

Synthesis and Characterization of Bifunctional Reactive Dyes Based from Naphthalimide Derivatives

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ABSTRACT

Series of bifunctional reactive dyes were synthesized based on naphthalimide derivatives. The intermediate A [6, 6'-diamino-1H, 1'H, 3H, 3'H-benzo[de]isoquinoline]-1, 1'3, 3'-tetraone,] which tetrazotised with cyanurated coupling component such as H-acid, R-acid, J-acid, *pr*-acid and Tobias acid. The synthesized dyes were purified by recrystallization method. The structure of the synthesized dyes were confirmed using UV – visible, FT-IR, MS and ¹HNMR spectroscopic technique. Spectrophotometric investigations of the dyes in solvents of different polarities were measured to obtain absorption maxima, molar extinction coefficient and solvatochromic effects. These dyes give percentage yield of 76-88%, molecular weight of 1262.85-1454.98 g/mol, melting point 300-306 °C with various hues such as blue, red, brown, black and orange respectively.

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INTRODUCTION

Reactive dyes are coloured dyes that contain functional groups which can form covalent binding with fibre active sites, such as cellulose, amino, thiol and hydroxyl groups [1]. The good washing fastness of cellulose fiber with reaction dyes results from the steady covalent bond between cellulose and reactive dyes [2]. As a consequence, there is still a demand for new reactive dyes that have improved properties [3]. The use of bifunctional reactive dyes grows quickly because of their improved physicochemical properties during use [4]. They are familiar for their excellent thinning efficiency and overall quickness. A diligent selection of the correct reactive groups and right chromophore creates reactive dyes with good dyeing properties [5].

In several researchers have reported on synthesis, characterization of bifunctional reactive dyes on cotton fabric but there is no existing literature with regards to synthesis of bifunctional reactive dyes derived from naphthalimide derivatives which is a new heterocyclic intermediate. The presence of the naphthalimide moieties in the dye structure will improve the

fastness properties of the dyes in cotton fabric and bring about deep shade, brilliant hues of high bathochromic effects due to donor acceptor character of the amino and carbonyl groups present in the naphthalimide moiety. This investigation aimed at synthesis, and characterization of bifunctional reactive dyes based from naphthalimide derivatives.

MATERIALS AND METHODS

The following are some of the major equipment that were used in the course of the research includes; UV-visible Spectrophotometer (Agilent Technology Cary 100), FT-IR Spectrophotometer (Agilent Technology Cary 630), Nuclear Magnetic Resonance (NMR) (Agilent Technology 400 MHz). Most commercial products used in the synthesis of bifunctional reactive dyes were purchased from Sigma-Aldrich and Weifang Senya chemical company limited, China. All the chemicals and reagent used in the present study such as Acenaphthene, Sodium dichromate, Hydrazine hydrate, Stannous chloride, 8-amino-naphthal-3-yl disulfuric acid (H acid), 2-naphthol-3-yl disulfuric acid (R-acid), 2-amino-1-naphthalene sulfuric acid, 4-amino

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butanoic acid, 2-amino -1- naphthalene sulfuric acid, Tridichloro -1, 3 5-triazine.

Synthesis of 5-nitroacenaphthene

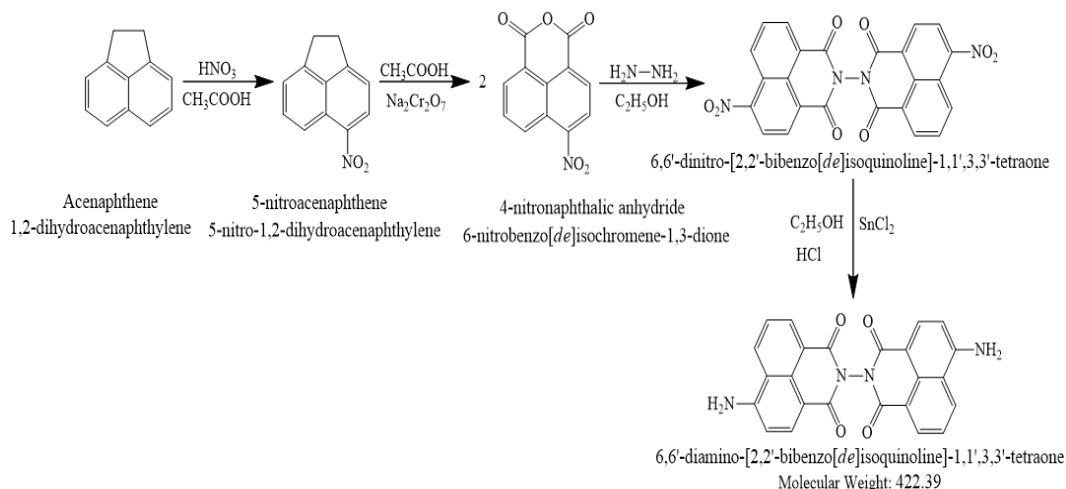
Acenaphthene (15.4 g, 0.1 mol) was dissolved in hot acetic acid (57.2 mL), cooled with vigorous stirring to separate the crystalline acenaphthene as fine as possible. Nitric acid (7.03 ml) was added drop wise for 1 hour at 22-27 °C, then stirred for 1 hour more at 25 °C, warmed to 68 °C gradually for 30 min. then cooled, and the crystals were filtered, washed with acetic acid - water (1: 1) followed by distilled water to give needle like crystals [7].

Synthesis of 4-nitro-1, 8-naphthalic anhydride 5-Nitroacenaphthene (24.87 g, 0.125 mol) was dissolved in hot acetic acid (248.75 mL), sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) (158.5 g) was added for 3 hour at 65-70 °C. This was warmed to 98-100 °C gradually for 30 min. and

further refluxed for 5 hours. The content was washed out with 0.6 L of hot water, cooled, filtered and the solid was washed with dilute HCl. It was further boiled for 30 min. with 200 mL of 5% Na_2CO_3 solution for 30 min., filtered, and the filtrate was acidified and the separated crystals was dried at 120 °C for 4 hours to obtain 4-nitro-1, 8-naphthalic anhydride, which was recrystallized from HNO_3 to afford the off-white needle like crystals [7]

Synthesis of 6, 6'-dinitro-[2,2'-bibenzo[de]isoquinoline]-1, 1'-3,3'-tetraone (a)

A suspension of 4-nitro-1'8-naphthalic anhydride (0.02 mol, 4.86 g) and hydrazine hydrate (0.03 mol, 4.71g) was stirred under reflux for 7 hrs in ethanol (102 ml). The cooled suspension was filtered out and recrystallized with ethanol as light brown.



