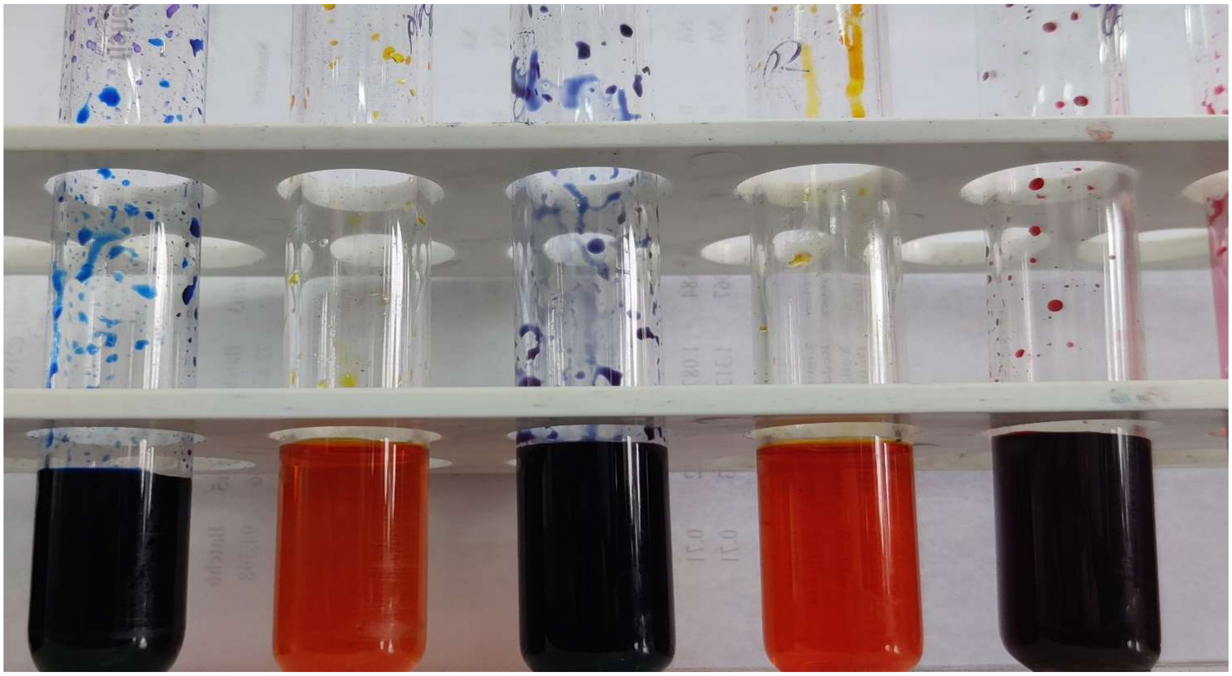
Experimental



2.0 Experimental

Reactive dyes are easy to use, flexible for dyeing and printing applications and they are economical. Reactive dyes have also only recently begun to penetrate the consumer market in comparison to direct dyes and vat dyes, which both offer low cost and quick application but poor wet intensity and great stability. Because of promising studies on the scientific applications of some of the phenyl urea reactive dyes, the synthesis and study of dyeing propriety phenyl urea derivatives related dyes were thought to be relevant. These are reactive dyes that contain monochlorotriazinyl and vinyl sulphone groups as reactive radicals and are useful for dyeing cellulosic fibers.

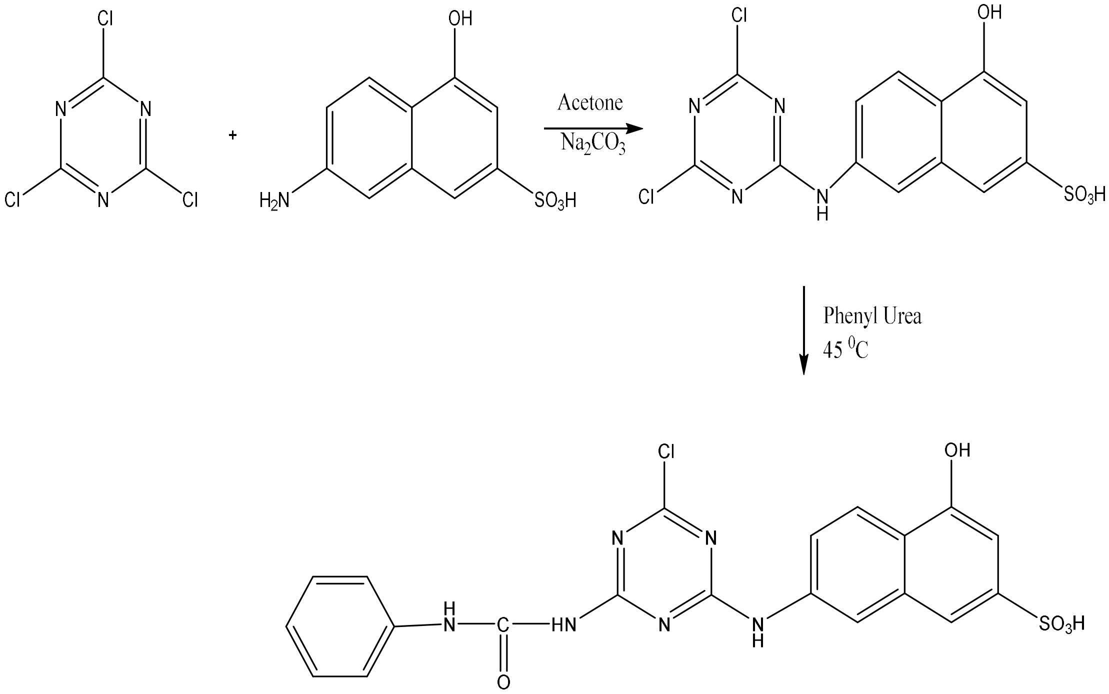
Under proper experimental conditions, the reactive dyes are manufactured and purified. To determine the purity of the dyes, thin layer chromatography technique was used. Each dye is assessed using elemental analysis and some of the chosen dyes was assessed using IR and ^{1}HNMR spectrum characteristics. By measuring the visible spectrum and noting the position of λ_{max} (nm), the colour of each dye in the specified solution is noted.

Novel six series of reactive dyes were synthesized. Phenyl urea derivatives were used for preparation of series I to IV, 2-Amino-5-naphthol-7-sulfonic acid(J-acid), 8-Amino-1-naphthol-3,6-sulfonic acid(H-acid), 2-Amino-8-naphthol-6-sulfonic acid (Gamma acid) and 1- hydroxy-6-(methylamino)-3-naphthalenesulphonic acid (methyl J-acid) were a used as coupling component. For the synthesis of series-V, 4-amino-4'-hydroxy benzylidene acetophenone (4-amino-4'-hydroxy chalcone) was used and K-acid, H-acid, J-acid, N-methyal J-acid, N-phenyl J-acid, Gamma acid and Peri acid were employed as coupling materials. In series VI mono azo reactive dyes of hot brand were prepared with diazo of diazotized o-anisidine was coupled with several 4-amino-4'-hydroxy benzylidene acetophenone cyanurated coupling component including H-acid, K-acid, Gamma acid, N-phenyl J-acid, J-Acid and Peri acid. A experimental work was carried out in distilled water. All the reagents and chemicals used as analytical grade and the coupling component was provided by Astik dyestuff, Ankleshwar. All dyeing auxiliaries and fabrics were provided by DyStar India Pvt Ltd., Ankleshwar. Application of exhaust, cold pad batch and print as well as all fastness properties evaluated in DyStar India Pvt Ltd.. Phenyl urea derivatives purchased from Merck Specialities Private Limited.

2.1 Preparation of bi-functional reactive dyes (Series-I)

2.1.1 Synthesis of Cyanurated coupling component:

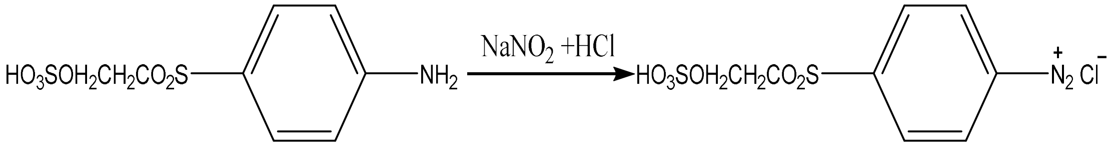
A solution of 0.01 mole cyanuric chloride was stimulated in acetone at temperatures below 5 ^{0}C for two hours. The pH of the cyanuric chloride solution was kept at 4.0 by using 20% (w/v) sodium carbonate, after that reaction mass temperature was kept below 5 ^{0}C for two hours. Cyanurated J-acid was formed in a clear solution. For second condensation the mixture of cyanurated J-acid was cooled, stirred and heated to 45 ^{0}C,. 0.01 Mol phenyl urea was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ^{0}C followed by next coupling reactions[1].



Cyanurated coupling component

2.1.2 Diazotization of 4-(β-sulfatoethylsulfonyl)aniline:

4-(β-Sulfatoethylsulfonyl)aniline diazotized with Xion Wei and Zhang Shufen process [2], 0.01 Mol of 4-(β-sulfatoethylsulfonyl)aniline was dissolved in a solution of sodium carbonate(10% w/v) and maintained pH 6-7 at 0-5 ^{0}C. In the solution of 4-(β-sulfatoethylsulfonyl)aniline, 0.0105 mol sodium nitrite solution was added. The reaction mass being introduced to chilled 0.015 mol conc. hydrochloric acid, which was kept at a constant temperature of 0-5 ^{0}C while stirring with ice cubes. The reaction mass was agitated for an hour and tested with starch iodide paper to detect the presence of nitrous acid. By adding sulfamic acid the excess nitrous acid was removed. The salt of diazo compound was used for next coupling reaction[3-5].

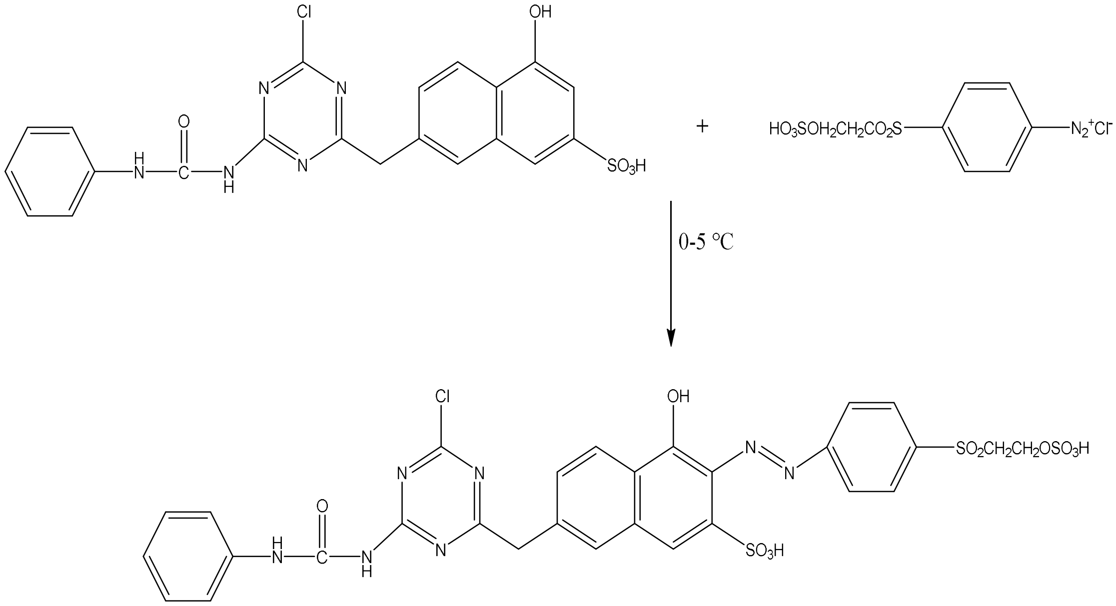


Diazotization of 4-(β-sulfatoethylsulfonyl)aniline

2.1.3 Coupling of 4-(β-sulfatoethylsulfonyl)aniline and 7-[(4-chloro-6-(3-phenylureido)-1,3,5-triazin-2-yl)amino]-4-hydroxynaphthalene-2-sulfonic acid:

A freshly synthesised 4-(β-sulfatoethylsulfonyl)aniline diazonium salt was transferred to the condensing product at 0–5 ^{0}C. by adding 10% w/v sodium carbonate solution. After that the solution was continue stirring for an hour at temperatures ranging from 0-5 ^{0}C and the pH 6-7 of the mass was kept constant. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z1) was filtered, washed with ethanol and dried in an electric oven at 40 ^{o}C. MP > 250 ^{0}C(d) [6-7].

Further reactive dyes Z2 to Z10 were produced using the above process using changing intermediates such as ortho tolyl urea, meta tolyl urea, para tolyl urea, para nitro phenyl urea, ortho nitro phenyl urea, ortho chloro phenyl urea, meta chloro phenyl urea, para chloro phenyl urea and para methoxy phenyl urea. All parameters were used same as per preparation of reactive dyes Z1.



Reactive dye Z1

2.1.4(a)Preparation of coupling component -A:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol ortho tolyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.5(b)Preparation of coupling component-B:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol meta tolyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.6(c)Preparation of coupling component-C:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol para tolyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.7(d)Preparation of coupling component-D:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol para nitro phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.8(e) Preparation of coupling component-E:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol ortho nitro phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.9(f) Preparation of coupling component-F:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol ortho chloro phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.10(g)Preparation of coupling component-G:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ºC. 0.01 mol meta chloro phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.11(h)Preparation of coupling component-H:

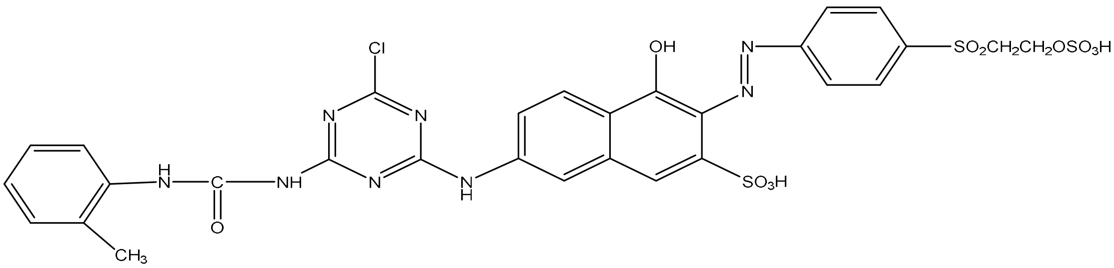
The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ^{0}C. 0.01 mol para chloro phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.12(i)Preparation of coupling component-I:

The solution of cyanurated J-acid (section 2.1.1) was heated to 45 ^{0}C. 0.01 mol para methoxy phenyl urea was introduced to this mixture slowly. The pH of this solution was kept neutral during reaction by adding sodium carbonate solution and after that the coloured reaction mixture was agitated for minimum three hours at 45 ^{0}C. For next coupling reactions, this reaction mass was utilized.

