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Aqueous & Microwave Synthesis & Spectral Behaviour of Some Selected Photosensitizer Zero-Methine *&* Self-Assembly Mero Cyanine Dyes

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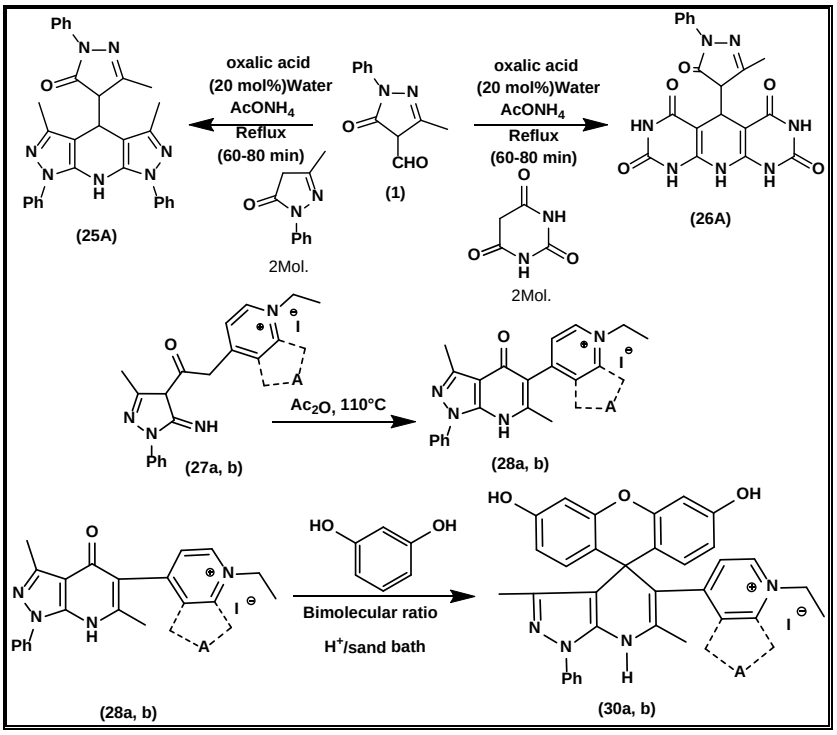
ABSTRACT

Aqueous Synthesis (water mediated) of three components Reactions resulted in dipyrazolo [3,4-b: 4',3'-e]pyridin-4-yl-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one and 5-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-9,10-di[H]pyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,5 H,7H)-tetra-one **(25, 26)A.** Thermal piperidine catalysis of the later **(25, 26)A** afforded bis-pyrazolo[3,4-b:4',3'-e] pyridin-4(1H, 7H, 8H)-pyrido [2, 3-d:6, 5-d'] dipyrimidine self-assembly **[ICT]**functional mero cyanine dyes **(25, 26)B** pyrazolo[3,4-b] pyridin-zero-5(4)-methine cyanine **(28a, b)** & related pyrazolo[3,4-b]pyridin-(7H)-zero(mono)-5[4(1)]-4-[2(4)]methine cyanine dyes **(29a-d)** were synthesised via acetic anhydride microwave irradiation of heterocyclization process of N-Ethyl-4-(2-(5-imino-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-2-keto-methylene-pyridin(quinolin)-1-ium **(27a,b)**flowingly interacted with 2-methyl-pyridin (quinolin)-2(4)-ium ethiodide salts under piperidine catalysis. Spiro [pyrazolo [3, 4-b] pyridin-4, 9'-xanthen]-N-ethyl-pyridin (quinolin)-zero (mono)-5(4)[15(4(1))] methine cyanine dyes were synthesised.to improve the specific characterization, photosensitization behaviour. The heterocyclic functional & related cyanine dyes were identified by elemental & spectral analyses. Special attention has been focus on absorption (emission) spectral, (media) chromic behaviour (acid-base properties).

Keywords: Recent Methodology, Aqueous Synthesis & Microwave synthesis, Absorption (Emission) Spectral, Solvato (Media) Chromic Behaviour

Graphical Abstract



Synthetic Routes of Starting Precursors

INTRODUCTION

Special attention was given to an implementation, preparations and Spectral Behaviour of heterocyclic cyanine to show the various aspects in order to satisfy the great demand in industrial and various biological fields. There was growing interest in the synthesis of heterocyclic compounds in view of their use in the cyanine dyes synthesis **[1-4].** Mero cyanine dyes had a large application as analytical reagents over a wide pH range this back to cyanine dyes had a permanent cationic charge in the basic media which then discharged on acidification **[5].** Mero cyanine was first synthesized from a century ago and continued to now days **[6-9]** but few of them focus on the synthesis of N-bridgehead mero cyanine dyes **[10-12].** Greener Synthesis of Heterocycles in Water Mediated Condition Technic of Some Selected Self-Assembly **[ICT]** Heterocyclic Functional & related methine cyanine dyes had been conducted by using of environmentally benign water as a solvent supports the green aspect of method as a simple and convenient one step method for synthesis of some heterocyclic compounds were reported and the major advantages of the proposed method were its simplicity, short reaction time, easy work-up, inexpensive catalyst, and good yields.