Synthesis of 6, 6'-diamino-1H, 1'H, 3H, 3'H-[bibenzo[de]isoquinoline]-1, 1', 3', 3'-tetraone,

General Procedure for Tetrazotization of intermediates A, was carry out using the same procedure and reaction condition. The intermediate (0.54g 0.005 mol) is suspend in distill water (60 cm³) and hydrochloric acid (0.36g) is add drop wise to the well stirred suspension. The mixture is gradually heat up to 70°C, till clear solution is obtained. The form solution is gradually

cool to below 5°C in an ice bath, then already cooled (0-5°C) NaNO_2 (0.6g in 4 ml of H_2O) is add over a period of 30 mins with continuous stirring. The stirring is continued for one (1) hour, maintaining the temperature of 0-5°C with positive test for nitrous with starch iodide paper. After completing destroying the excess of nitrous acid with the require amount of sulphamic acid the clear tetrazonium solution at 0-5°C obtain is use for next coupling as shown in scheme A [7].

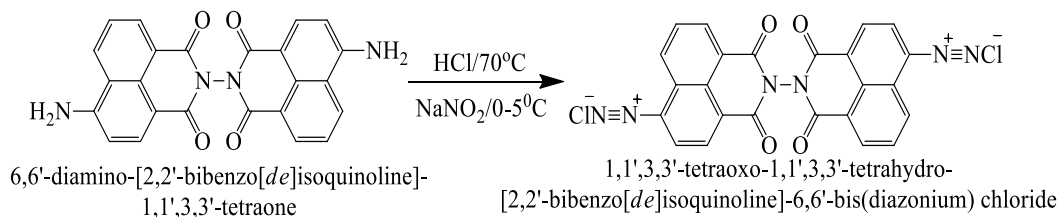
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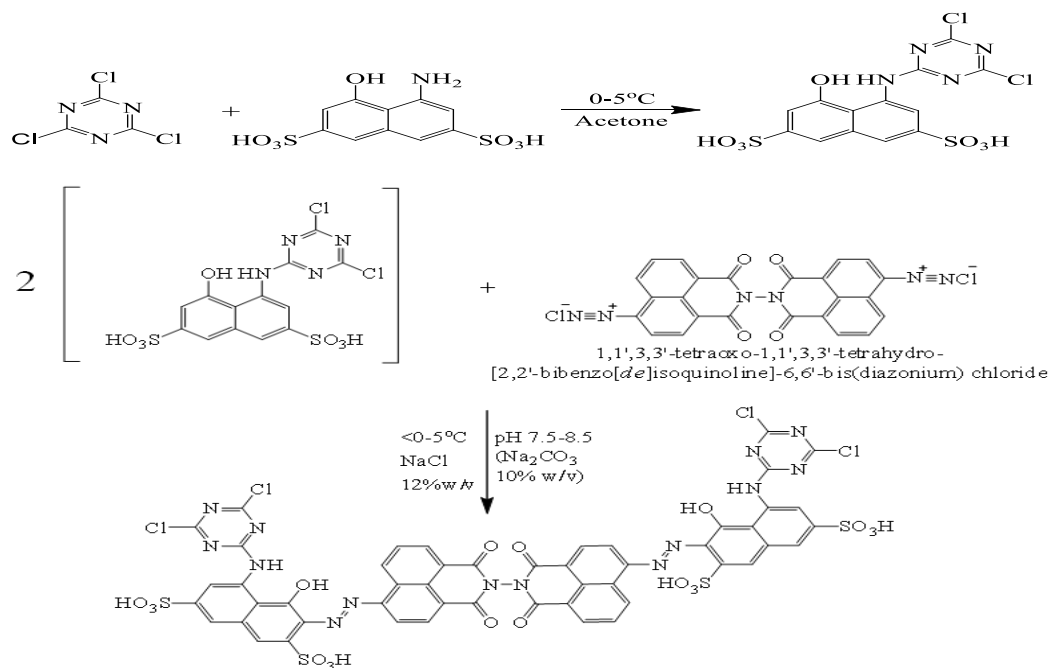
Synthesis of tetrazonium salt



Scheme General procedure for cyanuration of coupling components.

Cyanuric chloride (1.85g 0.01 mol) is stirred in acetone (25cm³) at temperature below 5°C for a period of an hour. A neutral solution of coupling component (3.19g 0.01 mol) in aqueous sodium carbonate solution (10% W/v) is then added in small lots for an hour. The pH is maintained

neutral by simultaneous addition of sodium carbonate solution (1% W/v). The reaction mass is then stirred at 0-5°C for further 4 hours. The cyanurated coupling component solution is used for subsequent coupling reaction in various acids such as H, Gamma, R, J, and Tobias acid respectively.[10]



Synthesis of A₁

3,3'-((1E,1'E)-(1,1',3,3'-tetraoxo-1,1',3,3'-tetrahydro-[2,2'-bibenzo[de]isoquinoline]-6,6'-diyl)bis(diazene-2,1-diyl))bis(7-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthalene-2-sulfonic acid). The synthesis of dye A₁-A₅ was done by adding freshly prepared solution of

tetrazotized ion 6,6'-diamino-1H,1'H,3H,3'H-[bibenzo[de]isoquinoline]-1,1',3,3'-tetraone. The pH 7.5-8.5 was maintained by simultaneous addition of sodium carbonate solutions (Na₂SO₃) (10% w/v) where a purple solution was obtained. The stirring was continued for 4 hrs at a constant temperature of 0-5°C for another one hr. The

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solid dye precipitates out and was filtered, with little amount of acetone and dried at room temperature [10] The same chemical reaction and controlled condition was use for synthesis of dye A₁-A₅

Purification of synthesized the Dyes

The synthesized dyes were purified by recrystallization from ethanol by adopting the method used by [6].

Determination of Percentage Yield of the synthesized Dyes

The percentage yield of the synthesized dyes was determined using equation 1. 1 [9]

$$\% \text{Yield} = \frac{\frac{MP}{MMP}}{\frac{MR}{MMR}} \times 100$$

..... 1. 1

where;

MP is the mass of the product

MMP is the molar mass of the product

MR is the mass of the reactant

MMR is the molar mass of the reactant

Determination Melting Point of the Dyes

The melting point of each dye was determined using Gallenkamp melting apparatus. Small amount of each dye was filled into a capillary tube and placed in to the apparatus, the melting point of each dye was obtained by consistently focusing on the apparatus as the apparatus gradually heat the dye in the tube where the melting point is obtained.

Determination of Molar Extinction Coefficient

The molar extinction coefficient (ε), which is a constant for each molecule at any given wavelength represents the absorbance substance

per litter. This was calculated using the relationship,

Log₁₀ (I₀/I) absorbance A or optical density

$$A = \epsilon CL \dots \dots \dots 1. 2$$

ε = Molar Extinction Coefficient

A = Absorbance at λ_{max}

C = Concentration of dye in Mol/dm³

L = Path length in cm

Infra-Red Spectra of the Dyes

About 1. 5mg of finely ground synthesized sample was intimately mixed with about 150mg of powdered potassium bromide (KBr) in a mortal with pestle. The finely ground mixtures were introduced in between the two bolts (A and A₁) and the upper screw A was tightened until the powder was compressed to a thin disc. After compressing, the sample bolts A and A₁ were removed and a steel cylinder with pellet inside it was placed in path of the beam of IR spectrometer and a blank KBr pellet was kept in the path of reference beam and run.