2.1.13 Preparation of Reactive Dye Z2:

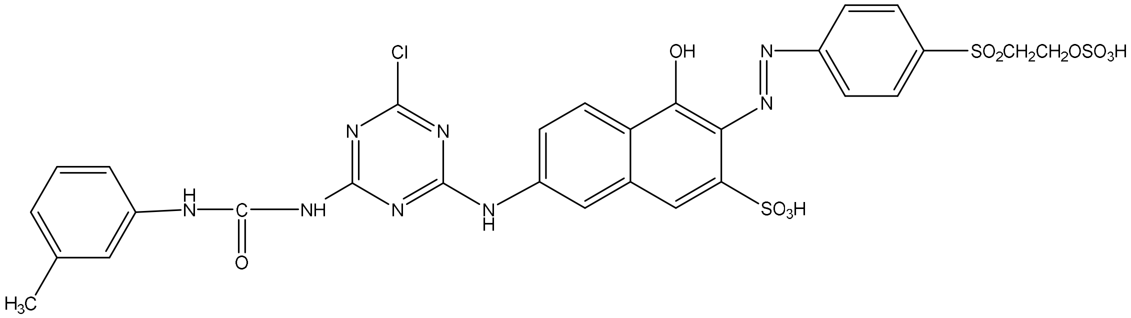
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.4A) with temperature 0-5 ^{0}C. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ^{0}C. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z2) was filtered, washed with ethanol and dried in an electric oven at 40 ^{0}C. MP > 250 ^{0}C(d).



Reactive dye Z2

2.1.14 Preparation of Reactive Dye Z3:

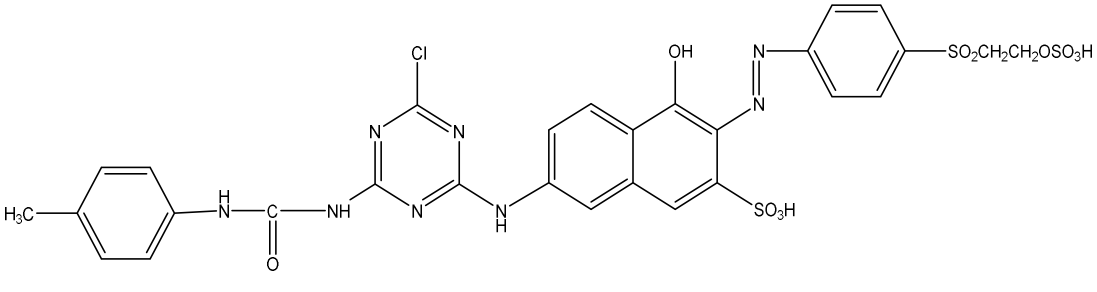
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.5B) with temperature 0-5 ^{o}C. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ^{o}C. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z3) was filtered, washed with ethanol and dried in an electric oven at 40 ^{o}C. MP > 250 ^{0}C(d).



Reactive dye Z3

2.1.15 Preparation of Reactive Dye Z4:

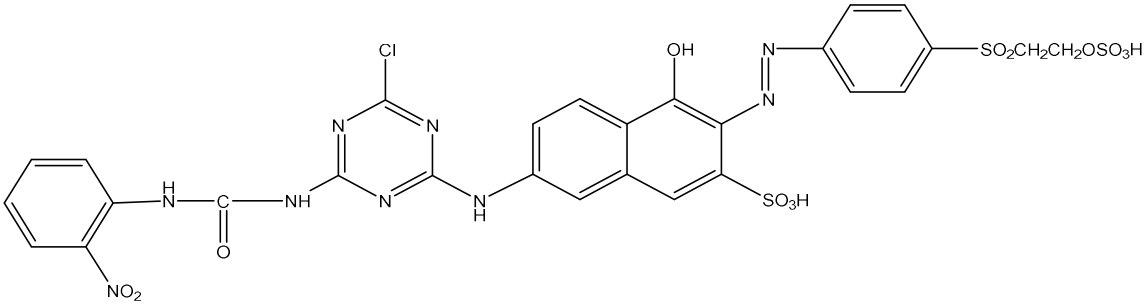
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.6C) with temperature 0-5 ^{o}C. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ^{o}C. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z4) was filtered, washed with ethanol and dried in an electric oven at 40 ^{o}C. MP > 250 ^{0}C(d).



Reactive dye Z4

2.1.16 Preparation of Reactive Dye Z5:

A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.7D) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z5) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).



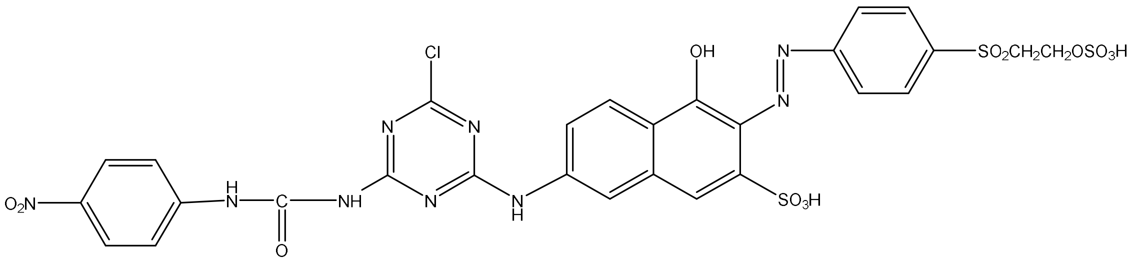
Reactive dye Z5

2.1.17 Preparation of Reactive Dye Z6:

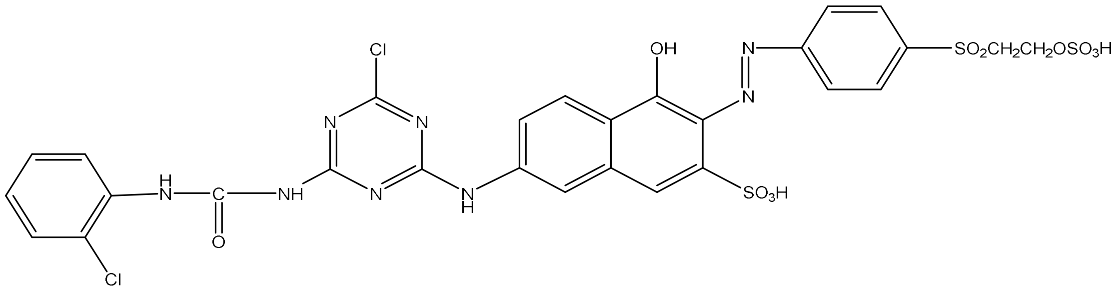
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.8F) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z6) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).

2.1.18 Preparation of Reactive Dye Z7:

A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.9F) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z7) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).



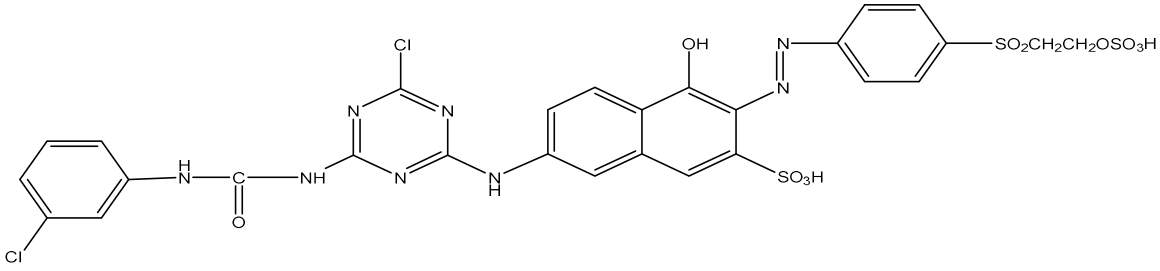
Reactive dye Z6



Reactive dye Z7

2.1.19 Preparation of Reactive Dye Z8:

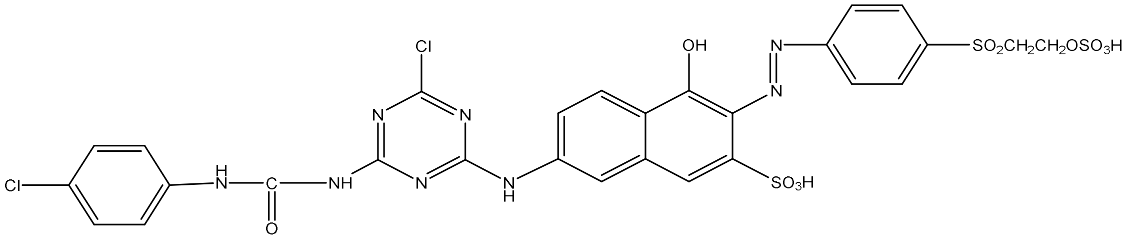
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.10G) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z8) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).



Reactive dye Z8

2.1.20 Preparation of Reactive Dye Z9:

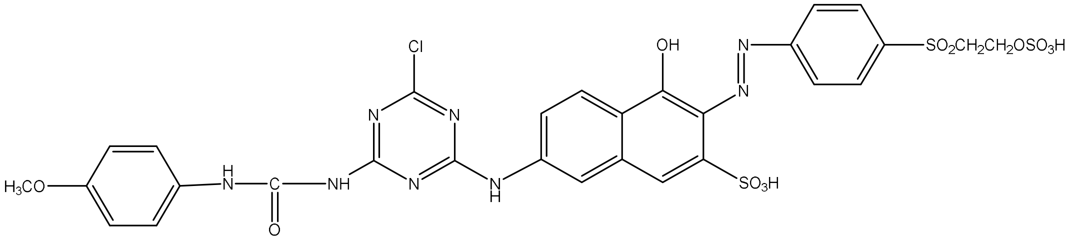
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.11H) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z9) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).



Reactive dyes Z9

2.1.21 Preparation of Reactive Dye Z10:

A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline was introduced slowly to the condensation product (section 2.1.11H) with temperature 0-5 ºC. The pH of mass was maintained by adding sodium carbonate (10%, w/v) and continued stirring for one hour with temperature 0-5 ºC. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z10) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).



Reactive dye Z10

The elemental analysis/TLC data of synthesized reactive dyes (Z1 to Z10) are recorded in Table:2.

Dye No	Molecular Formula	Mol. Wt. (g/mole)	Yield %	% of nitrogen		R_f value
				found	required	
Z1	$C_{28}H_{23}ClN_8O_{11}S_3$	779.17	87	14.29	14.38	0.45
Z2	$C_{28}H_{22}ClN_9O_{13}S_3$	824.16	84	15.22	15.30	0.32
Z3	$C_{28}H_{22}ClN_9O_{13}S_3$	824.16	84	15.23	15.30	0.36
Z4	$C_{28}H_{22}ClN_9O_{13}S_3$	824.16	87	15.22	15.30	0.38
Z5	$C_{28}H_{23}Cl_2N_9O_{13}S_3$	860.64	85	14.59	14.65	0.41
Z6	$C_{28}H_{23}Cl_2N_9O_{13}S_3$	860.64	75	14.58	14.65	0.39
Z7	$C_{28}H_{22}Cl_2N_8O_{11}S_3$	813.61	77	13.13	13.18	0.42
Z8	$C_{28}H_{22}Cl_2N_8O_{11}S_3$	813.61	85	13.14	13.18	0.35
Z9	$C_{28}H_{22}Cl_2N_8O_{11}S_3$	813.61	88	13.13	13.77	0.40
Z10	$C_{29}H_{25}ClN_8O_{12}S_3$	809.19	84	13.19	13.85	0.38

Table:2 Elemental analysis/TLC data of bi-functional reactive dyes Z1-Z10

2.2 Preparation of bi-functional reactive dyes (Series-II)

Bi-functional reactive dyes for series-II was prepared with cyanurated 8-amino-1-naphthol-3,6-disulfonic acid(H-acid) and phenyl urea derivatives then coupled with 4-(β-sulfatoethylsulfonyl)aniline gives dyes Z11-Z20.

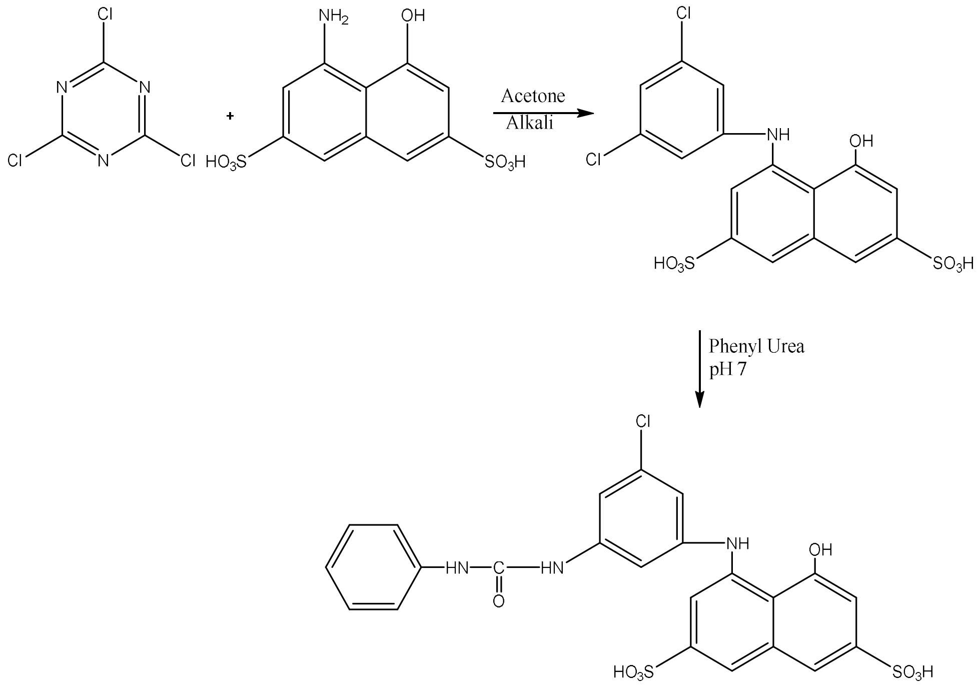
2.2.1 Synthesis of Cyanurated coupling component:

A solution of 0.01 mole cyanuric chloride was stimulated in acetone at temperatures below 5 °C for two hours. The pH of the cyanuric chloride solution was kept at 4.0 by using 20% (w/v) sodium carbonate, after that reaction mass temperature was kept below 5 °C for two hours. Cyanurated 8-amino-1-naphthol-3,6-disulfonic acid (H-acid) was formed in a clear solution. For second condensation the mixture of cyanurated 8-amino-1-naphthol-3,6-disulfonic acid (H-acid) was cooled, stirred and heated to 45 °C,. 0.01 Mol phenyl urea was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ^{o}C followed by next coupling reactions.