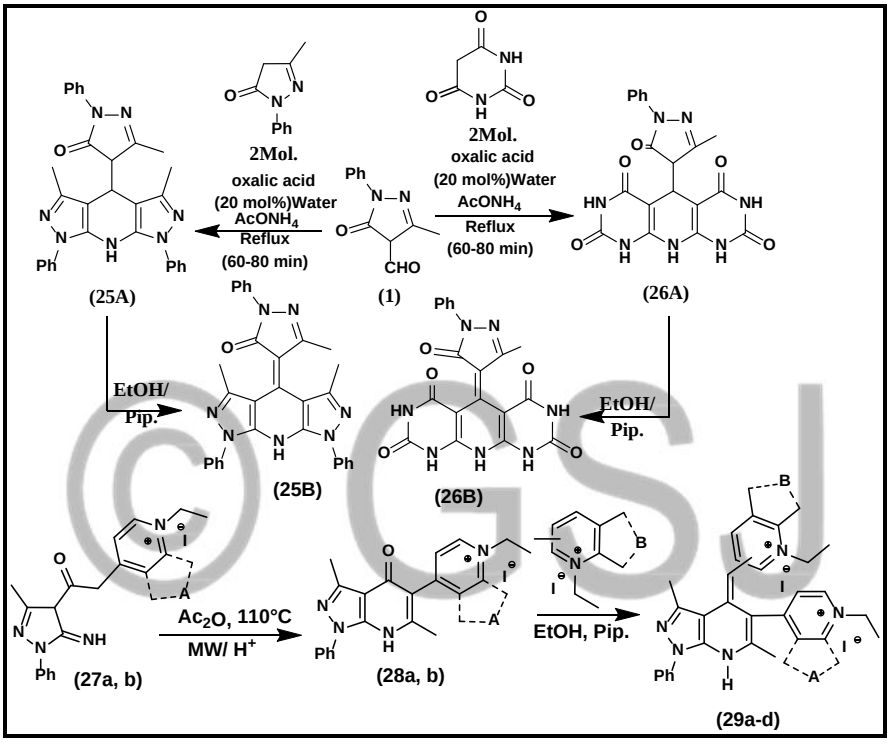
[13-20]. Aqueous synthesis is a simple & convenient one step method for synthesis of heterocyclic moieties & related methine cyanine dyes. Such new water reaction medium catalysis was reported & provides several advantages such as good yields, cheap catalyst, short reaction time, easy work-up, simplicity in operation & a rapid, high yielding. The use of environmentally benign water as a solvent supports the green aspect of method and

significant advancement toward an environmentally friendly reaction **[21].** New methodology (aqueous synthesis) was conducted for self-assembly **[ICT]** functional & related methine cyanine dyes synthesis **[29, 30]**. Thus, one pot synthesis of three component reaction under aqueous synthesis achieved the green aspect of the process.