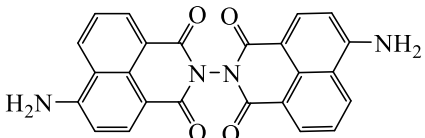
UV-Visible Absorption Measurements

The wavelength of maximum absorption of each dye was determined in distilled water, ethanol Ethanol ± HCl and dimethylformamide (DMF). 0. 001g of each dye was dissolved in 5 cm³ of each of the solvent. The spectra of each dye solution determined and recorded using UV-Visible spectra scanning (Agilent CARY 300 UV-Visible spectrophotometer).

RESULTS AND DISCUSSION

The results and discussion of the dye synthesized intermediate and dyes

Table 1.1: Structures of Synthesized intermediate, molecular formular their IUPAC Name

Intermediate no.	Name	Structure	Molecular formula
A	6, 6'-diamino-1H, 1'H, 3H, 3'H-[2, 2'-bibenzo[de]isoquinoline]-1, 1', 3, 3'-tetraone		C ₂₄ H ₁₄ N ₄ O ₄

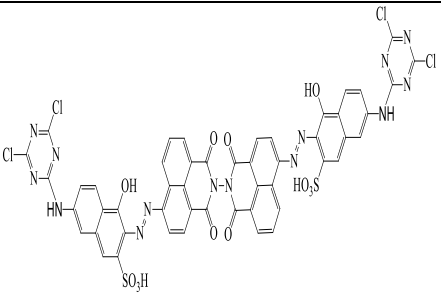
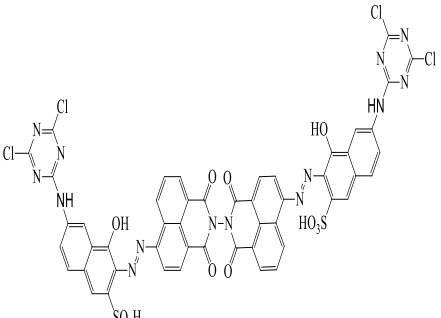
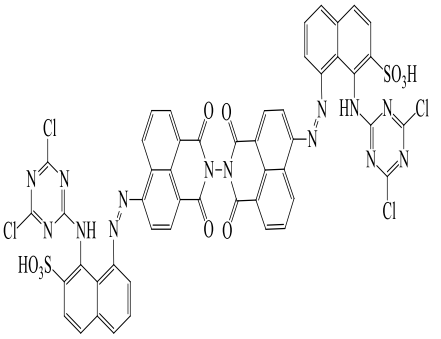
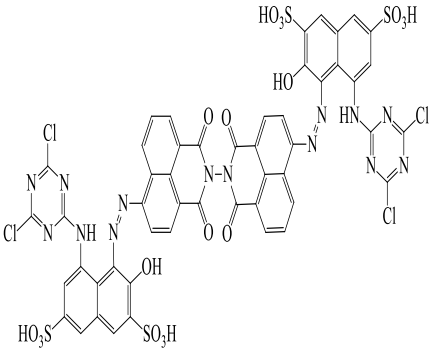
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Table 1.2: Structures of Synthesized reactive dyes, molecular formular and their IUPAC Name

DY E No	STRUCTURE	MOLECULAR FORMULA
A ₁	3, 3'-((1E, 1'E)-(1, 1', 3, 3'-tetraoxo-1, 1', 3, 3'-tetrahydro-[2, 2'-bibenzo[de]isoquinolin e]-6, 6'-diyl)bis(diazeno-2, 1-diyl))bis(7-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino)-4-hydroxynaphthalene-2-sulfonic acid)	 C ₅₀ H ₂₄ Cl ₄ N ₁₄ O ₁₂ S ₂
A ₂	3, 3'-((1E, 1'E)-(1, 1', 3, 3'-tetraoxo-1, 1', 3, 3'-tetrahydro-[2, 2'-bibenzo[de]isoquinolin e]-6, 6'-diyl)bis(diazeno-2, 1-diyl))bis(6-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino)-4-hydroxynaphthalene-2-sulfonic acid)	 C ₅₀ H ₂₄ Cl ₄ N ₁₄ O ₁₂ S ₂
A ₃	8, 8'-((1Z, 1'Z)-(1, 1', 3, 3'-tetraoxo-1, 1', 3, 3'-tetrahydro-[2, 2'-bibenzo[de]isoquinolin e]-6, 6'-diyl)bis(diazeno-2, 1-diyl))bis(1-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino)naphthalene-2-sulfonic acid)	 C ₅₀ H ₂₄ Cl ₄ N ₁₄ O ₁₀ S ₂
A ₄	4, 4'-((1Z, 1'Z)-(1, 1', 3, 3'-tetraoxo-1, 1', 3, 3'-tetrahydro-[2, 2'-bibenzo[de]isoquinolin e]-6, 6'-diyl)bis(diazeno-2, 1-diyl))bis(5-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino)-3-hydroxynaphthalene-2, 7-disulfonic acid)	 C ₅₀ H ₂₄ Cl ₄ N ₁₄ O ₁₈ S ₄

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A₅ 3, 3'-((1E, 1'E)-(1, 1', 3, 3'-tetraoxo-1, 1', 3, 3'-tetrahydro-[2, 2'-bibenzo[de]isoquinolin e]-6, 6'-diyl)bis(diazene-2, 1-diyl))bis(5-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino)-4-hydroxynaphthalene-2, 7-disulfonic acid)

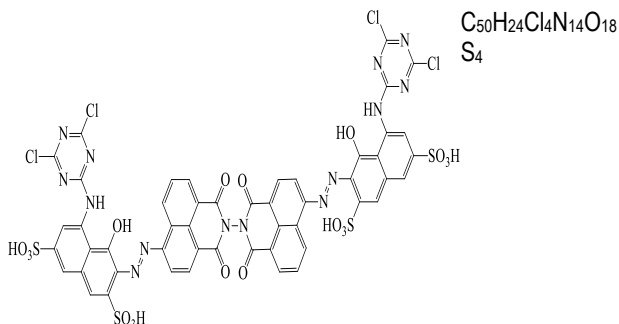


Table 1.3: Physical properties of the synthesized dye intermediates.