Diazotization of 4-(β-sulfatoethylsulfonyl)aniline was performed as described in the first series (section 2.1.2).

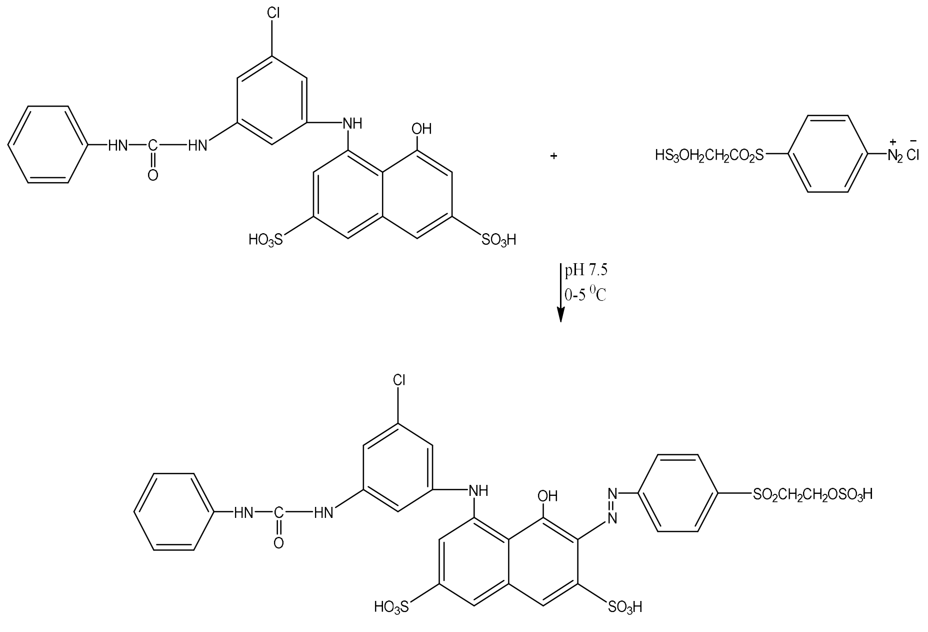
2.2.2 Coupling of 4-(β-sulfatoethylsulfonyl)aniline and 4-[(4-chloro-6-(3-phenylureido)-1,3,5-triazin-2-yl)amino]-5-hydroxynaphthalene-2,7-disulfonic acid:

A freshly synthesised 4-(β- sulfatoethylsulfonyl)aniline diazonium salt was transferred to the condensing product at 0–5 ^{0}C. by adding 10% w/v sodium carbonate solution. After that the solution was continue stirring for an hour at temperatures ranging from 0-5 ^{0}C and the pH 6-7 of the mass was kept constant. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z11) was filtered, washed with ethanol and dried in an electric oven at 40 ^{o}C. MP > 250 ^{0}C(d).



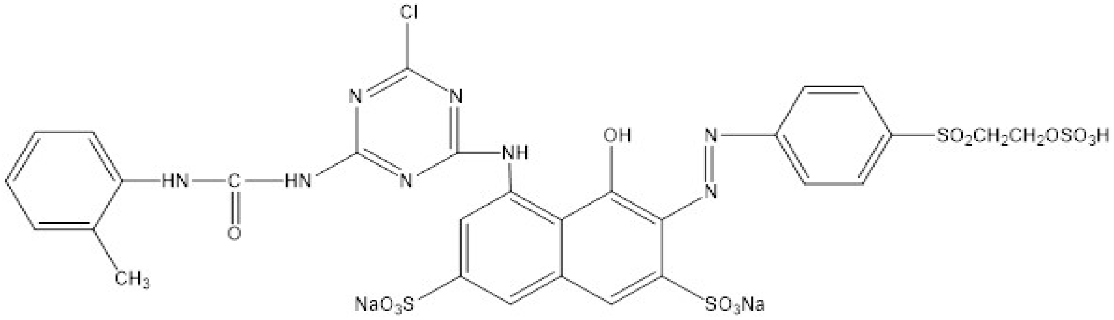
Cyanurated coupling component

Reactive dyes Z12 to Z20 were produced using the steps described in series-I by only changing the intermediates phenyl urea derivative such as ortho tolyl urea, meta tolyl urea, para tolyl urea, para nitro phenyl urea, ortho nitro phenyl urea, ortho chloro phenyl urea, meta chloro phenyl urea, para chloro phenyl urea and para methoxy phenyl urea.

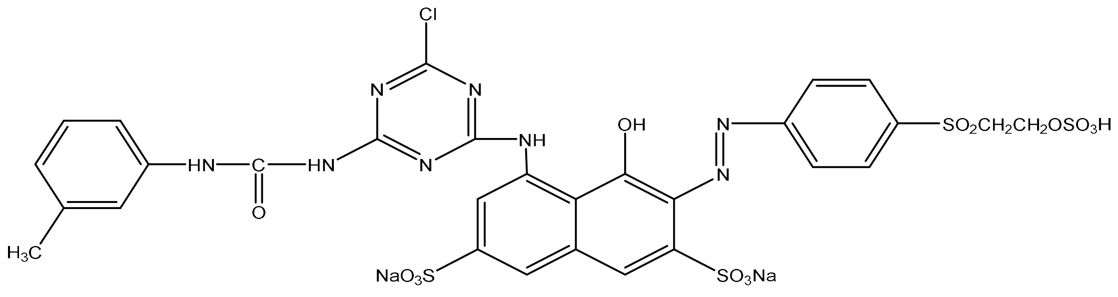


Reactive dye Z11

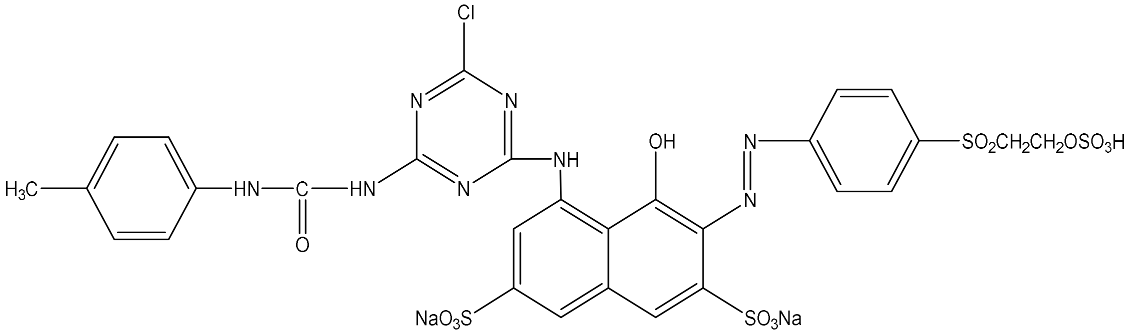
The Final structures of synthesized reactive dyes (Z12 to Z20) are as below:



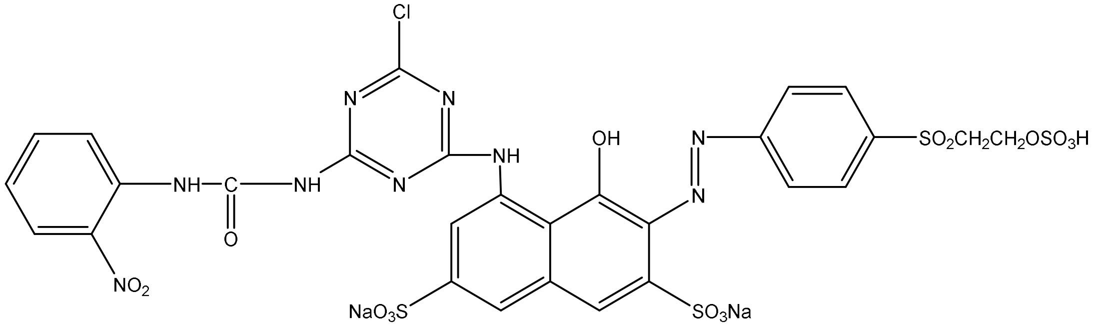
Reactive dye Z12



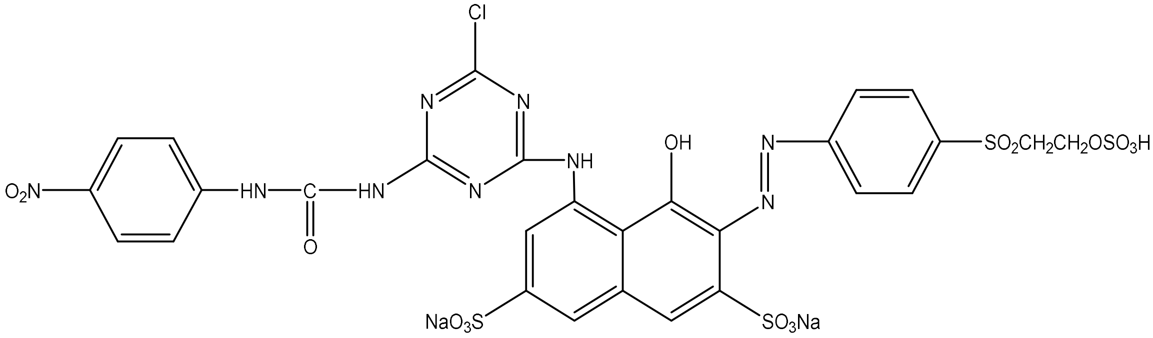
Reactive dye Z13



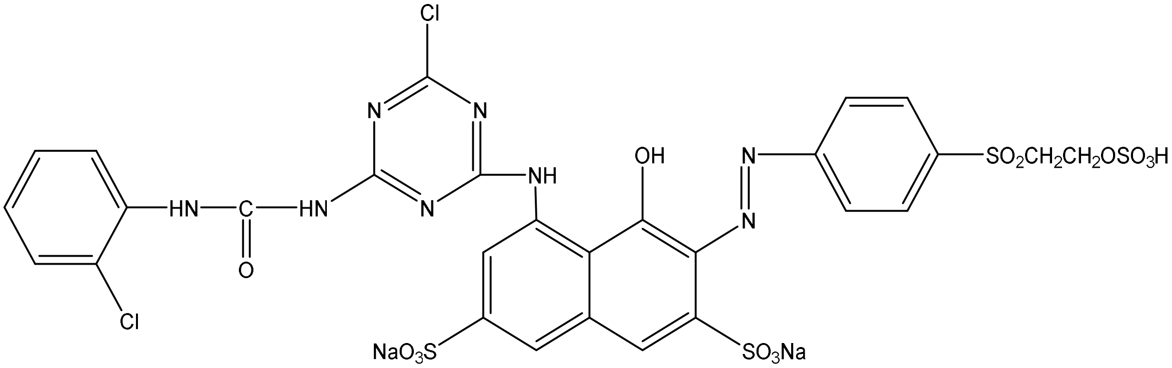
Reactive dye Z14



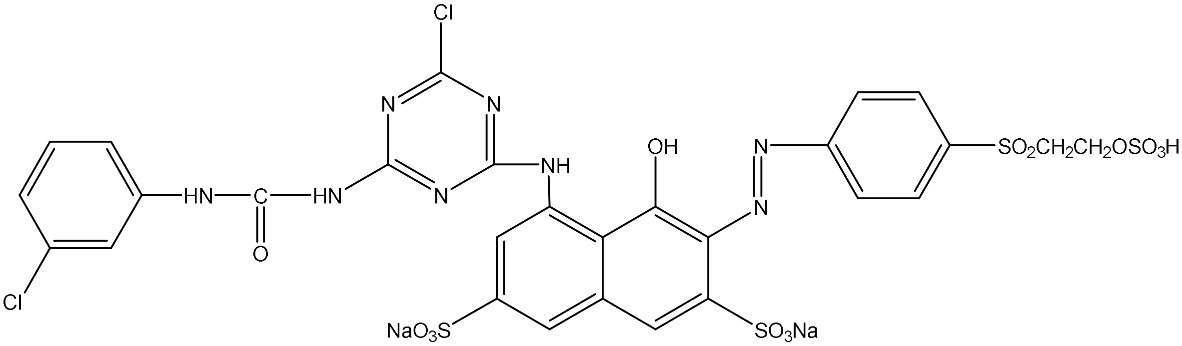
Reactive dye Z15



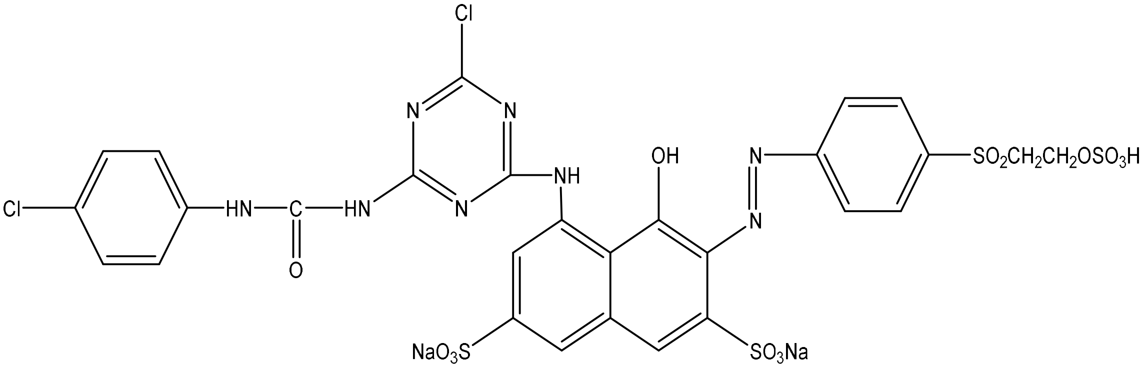
Reactive dye Z16



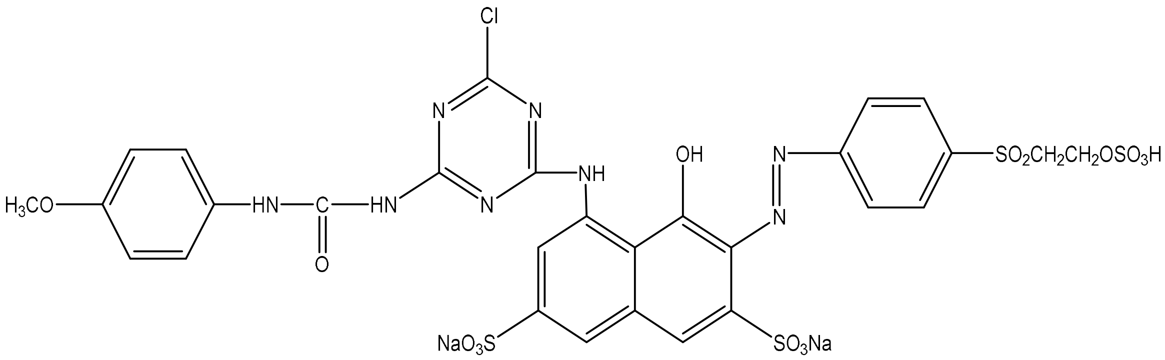
Reactive dye Z17



Reactive dye Z18



Reactive dye Z19



Reactive dye Z20

The elemental analysis/TLC data of synthesized reactive dyes (Z1 to Z10) are recorded in Table:3.