RESULTS AND DISCUSSION

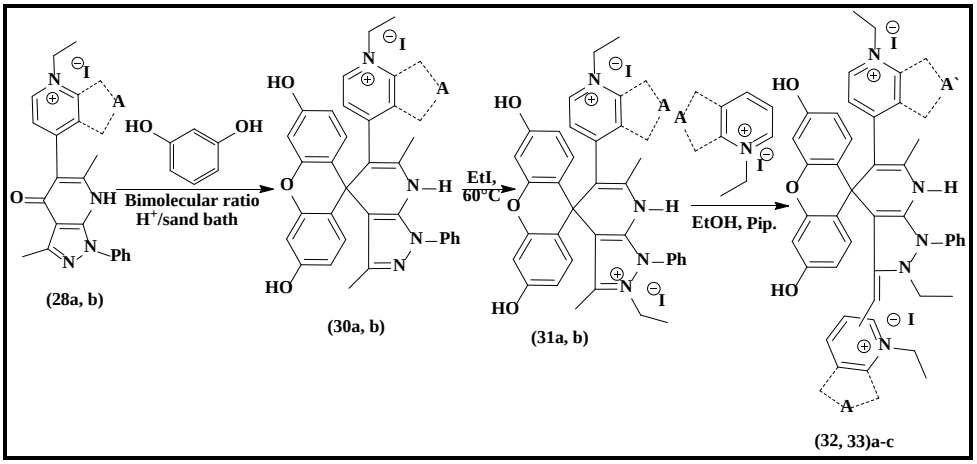
Interaction of an ethanolic solution of 4-formyl-3-methyl-1-phenyl-pyrazolin-5-one **(1),** equimolar ratio**, [22; 23]** and 3-methyl-1-phenyl-1H-pyrazolin-5-one and/or barbituric acid, in bimolecular ratio & ammonium acetate in aqueous solution of oxalic acid afforded 4-(3,5-dimethyl-1,7-diphenyl-1,4,7,8-tetra[H]dipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one & 5-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-9,10-di[H] pyrido[2,3-d:6,5-d'] dipyrimidin-2,4,6,8(1H,3H,5H,7H)-tetra-one **(25,26)A,** respectively,**.** Thermal piperidine catalysis flowingly 4-(3,5-dimethyl-1, 7-diphenyl-1, 4, 7, 8-tetra[H]di-pyrazolo[3, 4-b:4', 3'-e] pyridin-4-yl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one and 5-(3-methyl-5-oxo-1-phenyl-4, 5-di[H]-1H-pyrazol-4-yl)-9, 10-di[H] pyrido [2,3-d:6,5-d']dipyrimidin-2, 4, 6, 8(1H, 3H, 5H, 7H)-tetra-one **(25A, 26A)** flowingly an ethanol extraction afforded 4-(3,5-dimethyl-1,7-diphenyl-bis-pyrazolo[3,4-b:4',3'-e] pyridin-4(1H, 7H, 8H)-pyrido [2, 3-d:6, 5-d'] dipyrimidine self-assembly endocyclic **[ICT]** functional mero cyanine dyes **(25, 26)B.** An eye-opening feat of building up pyrazolo [3,4-b]pyridin-zero(mono) was synthesized. Thus, acetic anhydride catalysis of 3-methyl-1-phenyl-pyrazolin-5-imine-4-keto-methylene-N-pyridin (quinolin)-4-ium-iodide) **(27a,b) [29;33]** undergoes molecular heterocyclization to afford 3,6-dimethyl-4-oxo-1-phenyl-4,7-di[H]-1H-pyrazolo[3,4-b]pyridin- zero-5(4)-methine cyanine **(28a, b).** The interaction of an ethanolic solution of **(28a, b)** and 2(4)-methyl-pyridin (quinolin)-[2(4)]ethiodide salt, in equimolar ratio, under piperidine catalysis afforded 3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-(7H)-zero(mono)-5[4(1)]-4-[2(4)]methine cyanine dyes **(29a-d).** Acetic anhydride catalysis of 3-methyl-1-phenyl-pyrazolin-5-imine-4-keto-methylene-N-pyridin(quinolin)-4-ium-iodide)**(27a,b),[29,30]**undergoes molecular hetero-cyclization under irradiation in microwave oven (appropriate time at 200 watt) afforded 3,6-dimethyl-4-oxo-1-phenyl-4,7-di[H]-1H-pyrazolo[3,4-b]pyridin-zero-5(4)-methine cyanine **(28a,b).** The interaction of an ethanolic solution of **(28a, b)** & 2(4)-methyl-pyridin(quinolin)-[2(4)] ethiodide salt, equimolar ratio, under piperidine catalysis afforded 3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-(7H)-zero (mono)-5[4(1)]-4-[2(4)]methine cyanine dyes **(29a-d), Scheme (1).** In continuation of our work, methine cyanine synthesis of 1-ethyl-4-(3-methyl-5-oxo-1-phenyl-1,5-di[H]spiro[pyrazole-4,3'-pyrrolo[3',4':3,4]pyrazolo[1,5-a]pyridin]-mono-1[4(1)] & 4-(5-(acetyl-imino)-1',3-dimethyl-1-phenyl-1,5-di[H] spiro [pyrazol-4,3'-pyrrolo [3, 4-a]indolizin]-zero[4(1)]methine cyanine dyes **(31a,b, (32,33)a-c** were synthesised via an ethanolic solution of 3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin(quinolin)-4(7H)-one-5-zero-[4(1)] methine **(28a, b)** & resorcinol, equi (bi) molar ratios, under acidic medium

undergoes cyclocondensation reaction flowingly cyclo-dehydration processes to afford 3',6'-dihydroxy-3,6-dimethyl-1-phenyl-1,7-di-[H]spiro[pyrazolo[3,4-b]pyridin-4,9'-xanthen]-zero-5[4(1)] methine cyanines **(30a, b).** Selective quaternization of an ethanolic solution of **(30a, b),** equimolar ratio, using excess ethyl iodide afforded 3',6'-dihydroxy-3,6-dimethyl-1-phenyl-1,7-di[H]spiro[pyrazolo[3,4-b]pyridine-4,9'-xanthen]-2-ium-ethiodide-zero-5[4(1)]methine cyanine **(31a, b).** The interaction of an ethanolic solution of **(31a, b)** & pyridin (quinolin)-4(1)-ium-ethiodide salts ,equimolar ratio, under piperidine catalysis afforded 3', 6'-dihydroxy-3,6-dimethyl-1-phenyl-1,7-di[H]spiro[pyrazolo[3,4-b]pyridin-4,9'-xanthen]-N-ethyl-pyridin (quinolin)-zero[mono]-5(4) **[15** (4(1))]methine cyanine dyes **(32, 33)a-c**, **Scheme (2).**



Scheme (1) Substituents:

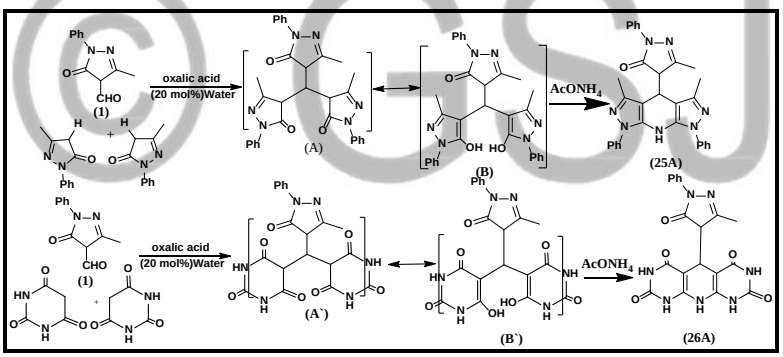
(27, 28)a, b: A=H-4-ium (a) A=C_4H_4-4-ium (b); **(29a-d):** A(B)=H-4-ium (C_4H_4-2-ium) (a); A(B)=H-4-ium (H-4-ium) (b); A(B)=C_4H_4-4-ium (C_4H_4-2-ium) (c); A(B)=C_4H_4-4-ium (H-4-ium) (d)



Scheme (2) Substituents

(28, 30) a, b: A=H-4-ium (a), C_4H_4-4(1)-ium (b), **(31, 32) a-c:** A=H-4-ium (a); A=C_4H_4-4-ium (b); A= H-4-ium (c).

The formation of **(25, 26)**A was suggested to proceed via bimolecular nucleophilic addition reaction of 3-methyl-1-phenyl-pyrazolin-5-(one) and/or barbituric acid to formyl group of 4-formyl-3-methyl-1-phenyl-pyrazolin-5-one to form an intermediate **(A, A`)** flowingly an enolization to give an intermediate **(B, B`).** The later intermediates **(B, B`)** undergo heterocyclization process under ammonium acetate to give desire **(25, 26)A Equation (1)**



Equation (1): Suggested Formation Mechanism of **(25, 26) A**

The structure of **(25A & 26A)** was confirmed by elemental & spectral analysis. IR (ν^{KBr} cm^{-1}) showed, in addition to, general frequency absorption bands at: 3306 cm^{-1} (γ NH cyclic pyridine), 3067 & 2926 cm^{-1} (γ CH, CH_3), 1713 cm^{-1} (γ cyclic C=O), 1594 cm^{-1} (γ C=C conj. Ar.), 757 cm^{-1} (γ phenyl mono-subs.) for **(25A);** 3313 cm^{-1} (γ NH cyclic pyridine and pyrimidine), 3067 & 2926 cm^{-1} (γ CH, CH_3), 1668 cm^{-1} (γ cyclic C=O), 1542 cm^{-1} (γ C=C Ar.), 751 cm^{-1} (γ phenyl mono-subs) for **(26A),** absorption bands at 3325 cm^{-1} (γ cyclic pyridine-NH), 2925 cm^{-1} (γ CH, CH_3), 1663 cm^{-1} (γ cyclic pyrazole C=O), 1595 cm^{-1} (γ conj. C=C Ar.), 756 cm^{-1} (γ phenyl mono-subs.) for (25B) and 3314 cm^{-1} (γ NH), 3061 cm^{-1} (γ CH, CH_3), 1686 cm^{-1} (γ C=O), 1594 cm^{-1} (γ C=C Ar.), 755 cm^{-1} (γ phenyl mono-subs.) for **(26B), [24,25].** IR (ν^{KBr} cm^{-1}) of **(30a, b)** showed, in addition to, general frequency absorption bands at 3214 cm^{-1} (γ OH, xanthene), 2966 cm^{-1} (CH, heterocyclic quaternary salt), 2928 cm^{-1} (γ

CH, CH_3), 1601 cm^{-1} (γ C=C conj. Ar), 1499 cm^{-1} (γ cyclic C=N), 758 cm^{-1} (γ phenyl mono-subs.) for (30a) and 3258 cm^{-1} (γ OH for xanthene), 2968 cm^{-1} (γ CH, heterocyclic quaternary salt), 2933 cm^{-1} (γ CH, CH_3), 1597 cm^{-1} (γ C=C conj.), 1500 cm^{-1} (γ cyclic C=N), 757 cm^{-1} (γ Ph mono subs) for **(30b), [24,25].**