Name of intermediate	Colour of Crystals	Melting point (°C)	Percentage yield (%)	Molecular weight(g/mol)	Molecular formula
A	Brown	278-280	96	498. 50	C ₂₄ H ₁₄ N ₄ O ₄

Table 1.4: Physical properties of the synthesized bifunctional reactive dyes derive from naphthalimides derivatives

Dyes No	Molecular formulae	Theoretical molecular weight (g/mol)	Melting point (°C)	Percentage yield (%)	Colour of the crystals
A ₁	C ₆₅ H ₂₈ Cl ₄ N ₁₄ O ₁₈ S ₄	1454. 98	304-306	82	Blue
A ₂	C ₆₅ H ₂₈ Cl ₄ N ₁₄ O ₁₈ S ₄	1454. 98	300-302	74	Red
A ₃	C ₅₆ H ₂₈ Cl ₄ N ₁₄ O ₁₈ S ₂	1294. 85	300-302	88	Brown
A ₄	C ₅₆ H ₂₈ Cl ₄ N ₁₄ O ₁₂ S ₂	1294. 85	308-310	80	Black
A ₅	C ₅₆ H ₂₈ Cl ₄ N ₁₄ O ₁₀ S ₂	1262. 85	300 302	76	Orange

Table 1.5: Wavelength of Maximum Absorption and Molar Extinction Coefficient of the Dyes

Dye No	ε _{max} in DMF × 10 ⁴ (Lmol ⁻¹ cm ⁻¹)	Distil H ₂ O λ _{max} (nm)	DMF λ _{max} (nm)	Ethanol λ _{max} (nm) (a)	Ethanol + HCl λ _{max} (nm) (b)	Change in λ _{max} (nm) (b-a)
A ₁	2. 77	511	525	509	514	+5
A ₂	2. 80	498	521	519	515	-4
A ₃	3. 28	494	511	510	494	-16
A ₄	2. 26	515	422	509	494	-15
A ₅	8. 21	449	511	510	511	+1

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Table 1.6: Infrared Spectra of the Synthesized Intermediates Based on Naphthalimide Derivatives

A-3067(N. H Str Vibr), 2784(C-H Str Vibr), 2583 (C-H Str Vibr Aliphatic), 2106 (C-H Str Vibr Ar), 1622 (C=O Str Vibr), 1670 (-N-C=O Str Vibr),

Table 1.7: FT-IR Analysis of the Synthesized Azo Reactive Dyes

Dye No	FT-IR (cm ⁻¹)
A ₁	3204 (OH Str Vibr) 3070 (C-H Str Vibr) 2121 (C-H Str Vibr) 1778-1707 (C=O Str Vibr) 1599-1299 (C-N Str Vibr) 1648 (N-H bend Vibr) 1372 (N=O Str Vibr) 709-743 (C-Cl Str Vibr) 877-862 (SO ₃ H Str Vibr)
A ₂	3432 (OH Str Vibr) 2840-2985 (C-H Str Vibr) 1797 (N=N Str Vibr) 1648 (N-H bend Vibr) 1439-1417 (C-N Str Vibr) 1041 (S=O Str Vibr) 862 (SO ₃ H Str Vibr) 709-766 (C-U Str Vibr) 1372 (N-O Str Vibr)
A ₃	3592 (OH Str Vibr) 3439 (NH Str Vibr) 2840-2996 (C-H Str Vibr) 2508-2162 (-SCN Str Vibr) 1748 (C=O Str Vibr) 1648 (N-H bend Vibr) 1588 (N=N Str Vibr) 1369 (N=O Str Vibr) 1417-1439 (C-N Str Vibr) 728-762 (C-CL Str Vibr) 829 (SO ₃ H Str Vibr) 992 (SO ₃ H Str Vibr)
A ₄	3435 (OH Str Vibr) 2870-2985 (C-H Str Vibr) 1819 (C-O Str Vibr) 1704-1745 (-N-C Str Vibr) 1588-1652 (-N=N Str Vibr) 724-762 (C-CL Str Vibr) 829-940 (SO ₃ H Str Vibr)
A ₅	3432 (OH Str Vibr) 3238 (NH Str Vibr) 2840 -2985 (C-H Str Vibr) 1704-1748 (C-O Str Vibr) 724-762 (C-CL Str Vibr) 829-992 (SO ₃ H Str Vibr) 1588-1648 (-N=N Str Vibr)

Table 1.8: Gas chromatography mass spectroscopy of synthesized intermediate based on naphthalimide derivatives

Intermediate code	Empirical formula	Experimental value of m/z fragment	Corresponding chare fragment	positive theoretical value
A	C ₂₄ H ₁₄ N ₄ O ₄	43. 0, 75. 0, 105. 0 177. 0, 207. 0 422. 0	C ₂ H ₅ NO ₂ ⁺ C ₆ H ₅ N ₂ ⁺ , C ₁₂ H ₅ NO ⁺ C ₁₂ H ₇ N ₄ ⁺ C ₁₇ H ₃ N ₃ O ₄ ⁺ , M ⁺	422.0