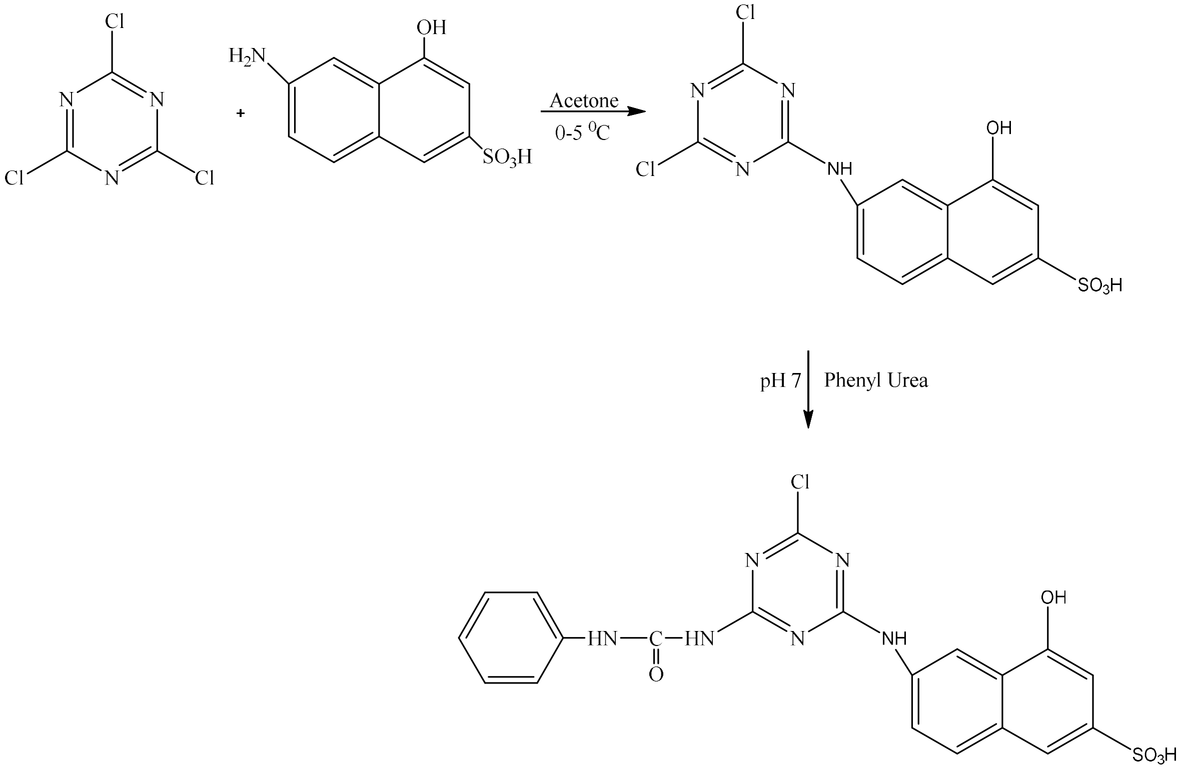
Dye No	Molecular Formula	Mol. Wt. (g/mole)	Yield %	% of nitrogen		Rf value
				found	required	
Z11	$C_{28}H_{23}ClN_8Na_2O_{11}S_3$	779.17	78	14.31	14.38	0.43
Z12	$C_{29}H_{23}ClN_8Na_2O_{14}S_4$	917.21	80	12.01	12.22	0.38
Z13	$C_{29}H_{23}ClN_8Na_2O_{14}S_4$	917.21	89	15.18	15.22	0.32
Z14	$C_{29}H_{23}ClN_8Na_2O_{14}S_4$	917.21	84	12.16	12.22	0.42
Z15	$C_{28}H_{20}ClN_9Na_2O_{16}S_4$	948.18	87	13.24	13.30	0.41
Z16	$C_{28}H_{20}ClN_9Na_2O_{16}S_4$	948.18	72	13.23	13.30	0.39
Z17	$C_{28}H_{20}Cl_2N_8Na_2O_{14}S_4$	937.63	76	11.86	11.95	0.32
Z18	$C_{28}H_{20}Cl_2N_8Na_2O_{14}S_4$	937.63	81	11.85	11.95	0.36
Z19	$C_{28}H_{20}Cl_2N_8Na_2O_{14}S_4$	937.63	83	11.90	11.95	0.45
Z20	$C_{29}H_{23}ClN_8Na_2O_{15}S_4$	933.21	82	11.98	12.01	0.37

Table:3 Elemental analysis/TLC data of bi-functional reactive dyes Z11-Z20

2.3 Preparation bi-functional reactive dyes (Series-III)

Bi-functional reactive dyes for series-II was prepared with cyanurated 2-amino-8-naphthol-6-sulfonic acid (gamma acid)and phenyl urea derivatives then coupled with 4-(β-sulfatoethylsulfonyl)aniline gives dyes Z21-Z30.

2.3.1 Synthesis of Cyanurated coupling component:



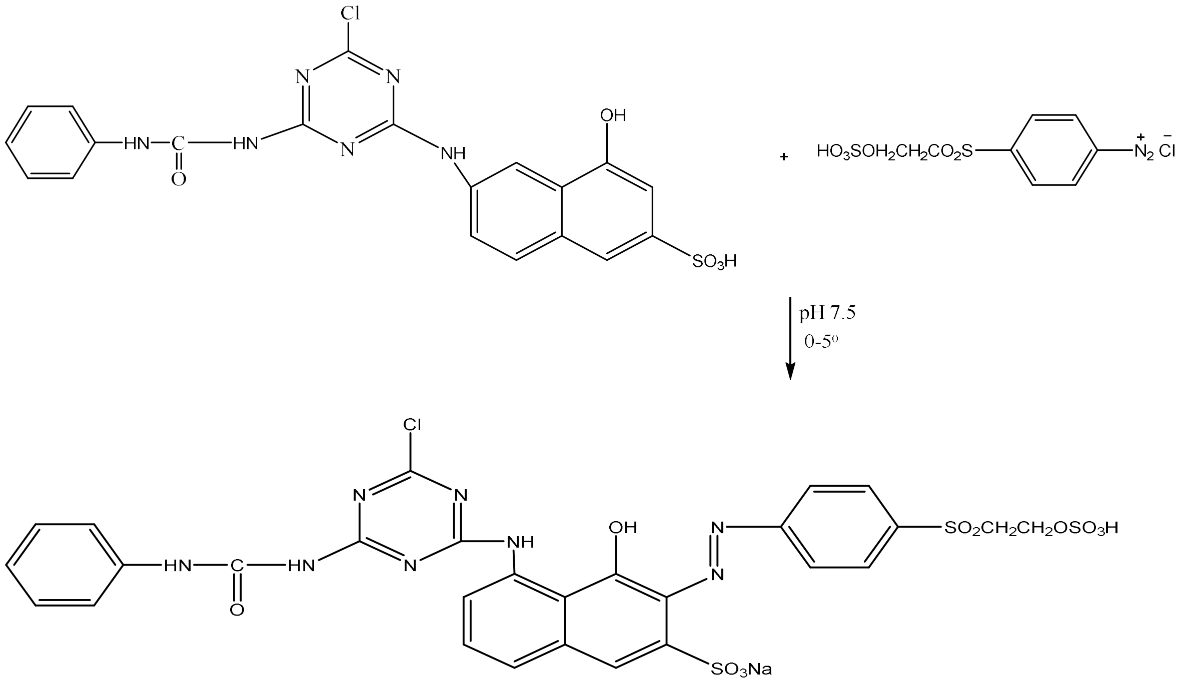
Cyanurated coupling component

A solution of 0.01 mole cyanuric chloride was stimulated in acetone at temperatures below 5 ⁰C for two hours. The pH of the cyanuric chloride solution was kept at 4.0 by using 20% (w/v) sodium carbonate, after that reaction mass temperature was kept below 5 ⁰C for two hours. Cyanurated 2-amino-8-naphthol-6-sulfonic acid (gamma acid) was formed in a clear solution. For second condensation the mixture of cyanurated 2-amino-8-naphthol-6-sulfonic acid (gamma acid) was cooled, stirred and heated to 45 ⁰C. 0.01 Mol phenyl urea was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ⁰C followed by next coupling reactions.

Diazotization of 4-(β-sulfatoethylsulfonyl)aniline was performed as described in the first series (section 2.1.2).

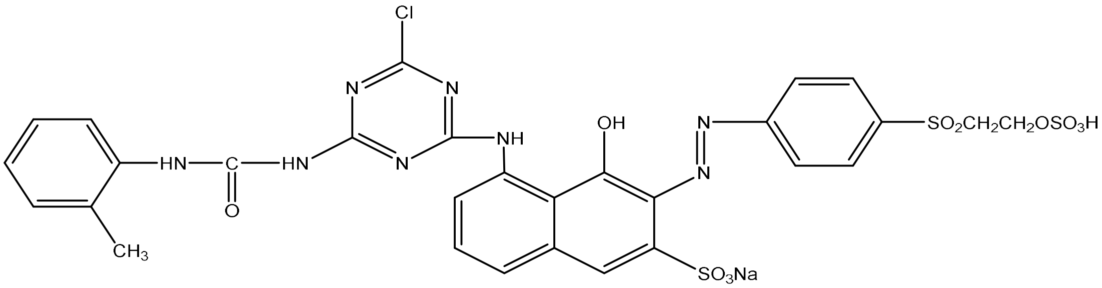
2.3.2 Coupling of 4-(β-sulfatoethylsulfonyl)aniline and 5-[(4-chloro-6-(3-phenylureido)-1,3,5-triazin-2-yl)amino]-4-hydroxynaphthalene-2-sulfonic acid:

A freshly synthesised 4-(β- sulfatoethylsulfonyl)aniline diazonium salt was transferred to the condensing product at 0–5 ^{0}C by adding 10% w/v sodium carbonate solution. After that the solution was continue stirring for an hour at temperatures ranging from 0-5 ^{0}C and the pH 6-7 of the mass was kept constant. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z21) was filtered, washed with ethanol and dried in an electric oven at 40 ^{0}C. MP > 250 ^{0}C(d).

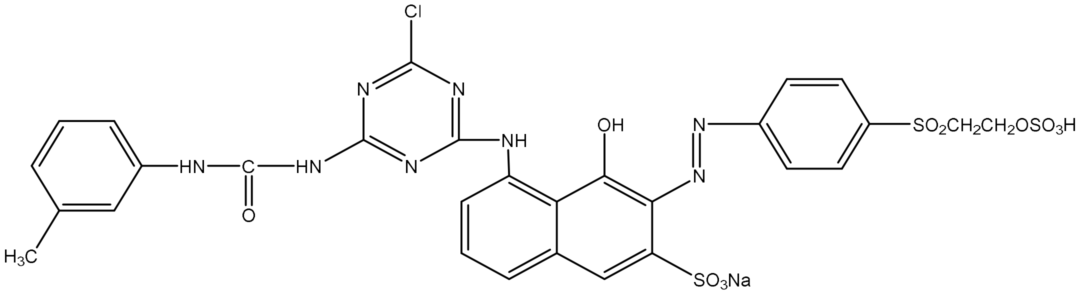


Reactive dye Z21

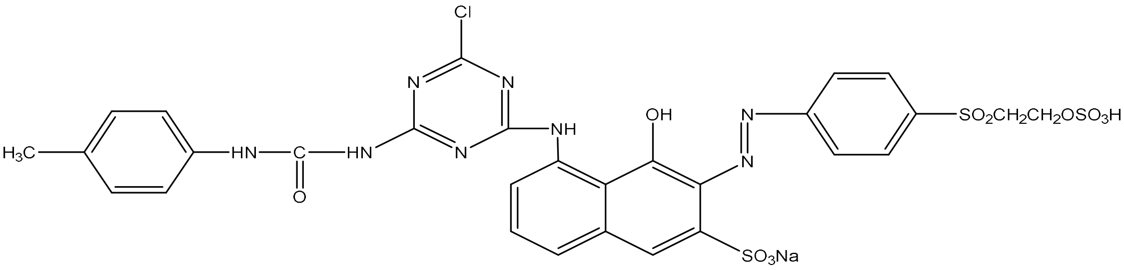
From the above procedure other reactive dyes Z22 to Z30 synthesized using changing intermediates such as ortho tolyl urea, meta tolyl urea, para tolyl urea, para nitro phenyl urea, ortho nitro phenyl urea, ortho chloro phenyl urea, meta chloro phenyl urea, para chloro phenyl urea and para methoxy phenyl urea. Final structures of synthesized reactive dyes (Z22 to Z30) are as below:



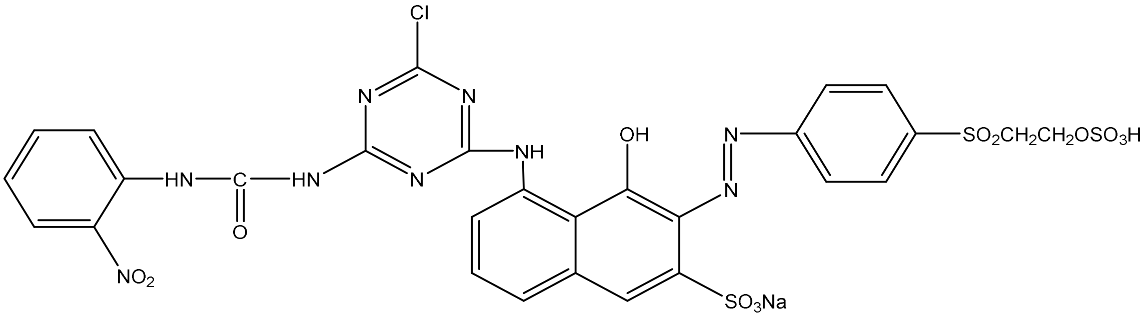
Reactive dye Z22



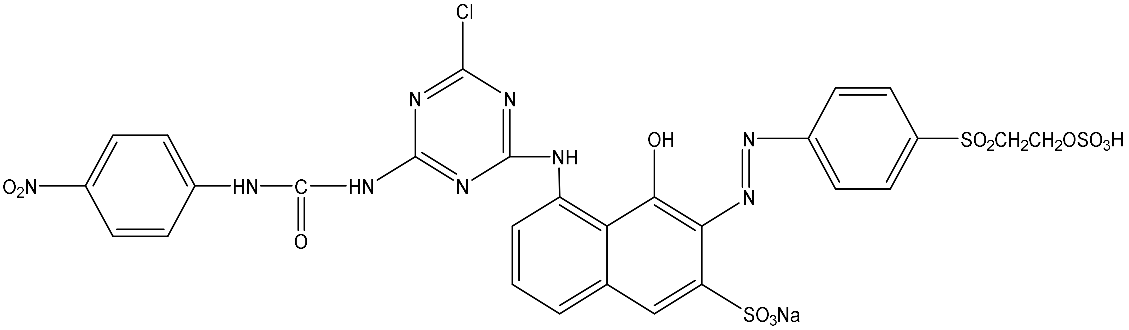
Reactive dye Z23



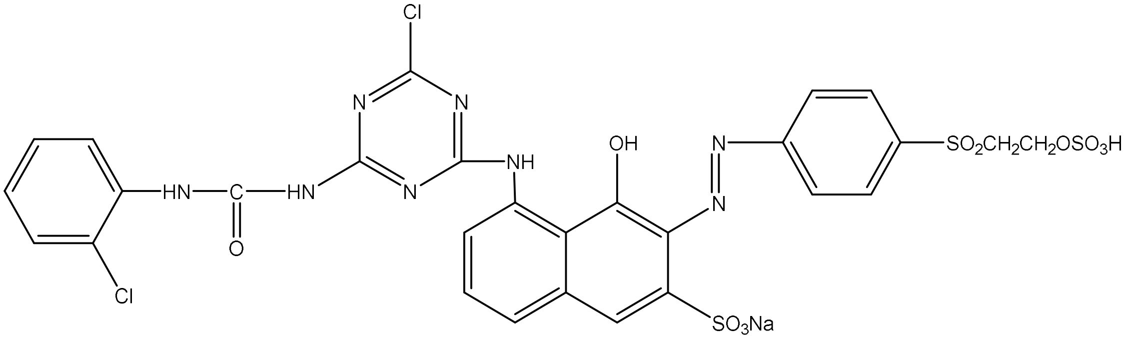
Reactive dye Z24



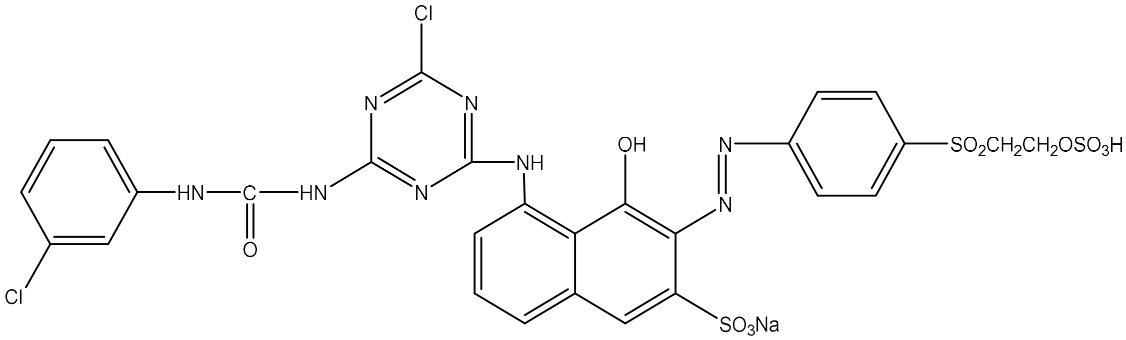
Reactive dye Z25



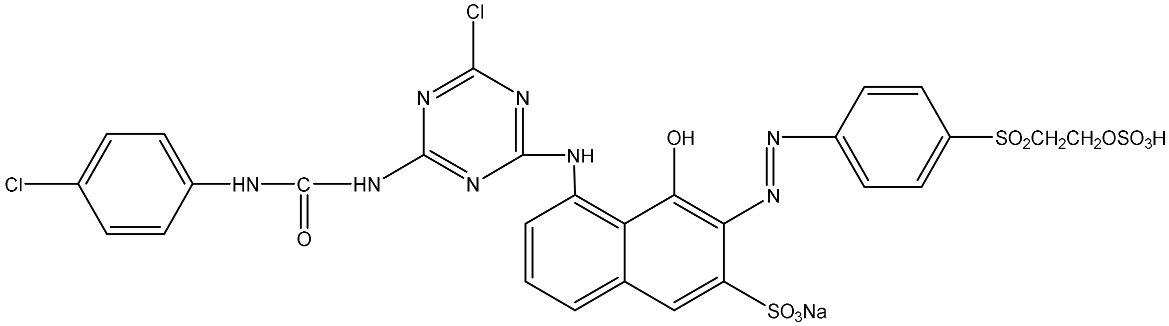
Reactive dye Z26



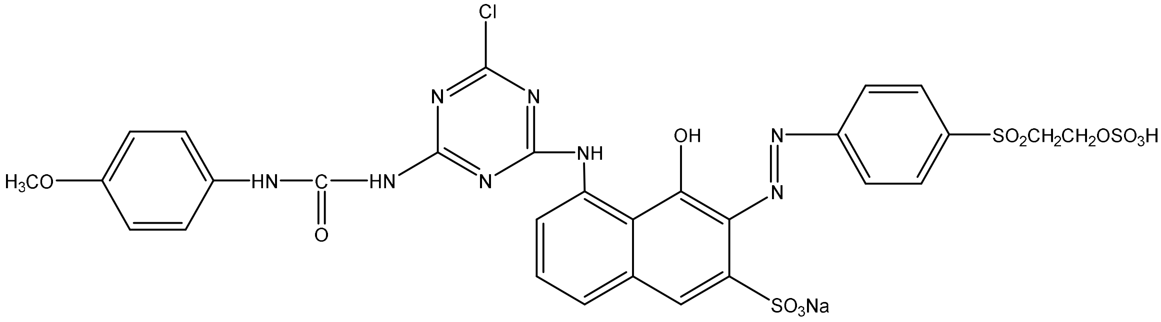
Reactive dye Z27



Reactive dye Z28



Reactive dye Z29



Reactive dye Z30

The elemental analysis/TLC data of synthesized reactive dyes (Z21 to Z30) are recorded in in Table:4.

Dye No	Molecular Formula	Mol. Wt. (g/mole)	Yield %	% of nitrogen		R_f value
				found	required	
Z21	$C_{28}H_{22}ClN_8NaO_{11}S_3$	801.15	81	13.85	13.99	0.45
Z22	$C_{29}H_{24}ClN_8NaO_{11}S_3$	815.18	82	13.68	13.75	0.36
Z23	$C_{29}H_{24}ClN_8NaO_{11}S_3$	815.18	87	13.71	13.75	0.38
Z24	$C_{29}H_{23}ClN_8Na_2O_{14}S_4$	815.18	89	13.60	13.75	0.41
Z25	$C_{28}H_{21}ClN_9NaO_{13}S_3$	846.15	83	14.88	14.90	0.32
Z26	$C_{28}H_{21}ClN_9NaO_{13}S_3$	846.15	72	14.78	14.90	0.36
Z27	$C_{28}H_{21}Cl_2N_8NaO_{11}S_3$	835.59	75	13.37	13.41	0.42
Z28	$C_{28}H_{21}Cl_2N_8NaO_{11}S_3$	835.59	86	13.31	13.41	0.40
Z29	$C_{28}H_{21}Cl_2N_8NaO_{11}S_3$	835.59	81	13.35	13.41	0.39
Z30	$C_{29}H_{24}ClN_8NaO_{12}S_3$	831.17	82	13.41	13.48	0.37

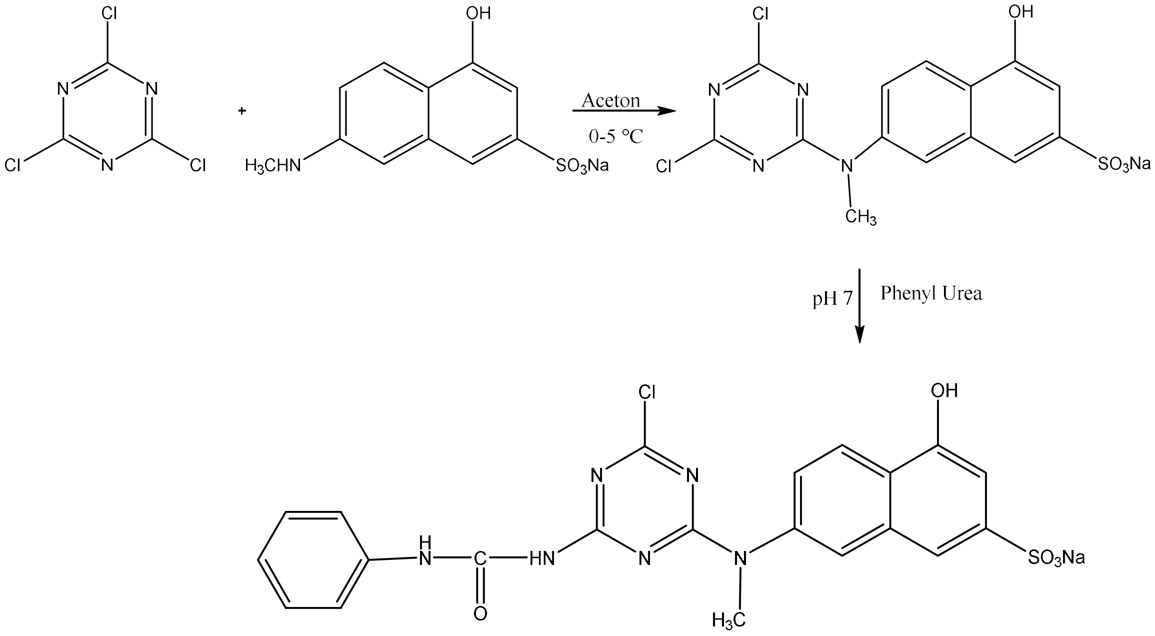
Table:4 Elemental analysis/TLC data of bi-functional reactive dyes Z21-Z30

2.4 Preparation bi-functional reactive dyes (Series IV)

Bi-functional reactive dyes for series-II was prepared with cyanurated 1-hydroxy-6-(methylamino)-3-naphthalenesulphonic acid (N methyl J- acid) and phenyl urea derivatives then coupled with 4-(β-sulfatoethylsulfonyl)aniline gives dyes Z31-Z40.

2.4.1 Synthesis of Cyanurated coupling component:

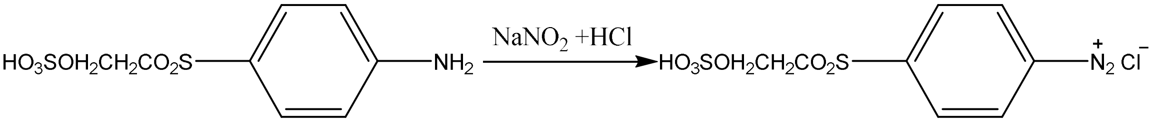
A solution of 0.01 mole cyanuric chloride was stimulated in acetone at temperatures below 5 ºC for two hours. The pH of the cyanuric chloride solution was kept at 4.0 by using 20% (w/v) sodium carbonate, after that reaction mass temperature was kept below 5 ºC for two hours. Cyanurated 1-hydroxy-6-(methylamino)-3-naphthalenesulphonic acid (N methyl J- acid) was formed in a clear solution. For second condensation the mixture of cyanurated 1-hydroxy-6-(methylamino)-3-naphthalenesulphonic acid (N methyl J-acid)was cooled, stirred and heated to 45 ºC,. 0.01 Mol phenyl urea was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ⁰C followed by next coupling reactions.



Cyanurated coupling component

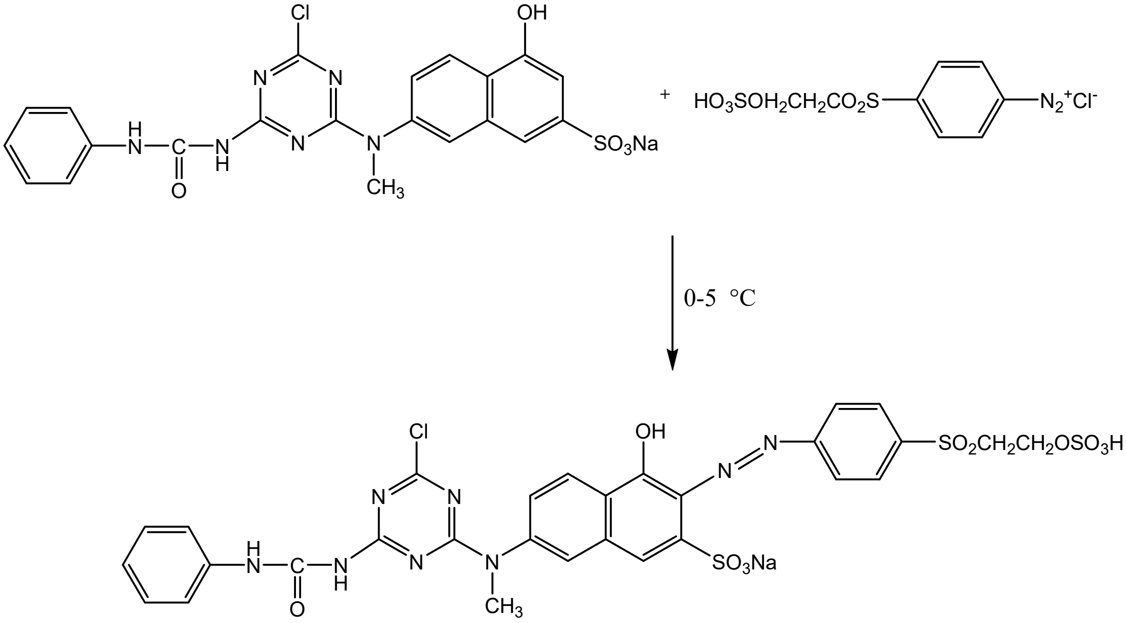
2.4.2 Diazotization of 4-(β-sulfatoethylsulfonyl)aniline:

4-(β-Sulfatoethylsulfonyl)aniline diazotized with Xion Wei and Zhang Shufen process, 0.01 Mol of 4-(β-sulfatoethylsulfonyl)aniline was dissolved in a solution of sodium carbonate(10% w/v) and maintained pH 6-7 at 0-5 ⁰C. In the solution of 4-(β-sulfatoethylsulfonyl)aniline, 0.0105 mol sodium nitrite solution was added. The reaction mass being introduced to chilled 0.015 mol conc. hydrochloric acid, which was kept at a constant temperature of 0-5 ⁰C while stirring with ice cubes. The reaction mass was agitated for an hour and tested with starch iodide paper to detect the presence of nitrous acid. By adding sulfamic acid the excess nitrous acid was removed. The salt of diazo compound was used for next coupling reaction.



