series of new monoazo bis reactive dyes (**6a-h** and 11a-h) have been synthesized in high yields from 4-NAP, H-acid, sulfanilic acid and γ-acid, respectively and examined for different properties. Reactive component was cyanuric chloride, which exhibited differential reactivity under different temperature and pH conditions to during preparation of dyes. Application of dyes on cotton fibers showed high light fastness, rubbing fastness and wash fastness values 6-7, 4-5 and 3-4, respectively. Moderate to high level of exhausion and fixation values of these compounds was observed on account of their high attraction and substantivity with cotton fibers. Furthermore, these compounds showed an incredible degree of levelness after washing, which demonstrated the good diffusion and excellent affinity to the fabric due to the accumulation of polar groups.

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