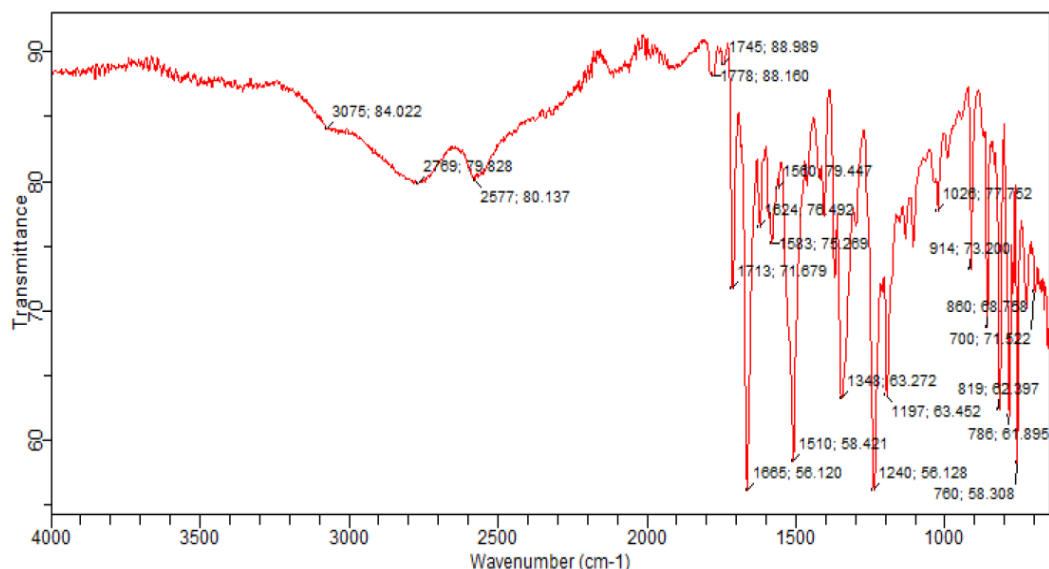


Figure A: TT-IR Spectra of Intermediate A

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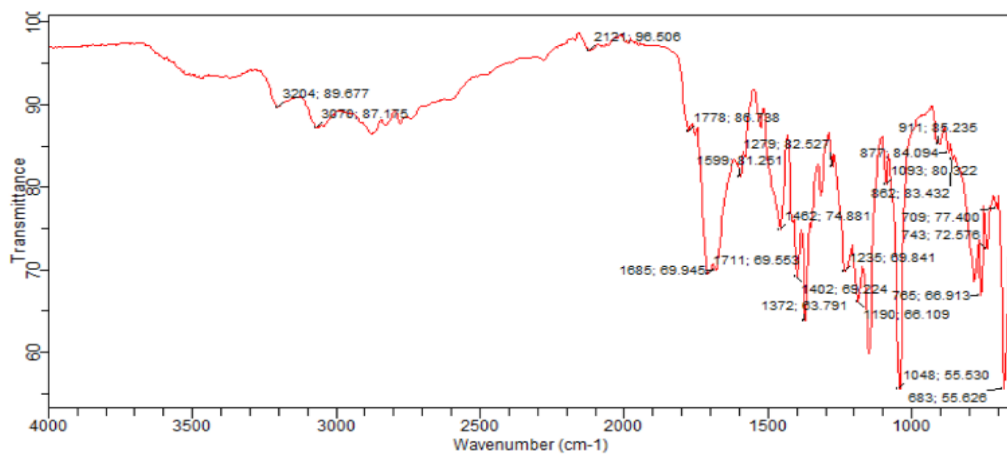


Figure A: 1. FT-IR Spectra of dye A₁

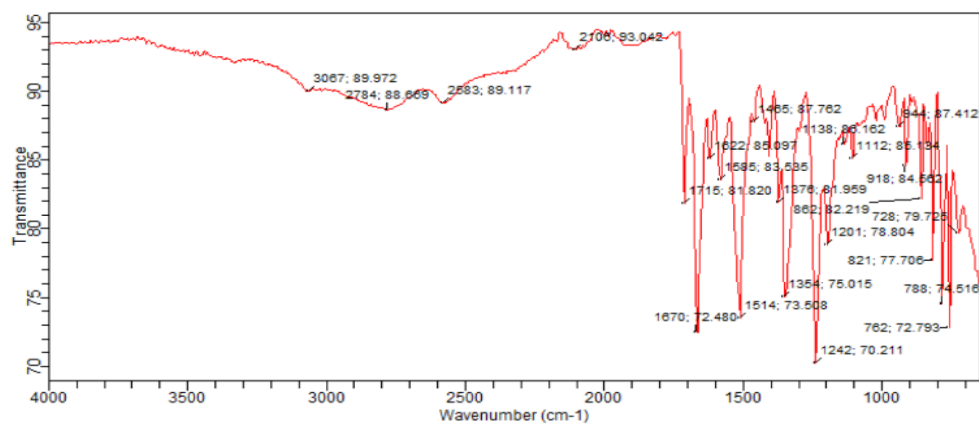


Figure A. 2. FT-IR Spectra of dye: A2

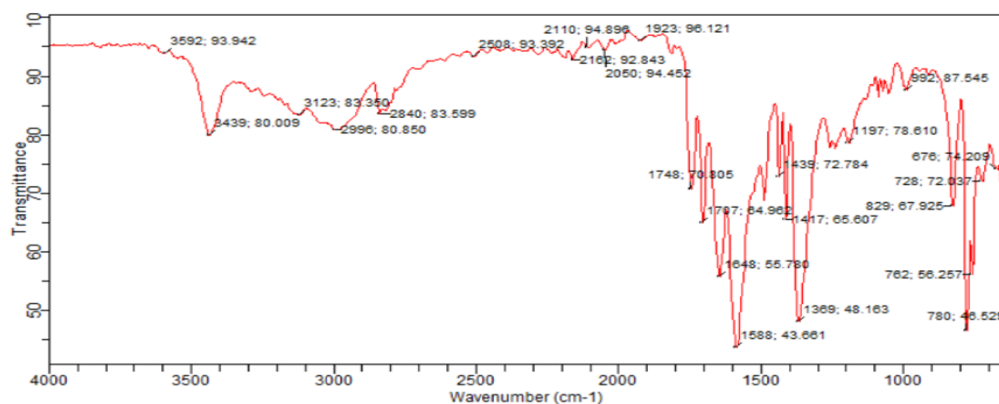


Figure A. 3. FT-IR Spectra of dye A3

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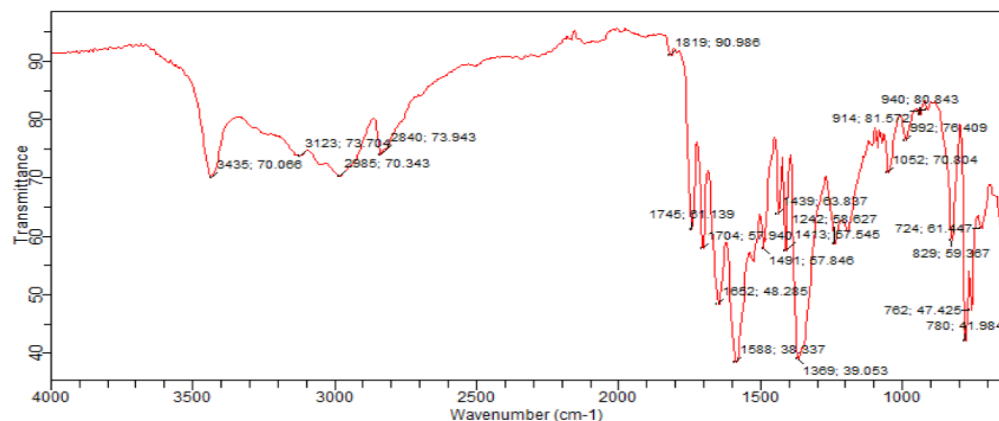