Diazotization of 4-(β-sulfatoethylsulfonyl)aniline

2.4.3 Coupling of 4-(β-sulfatoethylsulfonyl)aniline and 7-[(4-chloro-6-(3-phenylureido)-1,3,5-triazin-2-yl)(methyl)amino]-4-hydroxynaphthalene-2-disulfonic acid:

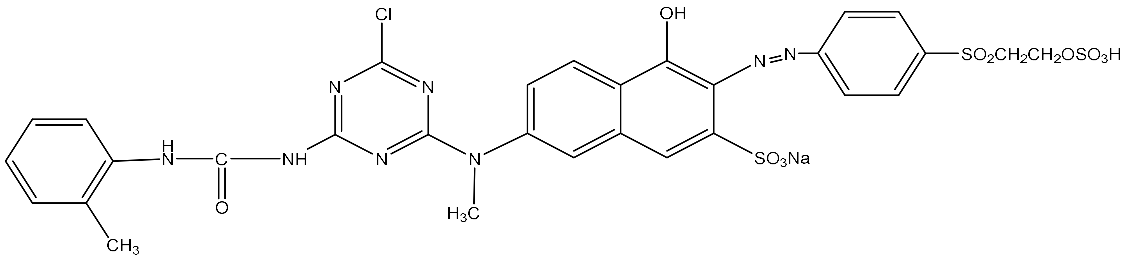


Reactive dye Z31

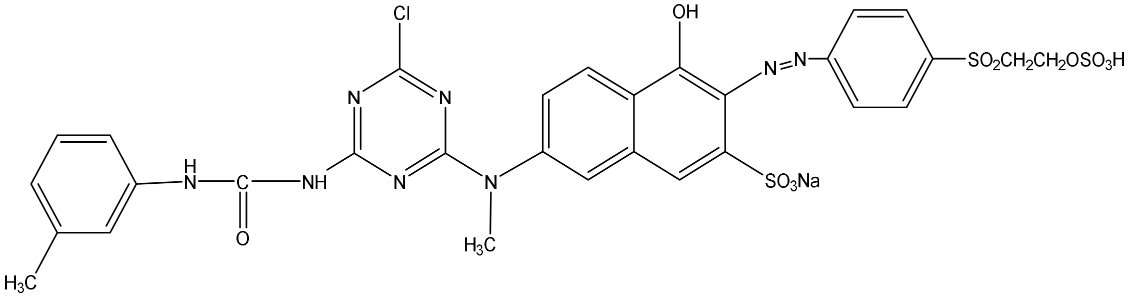
A diazonium salt of 4-(β-sulfatoethylsulfonyl)aniline which prepared freshly was introduced slowly to the condensation product with temperature 0-5 ºC. The pH of mass 7.5 was maintained with adding sodium carbonate (10%, w/v) and continue well-stirred for one hour with temperature 0-5 ºC. After the completion of reaction the synthesized dye was precipitated using potassium acetate (5% w/v), to get dye filtered product was washed with ethanol then dye Z31 was dried in oven at 40ºC. MP > 250 ⁰C(d).

From the above procedure other reactive dyes Z32 to Z40 synthesized using changing intermediates such as ortho tolyl urea, meta tolyl urea, para tolyl urea, para nitro phenyl urea, ortho nitro phenyl urea, ortho chloro phenyl urea, meta chloro phenyl urea, para chloro phenyl urea and para methoxy phenyl urea.

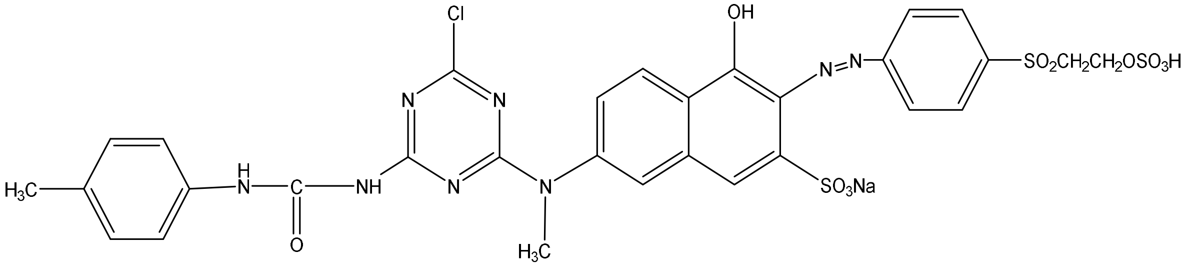
Final structures of synthesized reactive dyes (Z32 to Z40) are as below:



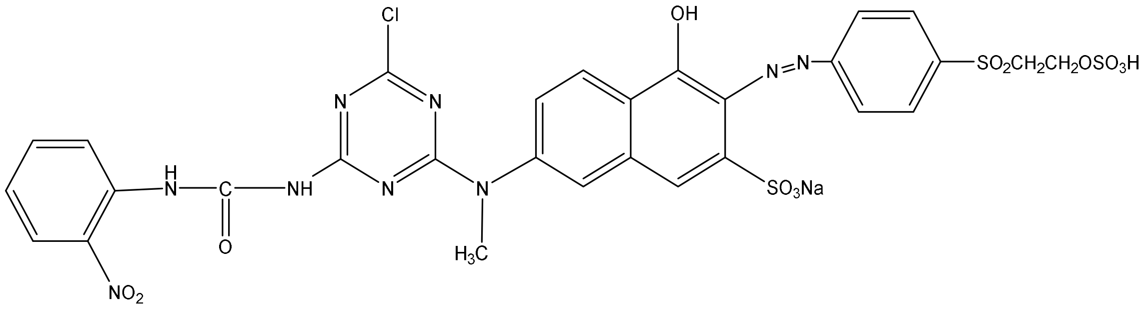
Reactive dye Z32



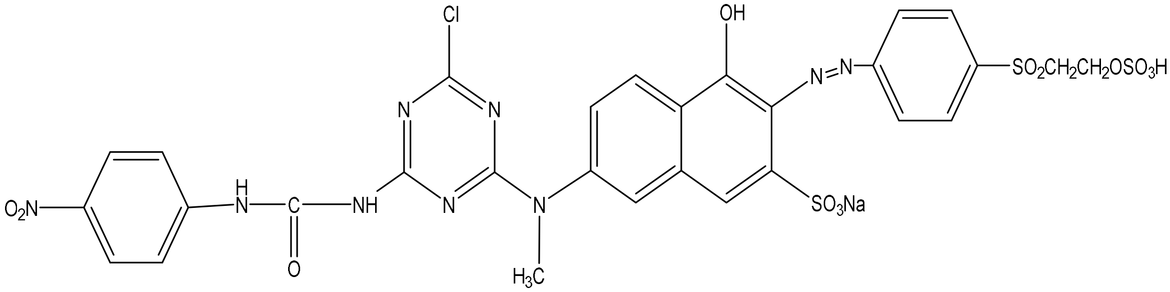
Reactive dye Z33



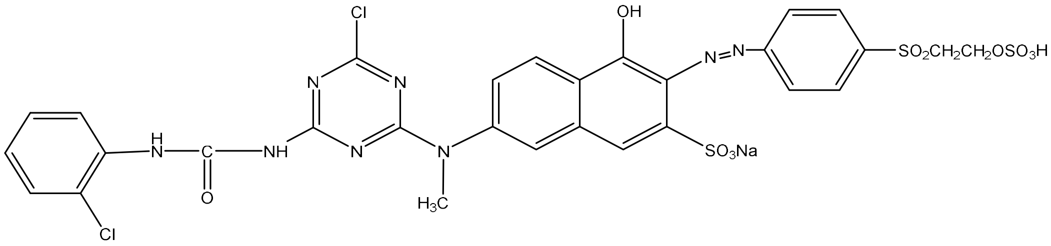
Reactive dye Z34



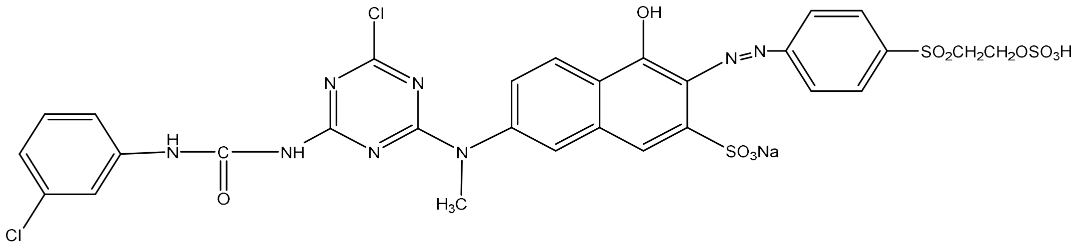
Reactive dye Z35



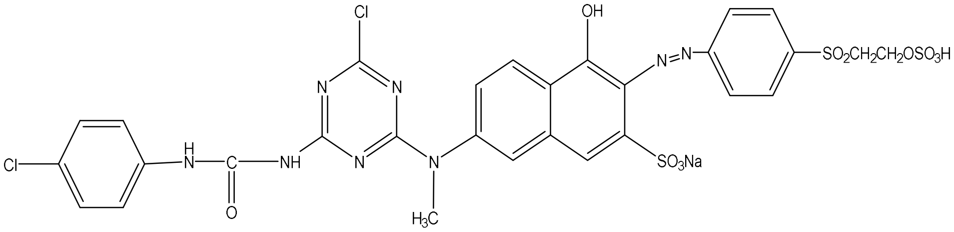
Reactive dye Z36



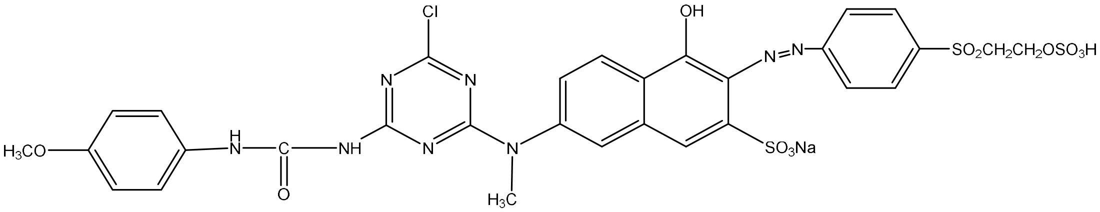
Reactive dye Z37



Reactive dye Z38



Reactive dye Z39



Reactive dye Z40

The elemental analysis/TLC data of synthesized reactive dyes (Z31 to Z40) are recorded in Table:4.

Dye No	**Molecular Formula**	**Mol. Wt. (g/mole)**	**Yield %**	**% of nitrogen**		**R_f value**
				found	**required**	
Z31	$C_{29}H_{24}ClN_8NaO_{11}S_3$	815.18	85	13.67	13.75	0.32
Z32	$C_{30}H_{26}ClN_8NaO_{11}S_3$	829.20	84	13.48	13.51	0.34

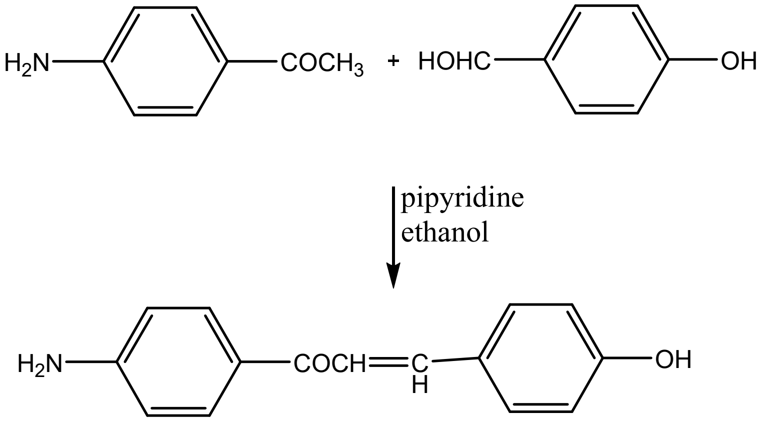
Z33	$C_{30}H_{26}ClN_8NaO_{11}S_3$	829.20	88	13.42	13.51	0.31
Z34	$C_{30}H_{26}ClN_8NaO_{11}S_3$	829.20	87	13.38	13.51	0.29
Z35	$C_{29}H_{23}ClN_9NaO_{13}S_3$	860.17	89	14.45	14.66	0.42
Z36	$C_{29}H_{23}ClN_9NaO_{13}S_3$	860.17	74	14.58	14.66	0.37
Z37	$C_{29}H_{23}Cl_2N_8NaO_{11}S_3$	849.62	75	12.09	13.19	0.32
Z38	$C_{29}H_{23}Cl_2N_8NaO_{11}S_3$	849.62	86	13.06	13.19	0.43
Z39	$C_{29}H_{23}Cl_2N_8NaO_{11}S_3$	849.62	89	13.06	13.19	0.40
Z40	$C_{30}H_{26}ClN_8NaO_{12}S_3$	845.20	85	13.12	13.26	0.41