^{1}H-NMR (DMSO-d_6, 500 MHz) spectra of **(30a)** showed, in addition to, general signals at observed [found]: δ 7.62-7.58 ppm [δ 9.14-7.80 ppm, ∆δ=0.22-1.52 ppm](m, 5H, ph), δ 7.36-6.57 ppm [δ 7.42 -6.82 ppm, ∆δ=0.06-0.25 ppm] (m, 10H, Ar), δ 4 ppm [δ 4.57 ppm, ∆δ=0.57 ppm] (s, 1H, NH), δ 5.35 ppm [δ 4.53 ppm, ∆δ=0.82 ppm] (s, 2H, 2OH), δ 4.07 ppm[δ 3.25 ppm, ∆δ=0.82 ppm](q, 2H, CH_2), δ 2.26-1.93 ppm[δ 2.37- 2.14 ppm, ∆δ=0.11-0.21 ppm] (s, 6H, $2CH_3$), δ 1.41 ppm[δ 1.53 ppm, ∆δ=0.12] (t, 3H, CH_3), **[26,27].** ^{1}HNMR (DMSO-d_6, 500 MHz) spectra of **(25A, 26A)** showed, in addition to, general signals at observed [found]: δ 7.94-7.43 ppm [δ 7.94 –7.28 ppm, ∆ δ=0.15 ppm (m, 15H, 3Ph)], δ 4 ppm [δ 5.45 ppm, ∆δ=1.45 ppm] (s, 1H, cyclic NH)], δ 4.3-3.2 ppm [δ 4.56 ppm, ∆δ=0.26 ppm] (d, 2H, CH cyclic), δ 1.94-1.93 ppm [δ 2.43-2.12 ppm, ∆δ=0.49 ppm] (s, 9H, $3CH_3$] for **(25A**) **[26 & 27].** ^{1}H-NMR spectra of **(29a)** showed, in addition to, general signals at observed [found]: δ 7.62-7.45 ppm [δ, 9.90–7.91 ppm, ∆δ=0.46-2.28 ppm] (m, 5H, Ph)], δ 8.81-7.57 ppm [δ 7.92–6.30 ppm, ∆δ=0.89-1.15 ppm] (m, 10H, 2Ar)], δ 7.15 ppm [δ 5.94, ∆δ=1.21 ppm] (s, 1H,=CH)], δ 4 ppm [δ 5.52 ppm, ∆δ=1.52 ppm] (s, 1H, NH), δ 4.51-4.43 ppm [δ 5.07-4.51 ppm, ∆δ=0.57-0.08 ppm] (q, 4H, $2CH_2$)], δ 2.47-1.63 ppm [δ 2.74-2.12 ppm, ∆δ=0.27-0.94 ppm] (s, 6H, $2CH_3$), δ 1.58-1.29 ppm [δ 1.52, ∆δ=0.0.6-0.23 ppm) (t, 6H, $2CH_3$)] for **(29a), [26,27].** Structure of **(25, 26)B** based on (ESI-Ft-mass) was considered most likely and in agreement with molecular formula ($C_{31}H_{25}N_7O$), resulted in m/z found=511.58453 (calcd. 511.58352 For $[M]^+$) with an error ΔM=2.799 ppm for **(25B).** Molecular formula ($C_{14}H_8IN_3O_4$) resulted in m/z found =409.14233 (calcd. 409.14367 For $[M]^+$) with an error of ΔM=2.23 ppm for **(26B).** Mass spectra 70 ev (m/z) of **(30a)** based on mass spectra was considered most likely & in agreement with molecular formula $C_{33}H_{29}IN_4O_3$ resulted, in addition to, general abundance peaks at general observed abundance peaks m/z= 658, 620, 591, 535, 512,213, 91, characteristic abundance molecular ion peaks (base peak) observes m/z [M^+] found m/z=357 (91), **[33,34]. [33, 34].**

COLOUR AND SPECTRAL BEHAVIOUR

4-(3,5-Dimethyl-1,7-diphenyl-1,4,7,8-tetra[H]dipyrazolo[3,4-b: 4',3'-e] pyridin-4-yl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one & 5-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-9,10-di[H]pyrido[2,3-d:6,5-d']dipyrimidin-2,4,6,8 (1H, 3H,5H,7H)-tetra-one **(25, 26) A &**4-(3,5-dimethyl-1,7-diphenyl-bis-pyrazolo[3,4-b:4',3'-e]pyridin-4(1H,7H,8H)-pyrido[2,3-d:6,5-d']di-pyrimidin-self-assembly endo-cyclic **[ICT]** functional mero cyanine dyes **(25, 26)B** are highly colour compounds. Their colour in