Figure A. 4. FT-IR Spectra of dye A₄

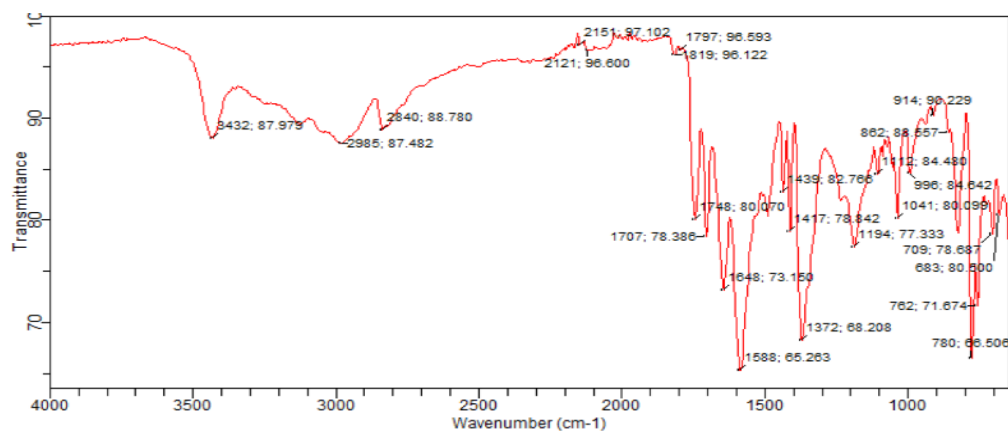


Figure A. 5. FT-IR Spectra of dye A₅

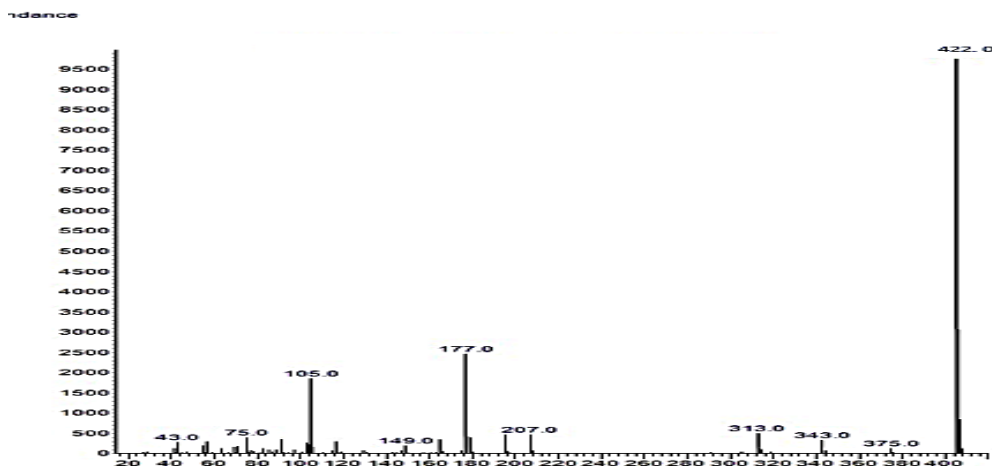


Figure A: GC-MS Spectra of Intermediate A

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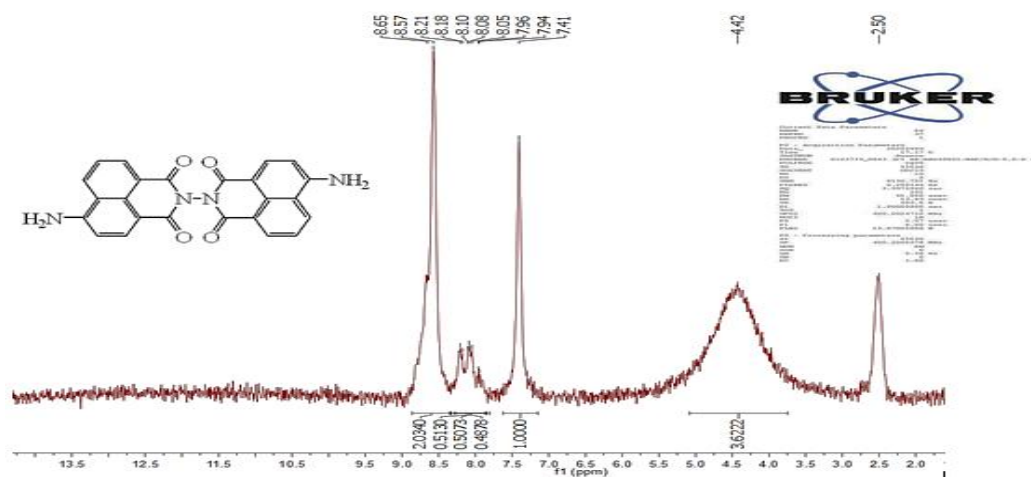