Table:5 Elemental analysis/TLC data of bi-functional reactive dyes Z31-Z40

2.5 Preparation of bi-functional reactive dyes (Series-V)

2.5.1 Synthesis of 4-amino-4'-hydroxy benzylidene acetophenone(4-amino-4'-hydroxy chalcone):

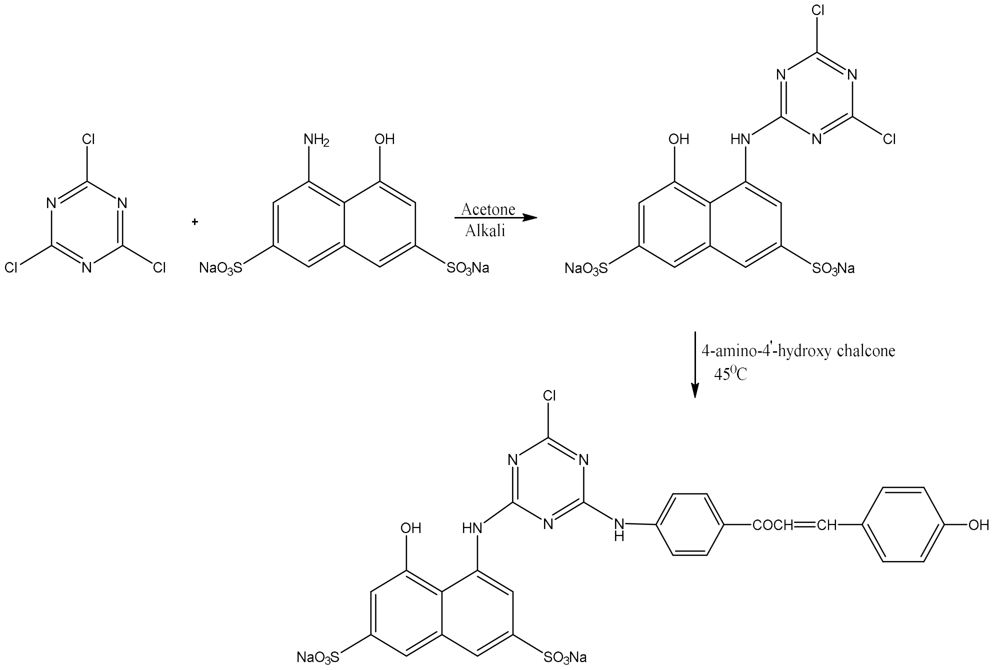
0.10 mole of 4-Amino acetophenone, 0.10 mole of 4-hydroxy benzaldehyde, a few drops of piperidine and absolute ethanol (40 ml) were taken in a round bottom flask. The mixture was refluxed for 12 hours. The reaction mass was concentrated up to its half the volume and after that, it was suspended in an ice-water mixture with stirring. Solid mass was separated, filtered, dried and crystallized from ethanol. Melting point 217 ^{0}C [8-9].



4-amino-4'-hydroxy chalcone

2.5.2 Synthesis of Cyanurated coupling component:

A solution of 0.01 mole cyanuric chloride was stimulated in acetone at temperatures below 5 ºC for two hours. The pH of the cyanuric chloride solution was kept at 4.0 by using 20% (w/v) sodium carbonate, after that reaction mass temperature was kept below 5 ºC for two hours. Cyanurated 8-amino-1-naphthol-3,6-disulfonic acid (H-acid) was formed in a clear solution. For second condensation the mixture of cyanurated 8-amino-1-naphthol-3,6-disulfonic acid (H-acid) was cooled, stirred and heated to 45 ºC,. 0.011 mole 4-amino-4'-hydroxy benzylidene acetophenone was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ºC followed by next coupling reactions.



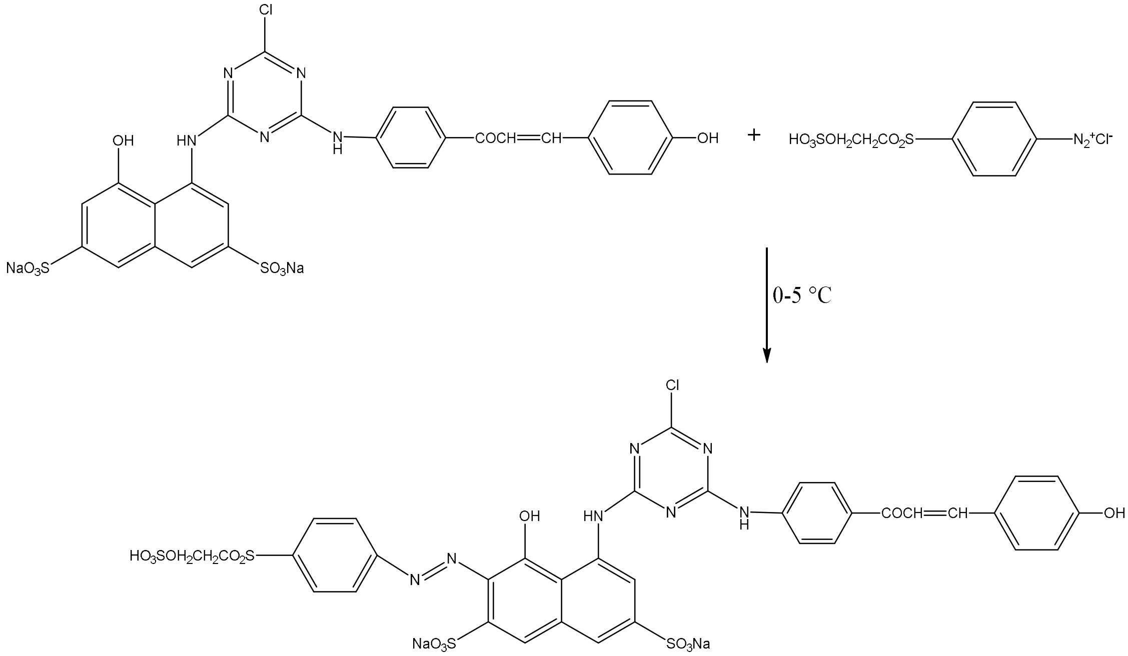
Cyanurated coupling component

2.5.3 Diazotization of 4-(β-sulfatoethylsulfonyl)aniline:

It was synthesized by the procedure as described above in Section 2.1.2.

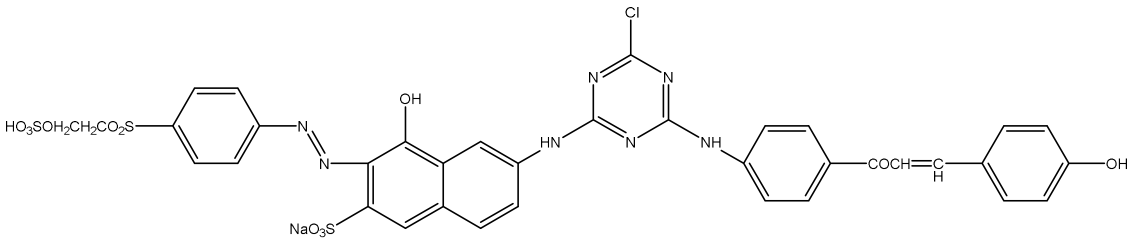
2.5.4 Coupling Reaction:

A freshly synthesised 4-(β- sulfatoethylsulfonyl)aniline diazonium salt was transferred to the condensing product (section 2.5.2) at 0–5 ^{0}C by adding 10% w/v sodium carbonate solution. After that the solution was continue stirring for an hour at temperatures ranging from 0-5 ^{0}C and the pH 6-7 of the mass was kept constant. The produced dye was precipitated using potassium acetate (5% w/v) once the reaction was completed. The dye(Z41) was filtered, washed with ethanol and dried in an electric oven at 40 ºC. MP > 250 ^{0}C(d).

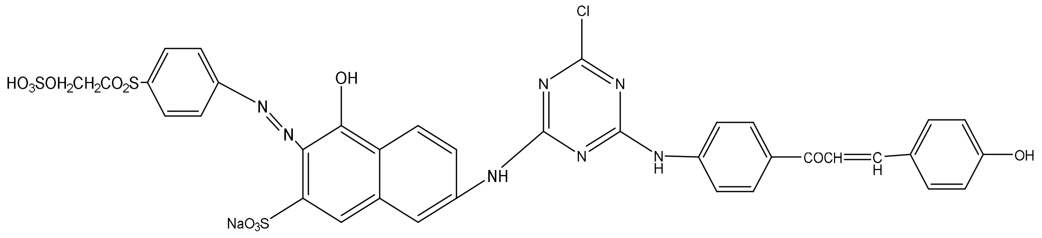


Reactive dye Z41

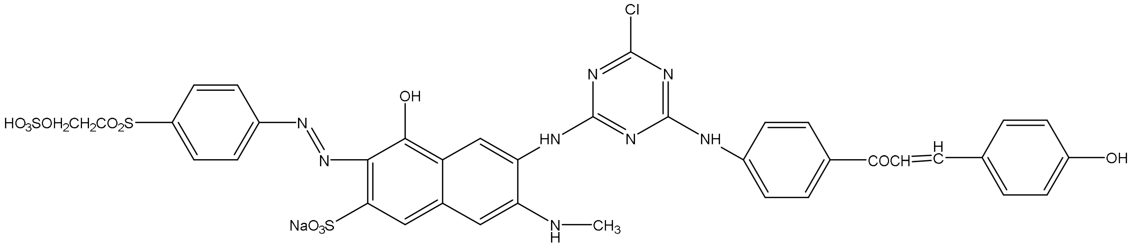
We have also synthesized novel reactive dyes(Z42-Z47) by substituting H-acid to appropriate substituted acid (Gamma acid, J-acid, N methyl J-acid, N-phenyl J-acid, K-acid and peri acid) using same procedure as mention above. The final structures of the dyes are as under:



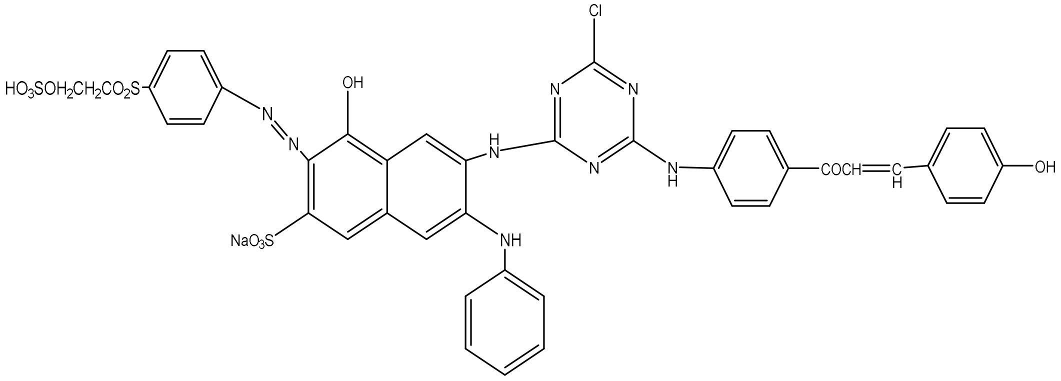
Reactive dye 42



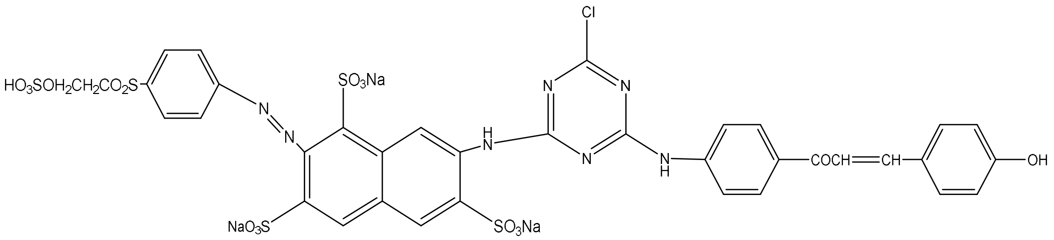
Reactive dye Z43



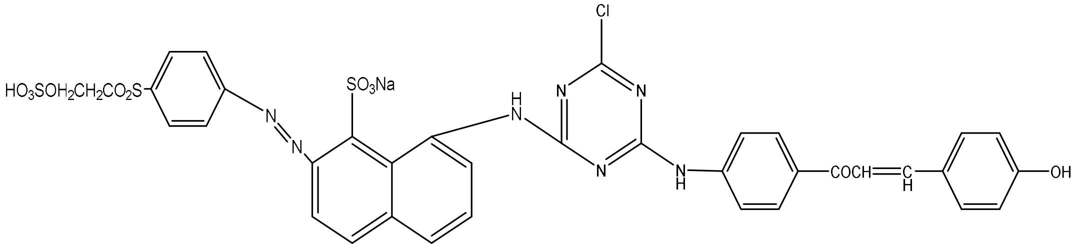
Reactive dye Z44



Reactive dye Z45



Reactive dye Z46



Reactive dye Z47

The elemental analysis/TLC data of synthesized reactive dyes (Z41 to Z47) are recorded in Table:6.