an ethanolic solution are ranging from pale brown to red (reddish brown to red), easily soluble in either polar or non-polar exhibiting colour solutions (violet), they are soluble in conc. H_2SO_4 exhibit no iodine vapour on warming, **Tables (8).** 3-Methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-(7H)-zero(mono)-5[4(1)]-4-[2(4)] methine cyanine dyes **(29a-d)** are highly colour compounds their colour are ranging from red to violet and in an ethanolic solution are ranging from red to violet, easily soluble in either polar or non-polar exhibiting colored solutions (green blue to green), they are soluble in conc. H_2SO_4 exhibit iodine vapour on warming. Such dyes **(29a-d)** exhibit on acidification green blue in colour, **Tables (1, 2 & 5).** 3',6'-Dihydroxy-3,6-dimethyl-1-phenyl-1,7-di[H]spiro[pyra-zolo[3,4-b]pyridin-4,9'-xanthen]-zero-5[4(1)]methine **(30a,b)** & 3', 6'-dihydroxy-3, 6-dimethyl-1-phenyl-1,7-di[H]spiro [pyrazolo [3,4-b]pyridin-4, 9'-xanthen]-N-ethyl-pyridin (quinolin)-zero (mono)-5(4)[15 (4(1))] methine cyanine dyes **(32, 33)a-c** are highly colour compounds. Their colour in an ethanolic solution are ranging from red brown to red for dyes **(30a, b)** and red to violet for **(32, 33)a-c,** they are easily soluble in either polar or non-polar) exhibiting colored solutions (violet/ blue) for **(30a, b)** & blue green to orange for **(32, 33)a-c**, they are soluble in conc. H_2SO_4 exhibit iodine vapour on warming. Such dyes **(30a, b & (32, 33) a-c** exhibit on acidification violet in colour. Meanwhile on basification exhibit green blue (green) in colour, **Tables (2 & 4-6).** In point view of spectral behavior of the absorption (emission) spectra of 4-(3,5-dimethyl-1,7-diphenyl-1,4,7,8-tetra[H]dipyrazolo [3,4-b:4',3'-e]pyridin-4-yl)-3-methyl-1-phenyl-1H-pyrazolin-5(4H)-one **(25A)** and/or 5-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-9,10-di[H]pyrido[2,3-d:6,5-d']dipyrimidin-2,4,6,8(1H,3H,5H,7H)-tetraone **(26A),** in 95% ethanol, the photosensitization resulted in absorption (emission) bands, batho(hypso) chromically shifted depending on the nature of heterocycle nuclei. Thus, dyes absorbed fundamental light of violet & emitted (yellow green) in colour as they have got absorption (emission) values at **(25A, 26A**; λ_{max}=399, 401 nm; ε_{max}=21395, 31810 $M^{-1}cm^{-1}$] **(25, 26) A, E** $_{max}$=460, 506 nm]. Meanwhile self-assembly-4-(3,5-dimethyl-1,7-diphenyl-dipyrazolo[3,4-b:4',3'-e]pyridin-4(1H,7H,8H)-3-methyl-1-phenyl-1H-pyrazol-5 (4H)-one functional endocyclic mero **(25B)** & self-assembly 9, 10-di[H]pyrido[2, 3-d:6, 5-d'] dipyrimidin-2,4,6,8(1,3,5,7[H])-tetraone functional endo cyclic mero cyanine dye **(26B)** in 95% ethanol, photosensitization resulted in absorption (emission) bands, batho(hypso) chromically shifted depending

on nature of heterocycle nuclei. Thus, the dyes absorbed fundamental light of violet & emitted (yellow green) in colour as they have got absorption (emission) values at **(25B, 26B**; λ_{max}=412, 422 nm; ε_{max}=1081, 937 $M^{-1}cm^{-1}$] (**25B, 26B,** E_{max}=118, 120 nm) **Table (1).** In comparing the absorption spectra of (25B and 26B), It was obvious that the dye **(25B)** is hypsochomic shift compared to **(26B)** attributed to highest stability of six membered ring (pyrimidine) in **(26B)** compared to five membered ring (pyrazole) in **(25B), Table (1).**

The spectral behavior & photosensitization of 3-methyl-1-phenyl-1H-pyrazolo [3,4-b] pyridin-(7H)-5-zero [4(1)] or mono [2(4)] methine cyanine dyes **(29a-d)** in 95% EtOH resulted in absorption (emission) bands, batho (hypso) chromically shifted depending on inserting heterocyclic quaternary salt and their linkage position. Thus, absorbed fundamental green blue-green and emitted (red-orange) colour, as they have got absorption (emission) values at (**29a**; λ_{max}=493 nm; ε_{max}=16050 $M^{-1}cm^{-1}$] **(29a**, E_{max}=568 nm (27 kcal/mol)]. Substituting of A=H-4-ium, B=C_4H_4-2-ium in **(29a)** by A=H-4-ium, B=H-4-ium in **(29b)** causes hypsochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 10 nm (Δ E_{max}=18 nm), as they have a got absorption (emission) values at **(29b);** λ_{max}=483 nm; ε_{max}=17880 $M^{-1}cm^{-1}$] **(29b;** E_{max}=550 nm (28 kcal/mol)). **Table (2).**This is due to decrease conjugation in pyridin-4-ium in **(29b)** than quinolin-2-ium **(29a)** as electron sink. Substituting of A= H-4-ium, B= H-4-ium in **(29b)** by A=C_4H_4-4-ium, B=C_4H_4-2-ium **(29c)** causes bathochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 53 nm (Δ E_{max}=39 nm), as they have a got absorption (emission) values at (**29c**; λ_{max}=536 nm; ε_{max}=18071 $M^{-1}cm^{-1}$) (**29c**; E_{max}=589 nm (26 kcal/mol)). This is due to more extended conjugation in quinolin-4(2)-ium than pyridin-4-ium as electron sink. Substituting of A=C_4H_4-4-ium, B= C_4H_4-2-ium in dye **(29c)** by A=C_4H_4-4-ium, B=H-4-ium in dye **(29d)** causes hypsochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 41 nm (Δ E_{max}=30 nm) as they have a got absorption (emission) values at **(29d);** λ_{max}=495 nm; ε_{max}=19808 $M^{-1}cm^{-1}$ [**29d;** E_{max}=559 nm (30 kcal/mol)]. This is due to the decrease extended conjugated in pyridine-4-ium as electron sink. It was obvious that dyes **(29a-d)** have further stock shift between fluorescence & emission spectra in 95% ethanol then underwent change to higher and lower depending on nature of heterocyclic quaternary salt, thus, dyes **(29a-d)** showed a range of $\Delta\lambda$ 53-75 nm concomitant with 26-30 x 10^5 kcal/mol respectively. Such diffuse and large stokes shifts for **(29a-d)** was suggested