Figure B. ¹H NMR spectra of Intermediate A

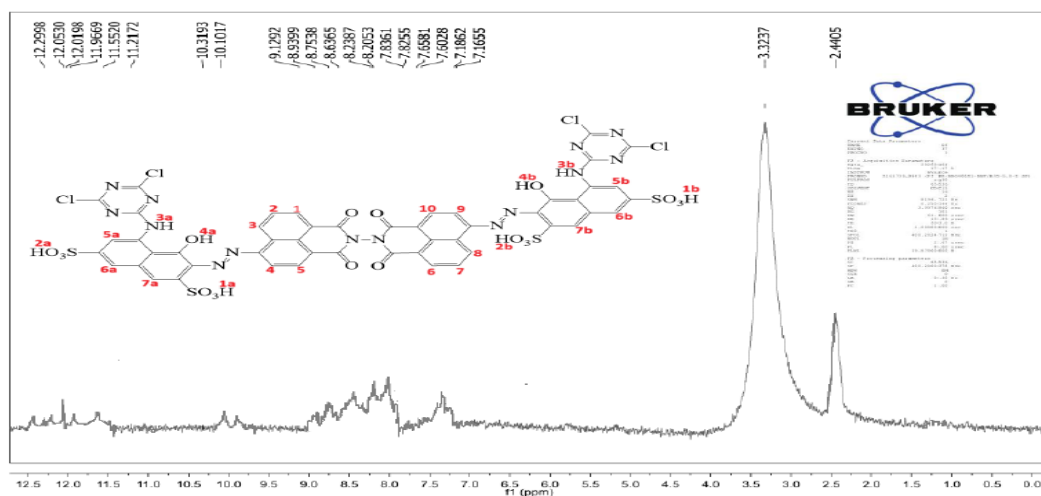


Figure B. ¹H NMR spectra of Dye A₁

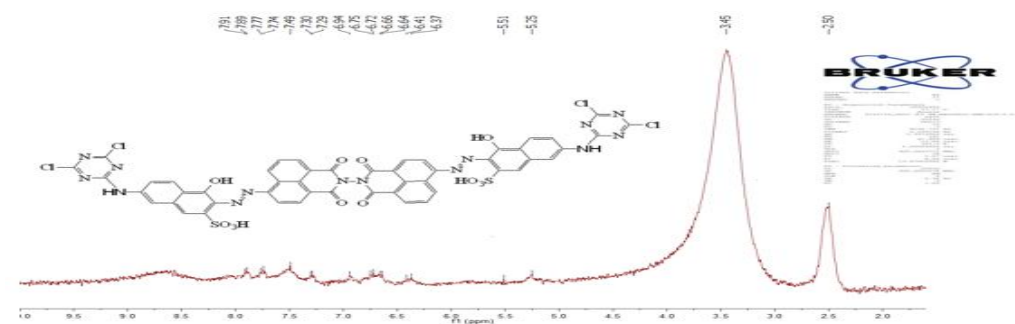


Figure B. ¹H NMR spectra of dye A₃

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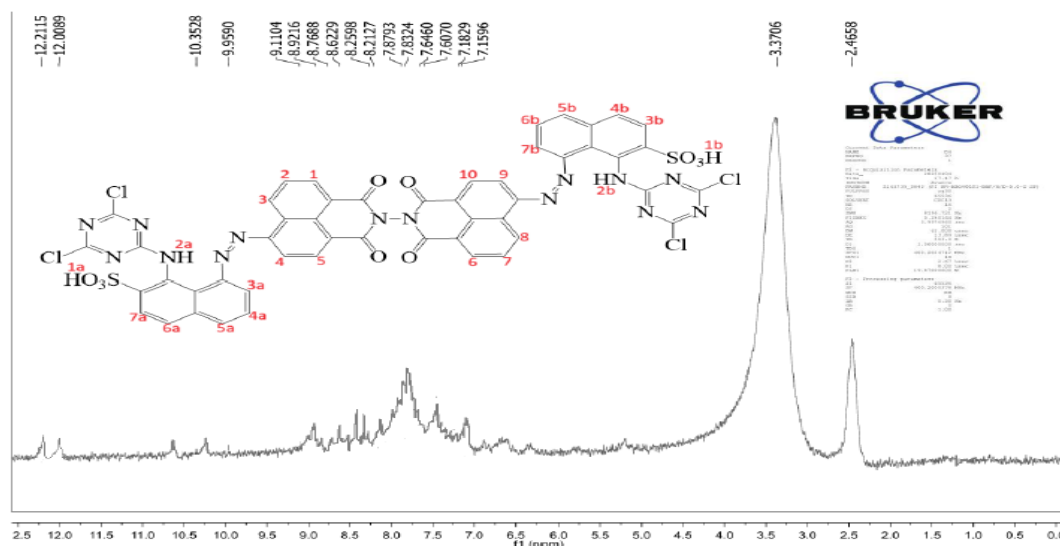


Figure B. ¹H NMR spectra of dye A₄

Displayed the structures of synthesized intermediates using acenaphthene as a starting material and several reaction steps like nitration, oxidation, amination and reduction were involved to obtain the various intermediates, with the colour crystals brown, yellow and dark brown, melting point ranging 276-290°C percentage yield ranged from 58-98% and the molecular weight range from 422. 40 (g/mol).

Physical properties of the synthesized bifunctional reactive dyes A₁-A₅ derive from Naphthalimide derivatives

The dichlorotriazine dyes **A₁-A₅** have moderate to higher molecular weight ranges from 1186. 76 -2097. 87 (g/mol) which translates to higher melting point ranges from 300-338 (°C). The percentage yield of the synthesized dyes is also very high although very few have low percentage yield which ranges from 68-92 %. The high percentage yield recorded is an indication that there was a control of the experimental conditions (Mousa *et al.*, 2014). The synthesized dyes were also very soluble in water which is an indication that the structure of the synthesized dyes are highly branched and the position of the functional groups in the carbon chains also favours the solubility of the dyes (OH, SO₃ H)[8]

[11];[12];. The colour or hue of the synthesized bifunctional dyes ranges from blue, brown, orange, black, purple, red, pink due to the presence of functional groups such as NH₂ and -OH on the dye structure

Spectroscopic characteristics of the synthesised bifunctional reactive dyes A₁-A₅ based on naphthalimide derivatives

The visible absorption maxima of the synthesised azo reactive dyes as recorded in Table 4. 3 felt within the visible region (400 - 700 nm) of the electromagnetic spectrum. The values of the molar extinction coefficient (ε) that were determined by Beer-Lambert's law are in the range of 2. 77×10⁻⁴ -8. 21×10⁻⁴ Lmol-cm⁻¹ which is an indication of high absorption intensity of the synthesised azo reactive dyes in DMF respectively. However, the synthesised azo reactive dyes have different chromophoric functionalities, but same bridging groups and it is also apparent that the value of λ_{max} depends on the coupling components used. The presence of electron donating or electron attracting (withdrawing) groups at the suitable position of the coupler ring affects the absorption characteristics of the synthesised azo reactive dyes [11].

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The wavelength of maximum absorption (λ_{max}) appeared in the visible region of the spectrum which is attributed to the π - π^* . Reaction of 6, 6-diamino 1H, 1'H, 3h, 3' H (2, 2' – bibenzo [de] isoquinoline) 1, 1'3, 3 – tetraone with cyanurated H-acid gave dye A₁, which absorbed at 525 nm in DMF, 511nm in distilled water, 509 nm in ethanol and 514 nm in ethanol plus HCL which dye A₁ in DMF is more bathochromic which could be attributed to the presence of electron donating or electron attracting (withdrawing) groups at the suitable position of the coupler ring and polar excited states of the synthesised azo reactive dyes are stabilized by polarization interactions forces as the polarisability of the solvent increases but when cyanurated H-acid was replaced with cyanurated R-acid which gave dye A₂ and absorbed at 521 nm, which gave hypsochromic shift of 4 nm when compared to dye A₁. This agrees with the findings of [13] and the presence of electron acceptor group of tetraazo components and electron donating group of the coupler.

Replacing cyanurated R with J-acid dye A₃ was synthesized which absorbed at 511 nm in DMF and gave a hypsochromic shift of 14 nm positive solvatochromic when compared to dye A₁ and hypsochromic shift of 10 nm negative solvatochromic when compared to dye A₂ due to the presence of sulphonate group and tetra azo component on the coupling components. Meanwhile replacing J-acid with gamma – acid dye A₄ was synthesized which absorbed at 422 in DMF and gave a hypsochromic shift of 103 nm when compared to dye A₁, hypsochromic shift of 99 nm when compared to A₂ and hypochromic shift of 87 nm when compared to dye A₃ respectively. However, replacing cyanurated gamma-acid with Tobias acid, dye A₅ was synthesized absorbed at 511 in DMF and gave a hypsochromic shift of 14 nm when compared to A₁, hypsochromic shift of 10 nm when compared to dye A₂ when compared to dye A₃ at on the same wavelength, when compared to dye A₄ bathochromic shift 89 nm respectively.

Infrared Spectra of the Synthesized bifunctional Reactive Dyes Based on Naphthalimide Derivatives

The FT-IR spectral of dye A₁

Dye A₁ was synthesized by tetrazotizing 6, 6-diamino 1H, 1'H, 3H, 3'H (2, 2-bibenzo[de] isoquinoline) 1, 1'3, 3-tetraone with cyanurated H-acid. The crystal colour, percentage yield and melting point were Blue, 82% and 304-306°C respectively. The IR spectrum of the synthesized dye A₁ showed all the basic functional groups indicated by the characteristics bands (stretching and bending vibration) at the IR spectra IR ν_{max} (cm^{-1}) figure A, 1 appendix A) of the dye A₁ showed stretching vibration at 3204 for OH, 3070 for C-H, N-H stretching vibration, at 2121. For C-H, 1599 for N=N 1648 for N-H bend vibration 1299 for C-N stretching vibration, at 1372 for N=O, C-C, 1709-743 cm^{-1} stretching vibration.