Dye No	Molecular Formula	Mol. Wt. (g/mole)	Yield %	% of nitrogen		R_f value
				found	required	
Z41	$C_{36}H_{26}ClN_7Na_2O_{15}S_4$	1006.31	84	9.67	9.74	0.32
Z42	$C_{36}H_{27}ClN_7NaO_{12}S_3$	904.27	79	10.76	10.84	0.41
Z43	$C_{36}H_{27}ClN_7NaO_{12}S_3$	904.27	83	10.78	10.84	0.36
Z44	$C_{37}H_{30}ClN_8NaO_{12}S_3$	933.31	88	11.98	12.01	0.35
Z45	$C_{42}H_{32}ClN_8NaO_{12}S_3$	995.38	83	11.12	11.26	0.31
Z46	$C_{36}H_{25}ClN_7Na_3O_{17}S_5$	1092.35	82	8.78	8.98	0.43
Z47	$C_{36}H_{27}ClN_7NaO_{11}S_3$	888.27	72	10.97	11.04	0.43

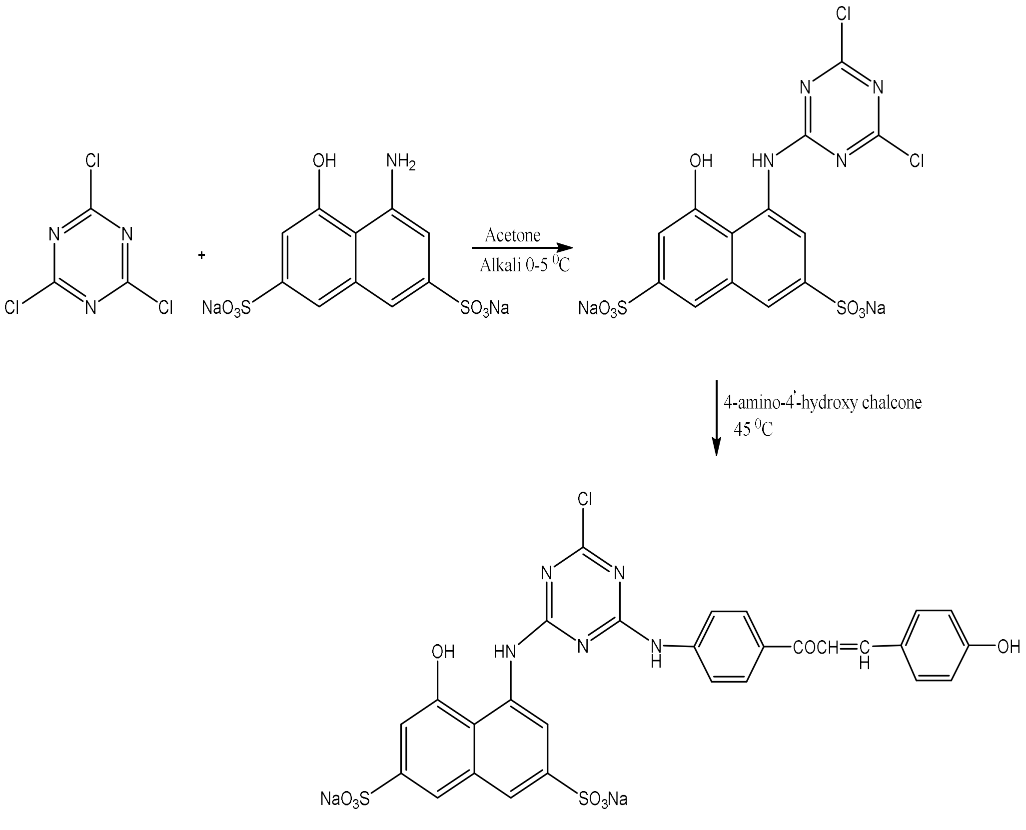
Table:6 Elemental analysis/TLC data of bi-functional reactive dyes Z41-Z47

2.6 Preparation of hot brand reactive dyes series VI

In this series hot brand reactive dyes were synthesized, diazotized o-anisidine was coupled with several 4-amino-4’-hydroxy benzylidene acetophenone cyanurated coupling component including H-acid, Gamma acid, J-Acid, N-phenyl J-acid, K-acid and Peri acid.

2.6.1 Synthesis of Cyanurated coupling component:

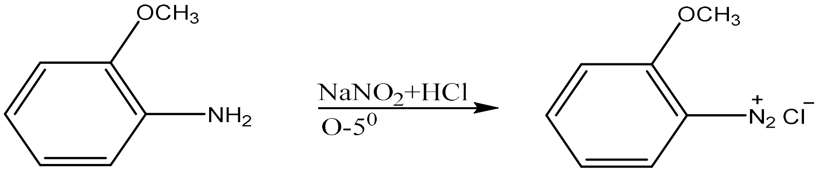
0.01 mol Cyanuric acid was stimulated in acetone at 0-5 ^{o}C for 2 hours, a solution of 0.01 mole H-acid was added in cyanuric chloride solution the pH was maintained 7 by adding sodium carbonate 20% (w/v) the reaction mass temperature was maintained below 5^{o} C for 2 hours. Cyanurated H-acid was formed as a clear solution. For second condensation the mixture of cyanurated H-acid was cooled, stirred and heated to 45 ^{o}C. 0.01 mol 4-amino-4’-hydroxy benzylidene acetophenone was introduced to this mixture slowly, pH was kept neutral during this reaction by using solution of sodium carbonate and the reaction mixture was agitated minimum three hours with temperature 45 ^{o}C followed by next coupling reactions



Cyanurated coupling component

2.6.2 Diazotization of o-Anisidine:

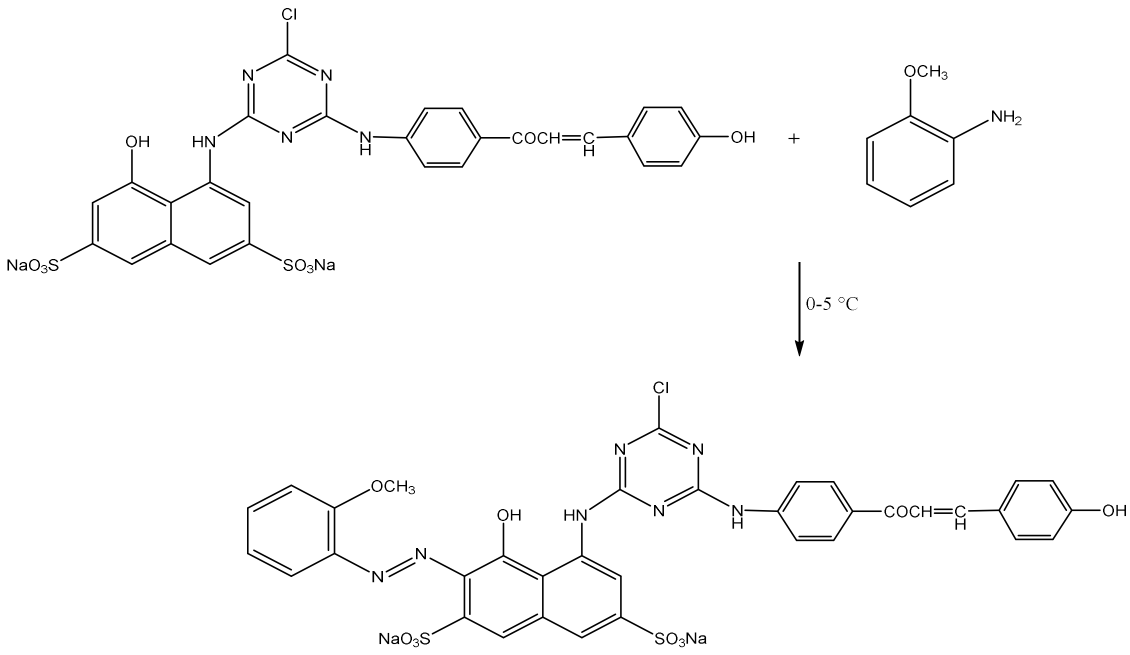
0.01 mol of o-Anisidine was suspended in water (120 ml). Dropwise additions of hydrochloric acid were made to this thoroughly agitated mixture. The mixture was raised to 70 °C gradually until a clear solution was achieved. In an ice bath, the solution was cooled to 0- 5°C. The addition of a $NaNO_2$ solution was done while stirring for five minutes. The reaction mass was agitated for an hour and tested with starch iodide paper to detect the presence of nitrous acid. By adding sulfamic acid the excess nitrous acid was removed. The salt of diazo compound was used for next coupling reaction[11-12].



Diazotization of o-anisidine

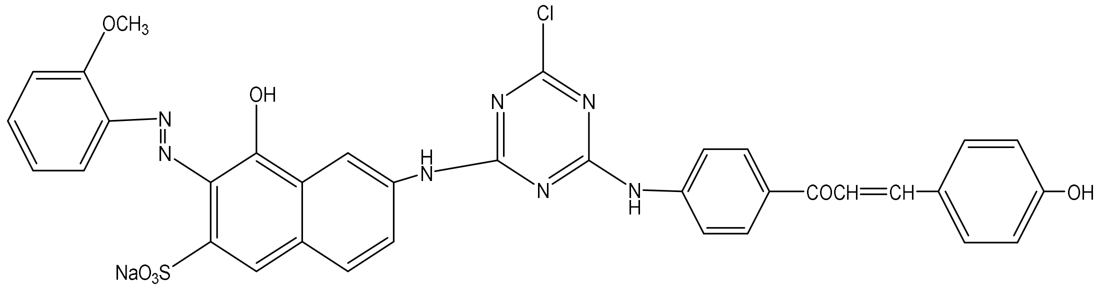
2.6.3 Coupling Reaction:

A diazonium salt of o-anisidine (section 2.6.3) which prepared freshly was introduced slowly to the condensation product (section 2.5.5) with temperature 0-5 ºC. The pH of mass 7.5 was maintained with adding sodium carbonate (10%, w/v) and continue well-stirred for one hour with temperature 0-5º C. After the completion reaction the synthesized dye was precipitated using potassium acetate (5% w/v), to get dye filtered product was washed with ethanol then dye Z48 was dried in oven at 40ºC. MP > 250 ^{0}C(d). For synthesis of dye Z49-56 follow the same process as describe in 2.5 only coupling component were change such as Gamma acid, J-acid, N methyl J-acid, N-phenyl J-acid, K-acid and peri acid [13-14].

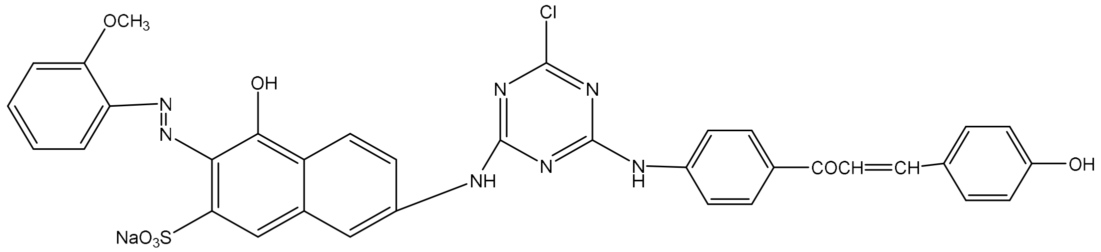


Reactive dye Z48

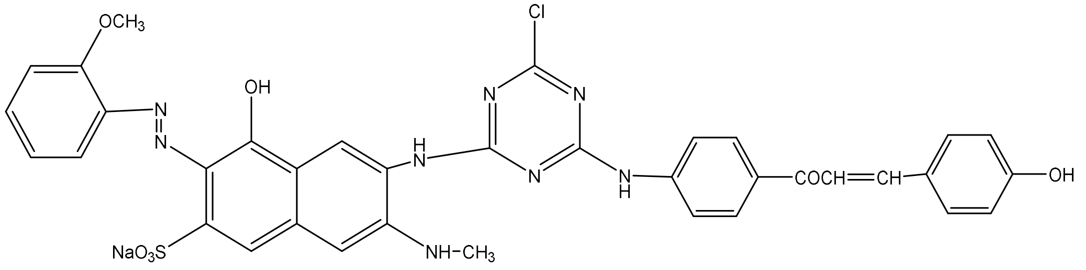
We have also synthesized novel reactive dyes(Z49-Z54) by substituting H-acid to appropriate substituted acid (Gamma acid, J-acid, N methyl J-acid, N-phenyl J-acid, K-acid and peri acid) using same procedure as mention above. The final structures of the dyes are as under:



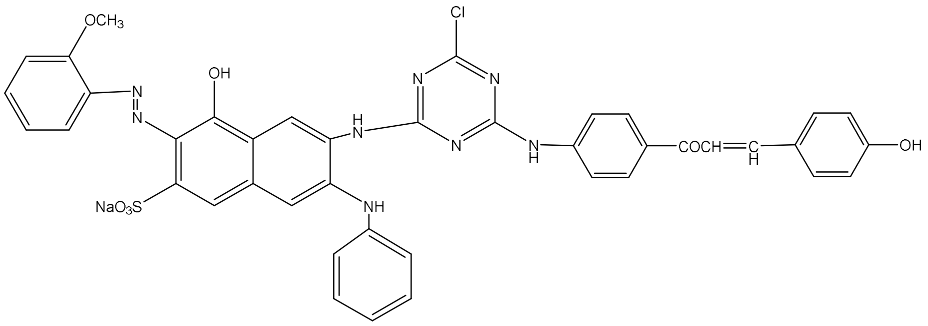
Reactive dye Z49



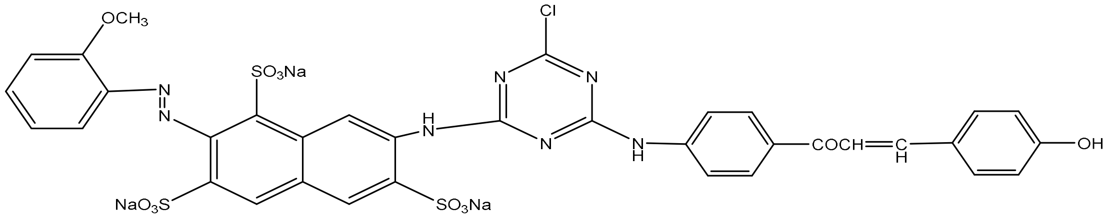
Reactive dye Z50



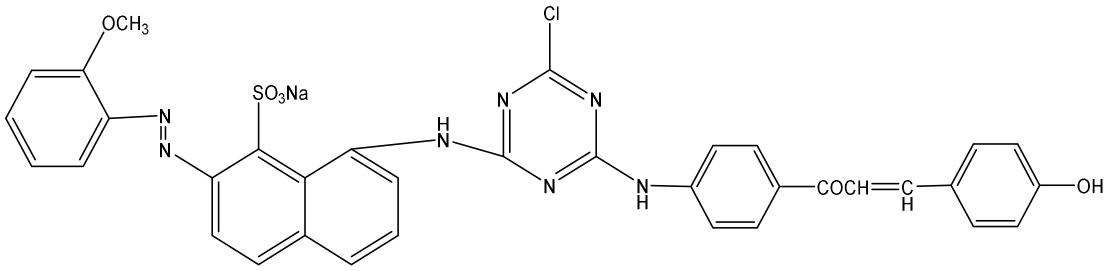
Reactive dye Z51



Reactive dye Z52



Reactive dye Z53



Reactive dye Z54

The elemental analysis/TLC data of synthesized reactive dyes (Z41 to Z47) are recorded in Table:6.

Dye No	Molecular Formula	Mol. Wt. (g/mole)	Yield %	% of nitrogen		Rf value
				found	required	
Z48	$C_{35}H_{24}ClN_7Na_2O_{10}S_2$	848.17	87	11.45	11.56	0.31
Z49	$C_{35}H_{25}ClN_7NaO_7S$	746.11	84	13.01	13.14	0.43
Z50	$C_{35}H_{25}ClN_7NaO_7S$	746.11	87	13.09	13.14	0.42
Z51	$C_{36}H_{28}ClN_8NaO_7S$	775.17	84	14.32	14.46	0.36
Z52	$C_{41}H_{30}ClN_8NaO_7S$	837.24	87	13.24	13.38	0.41
Z53	$C_{35}H_{23}ClN_7Na_3O_{12}S_3$	934.21	85	10.42	10.50	0.32
Z54	$C_{35}H_{25}ClN_7NaO_6S$	730.13	75	13.31	13.43	0.37

Table:7 Elemental analysis/TLC data of bi-functional reactive dyes

2.7 References

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