to be partly result of charge transfer (solute-solvent) interaction of such dyes, in addition to, stokes shift effects the generation properties were explained by change in the mobility of π-electron in conjugated chromophore of such dyes, **Table (1).** The excitation energy ($E_{0\text{-}0}$) of dyes depend basically on type of substituents and nature of heterocyclic quaternary salt (A) which have a great effect on number of π-conjugations in fluorophore. Thus, the first (lower) excitation energy ($E_{0\text{-}0}$) of **(29a**; $E_{0\text{-}0}$=2.31). A=H-4-yl, B=C_4H_4-2-ium in dye **(29a)** by A=H-4-yl, B= H-4-ium in dye **(29b) (29b**; $E_{0\text{-}0}$=2.37) causes higher value of gap ($E_{0\text{-}0}$). This is due to decreasing conjugation in dyes **(29b)** than **(29a).** Substituting A=H-4-yl, B=H-4-yl in dye **(29b)** by A=C_4H_4-4-ium, B=C_4H_4-2-ium **(29c;** $E_{0\text{-}0}$=2.21) causes lower value of gap ($E_{0\text{-}0}$). This is due to increasing conjugation in dye (29c) compared to **(29b).** Substituting of A=quinolin-4-ium, B=quinolin-2-ium in **(29c)** by quinolin-4-ium, B=pyridin-4-ium in **(29d**; $E_{0\text{-}0}$=2.28) causes high value of gap ($E_{0\text{-}0}$). This is due to decreasing conjugation in **(29d)** compared to **(29c).** In point view of spectral behavior of 3-methyl-1-phenyl-1,7-di[H]spiro[pyrazolo[3,4-b]pyridin(quinolin)-4, 9'-xanthene]-3', 6'-diol-5-zero-[4(1)]methine **(30a, b)** in 95% EtOH. photosensitization of such dyes resulted in absorption (emission) bands, batho (hypso) chromically shifted depending on inserting heterocyclic quaternary salt and their linkage position thus, absorbed fundamental light of blue-green (yellow-purple) colour as they have got absorption (emission) values at **(30a ;** λ_{max}=428 nm; ε_{max}=10050 $M^{-1}cm^{-1}$] (**30a**, E_{max}=570 nm (60 kcal/mol)]. Substituting of pyridin-4-ium in dye **(30a)** by quinolin-4-ium in dye **(30b)** causes bathochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 42 nm (Δ E_{max}=14 nm), as they have a got absorption (emission) values at **(30b;** λ_{max}=470 nm; ε_{max}=10780 $M^{-1}cm^{-1}$),(**30b**; E_{max}=584 nm (55 kcal/mol)], **Table (2)**. This is due to more extended conjugated in quinolin-4-ium than pyridin-1-ium as electron sink. In point view of spectral behavior of 2'-ethyl-6'-methyl-1'-phenyl-1',2',3',7'-tetra [H]-10H-spiro[anthracene-9,4'-pyrazolo[3,4-b]pyridine]-3,6-di-ol-3'-mono-3[4(1)]-5'-zero-[4(1)] methine cyanine **(32, 33 a-c)** & photosensitization in 95% EtOH of such dyes resulted in absorption (emission) bands, batho(hypso) chromically shifted depending on inserting heterocyclic quaternary salt linkage position. Thus, absorbed fundamental blue green-orange light and emitted (red-green blue) colour as they have got absorption (emission) values at **(32a;** λ_{max}=493 nm; ε_{max}=12550 $M^{-1}cm^{-1}$), (**32a**, E_{max}=566 nm (60 kcal/mol)]. Substituting of A=H-4-ium in dye **(32a)** by A=C_4H_4-