The ¹H NMR spectrum (figure B, 2 Appendix B) (400 MHz, DMSO) shows peak at 2. 0-3. 43 δ ppm correspond to the proton on the sulphonate group (SO₃H), the peak at 4. 0-5. 25 δ ppm correspond to the proton on the amine group (NH), the peak at 5. 35-5. 51 δ ppm correspond to the proton on the hydroxyl group (OH). The peak at 7. 22-6. 94 δ ppm correspond to the aromatic region of the spectrum. The peak at 7. 78-7. 74 δ ppm correspond to the aromatic region of the spectrum.

The FT-IR spectral of dye A₂

Dye A₂ was synthesized by tetrazotizing 6, 6-diamino 1H, 1'H, 3H, 3'H (2, 2-bibenzo [de] isoquinoline) 1, 1'3, 3-tetraone with cyanurated R-acid. The crystal colour, percentage yield and melting point were red, 74% and 300-302 °C respectively. The IR spectrum of the synthesized dye A₂ showed all the basic functional groups indicated by the characteristics band (stretching and bending vibration). The IR spectrum (IR ν_{max} (cm^{-1}) figure A2 appendix A) of the dye A₂ showed stretching vibration at 3432 O-H, -2840-2985 C-H stretching vibration 1791 N=N stretching vibration, 1648 N-H bending vibration 1439-1417 C-N stretching vibration, 1372 N-O stretching vibration.

709-766 cm^{-1} C-Cl stretching vibration. The ^1H NMR spectrum (figure B, 2 Appendix B) (400 MHz, DMSO) shows peak at 2. 0-3. 43 δ ppm correspond to the proton on the amine groups (NH), the peak at 10.05-10. 25 δ ppm correspond to the proton on the hydroxyl group protons (OH), the peak at 11. 35-12. 25 δ ppm correspond to the proton on the sulphuric group (SO_3H). The peak at 7. 16- 8. 15 δ ppm correspond to the aromatic group protons of the spectrum.

The FT-IR spectral t of dye A₃

Dye A was synthesized by tetrazotizing 6, 6-diamino 1H, 1H, 3H, 3'H (2, 2-bibenzo (de) isoquinoline) 1, 1'3, 3-tetraone with cyanurated J-acid. The crystal colour, percentage yield and melting point were Brown, 88% and 300-302 $^{\circ}\text{C}$ respectively. The IR spectrum of the synthesized dye A₃ showed all the basic functional groups indicated by the characteristic of the band. (Stretching and bending vibration. The (IR Vmax cm^{-1}) (figure A. 3, Appendix A) of the dye A₃ showed stretching vibration at O-H 3592, N-H stretching vibration at 3439 C-H stretching vibration at 2840-2996, -S-C-N stretching vibration 2508-2162, C-O stretching vibration at 1748, N-H bending vibration at 1648, N-O stretching vibration 1369 C-N stretching vibration 1417-1439, N=N stretching vibration at 1588, C-Cl stretching vibration at 728-762 cm^{-1} .

The ^1H NMR spectrum (figure B, 2 Appendix B) (400 MHz, DMSO) shows peak at 12.00-12. 30 δ ppm correspond to the proton on the sulphonic group (SO_3H), the peak at 9.95-10.35. δ ppm correspond to the proton on the amine group (NH), the peak at 5. 35-5. 51 δ ppm correspond to the proton on the hydroxyl group (OH). The peak at 7. 78-9. 95 δ ppm correspond to the aromatic protons region of the spectrum.

The FT-IR spectral of dye A₄

Dye A₄ was synthesized by tetrazotizing 6, 6-diamino 1H, 1H, 3H, 3'H (2, 2-bibenzo [de] isoquinoline) 1, 1'3, 3-tetraone with cyanurated γ -acid. The crystal colour, percentage yield and melting point were Black, 80 % and 308-3010 $^{\circ}\text{C}$ respectively. The IR spectrum of synthesized dye

A₄ showed all the basic functional groups indicated by the characteristics bands (stretching and bending vibration). The IR spectrum (IR Vmax cm^{-1}) Figure A-4 Appendix A) of the dye A₄ showed stretching vibration at O-H 3435, C-H stretching vibration at 2840-2985, C-O stretching vibration at 1819 N-C stretching vibration at 1704-1745, N=N stretching vibration at 1588-1652, C-Cl stretching vibration at 724-762 SO_3H stretching vibration 829-940 cm^{-1} .

The FT IR spectral of dye A₅

Dye A₅ was synthesized by tetrazotizing 6, 6-diamino 1H, 1H, 3H, 3'H (2, 2-bibenzo [de] isoquinoline) 1, 1'3, 3-tetraone with cyanurated Tobias-acid. The crystal colour, percentage yield and melting point were Orange, 76% and 300-302 $^{\circ}\text{C}$ respectively. The IR spectrum of synthesized dye A₅ showed all the basic functional groups indicated by the characteristics band (stretching and bending vibration). The IR spectrum (IR Vmax cm^{-1}) figure A-5 Appendix A) of the dye A₅ showed stretching vibration at OH 3432, N-H stretching vibration 3238, C-H stretching vibration at 2840-2985, C-O stretching vibration at 1704-1748, C-Cl stretching vibration at 724-762, SO_3H stretching vibration at 829-992 N=N stretching vibration at 1588-1648 cm^{-1} .

CONCLUSIONS

In conclusion, we reported the synthesis of 488ifunctional reactive dyes with naphthalimide derivative were synthesized starting with the following reaction nitration, oxidation, amination and reduction to synthesized the intermediate A [6, 6'-diamino-1H, 1'H, 3H, 3'H-[bibenzo[de]isoquinoline]-1, 1'3, 3'-tetraone,] which tetrazotised with cyanurated coupling component such as H-acid, R-acid, J-acid, γ -acid and Tobias acid. The synthesized dyes were purified by recrystallization method. The structure of the synthesized dyes were confirm using UV – visible,, FT-IR, MS and ^1H NMR spectroscopic technique., Spectrophotometric investigations of the dyes in solvents of different polarities were measured to obtain absorption maxima, molar extinction coefficient ana salvatochromic effects These dyes givss percentage yieldd of 76-

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88%, molecular weight of 1262.85-1454.98 g/mol, melting point 300-306°C with various hues such as blue, red, brown, black and orange respectively. The planarity of molecules and solvent polarity play an important role in emission spectra of dyes.

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