4-ium in dye **(32b)** causes bathochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 52 nm (ΔE_{max}=60 nm), as they have got absorption (emission) values at **(32b);** λ_{max}=545 nm; ε_{max}=16520 $M^{-1}cm^{-1}$ (**32b;** E_{max}=626 nm (54 kcal/mol)], **Table (1).** This is due to the more extended conjugated in quinolin-4-ium than pyridin-1-ium as electron sink. Substituting of $A=C_4H_4$-4-ium in dye **(32b)** by $A=C_4H_4$-1-ium in dye **(32c)** causes hypsochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 15 nm (ΔE_{max}=21 nm), as they have a got absorption (emission) values at **(32c);** λ_{max}=530 nm; ε_{max}=6721 $M^{-1}cm^{-1}$ **(32c**; E_{max}=605 nm (54 kcal/mol)]. This is due to the decrease extended conjugation in quinolin-2-ium than quinolin-4-ium as electron sink. In point view of the spectral behaviour dye **(33a)** absorbed fundamental light green & emitted purple as they have got absorption (emission) values at (**33a**; λ_{max}=503 nm; ε_{max}=12010 $M^{-1}cm^{-1}$), (**33a;** E_{max}=584 nm (55 kcal/mol)]. This is due to the decrease extended conjugation in quinolin-4-ium as electron sink. Substituting of A=H-4-ium in dye in **(33a)** by $A=C_4H_4$-4-ium **(33b)** causes bathochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 95 nm (ΔE_{max}=69 nm) as they have got absorption (emission) values at **(33b;** λ_{max}=598 nm; ε_{max}=16430 $M^{-1}cm^{-1}$) **(33b**; E_{max}=653 nm (61 kcal/mol)]. This is due to the increase extended conjugation in two quinolin-4-ium units as electron sink. Substituting of $A=C_4H_4$-4-ium in **(33b)** by $A=C_4H_4$-1-ium **(33c)** causes hypsochromic shift of absorption (emission) by $\Delta\lambda_{max}$ = 55 nm (ΔE_{max}=33 nm) as they have got absorption (emission) values at **(33c);** λ_{max}=543 nm; ε_{max}=15830 $M^{-1}cm^{-1}$ (**33c;** E_{max}=620 nm (56 kcal/mol)). This is due to the decrease extended conjugation in quinolin-2-ium than quinolin-4-ium as electron sink. It was obvious that dyes **(32, 33 a-c)** have further stock shift between the fluorescence (emission) spectra in 95% EtOH underwent change to higher & lower depending on alkyl substituent & nature of heterocyclic quaternary salt. Thus, dyes **(32, 33 a-c)** showed a range of Δ λ 55-81 nm concomitant with 54-61 x 10^5 kcal/mol kcal/mol respectively. Such diffuse & large stokes shifts for **(32, 33 a-c)** was suggested to be partly result of charge transfer (solute-solvent) interaction of such dyes, in addition to, stokes shift effects the generation properties were explained by change in the mobility of π-electron in conjugated chromophore of such dyes, **Table (1).** The excitation energy ($E_{0\text{-}0}$) of dyes depend basically on the type of substituents and the nature of heterocyclic quaternary salt (A) which have a great effect on the number of π-conjugations in fluorophore and calculated from the intersection of absorption

(emission) spectra, the first (lower) excitation energy ($E_{0\text{-}0}$) of **(32a;** $E_{0\text{-}0}$=2.33). Substituting of A=H-4-ium in dye **(32a)** by A=C_4H_4-4-ium in dye **(32b;** $E_{0\text{-}0}$=2.10) causes lower in gap ($E_{0\text{-}0}$). This is due to increasing conjugation in dye **(32b)** than **(32a).** Substituting A=C_4H_4-4-ium in dye **(32b)** by A=C_4H_4-1-ium in dye **(32c)** resulted in high $E_{0\text{-}0}$ **(32c;** $E_{0\text{-}0}$=2.21). This is due to decreasing conjugation in dye **(32c)** compared to **(32b).** Substituting of A=C_4H_4-4-ium in dye **(32c)** by A=C_4H_4-1-ium in dye **(33a)** increasing $E_{0\text{-}0}$ value (**33a**; $E_{0\text{-}0}$=2.27). This is due to decreasing the conjugation inside the dye molecule. Substituting A=H-4-ium in dye **(33a)** by A=C_4H_4-4-ium in dye **(33b)** causes decrease in $E_{0\text{-}0}$ value **(33b**; $E_{0\text{-}0}$=2.01). This is due to increasing conjugation. Substituting A=C_4H_4-4-ium in dye **(33b)** by A=C_4H_4-1-ium in dye **(33c)** causes increase in $E_{0\text{-}0}$ value **(33c;** $E_{0\text{-}0}$=2.13). This is due to decreasing conjugation in dye **(33c)** compared to dye **(33b)**. On comparison of dyes **(29a-d & 30a, b & 32, 33 a-c)**, It was observed that, the absorption maximum of **(29a-d & 32, 33 a-c)** are red-shifted that those of **(30a, b)** attributed that dyes **(30a, b)** possess only one **[ICT]** pathway compared to dyes **(29a-d & 32, 33 a-c)** which have two **[ICT]** pathways.

Table (1): Normalized Absorption and Emission Spectra of (25A, B & 26A,B, 29a-d, 30a, b & 32, 33 a-c) in (10^{-4} M) EtOH

Comp. No.	λ_{max} (ε_{max})	Absorbed Colour	E_{max} (nm) (Intensity 10^5)	Transmitted Colour	Stokes shift	I $E_{0\text{-}0}$
25A	399 (2.1395)	_	460	_	61	425 (2.917)
25B	412 (0.1081)	Violet	530	Yellow- green	118	443 (2.798)
26A	401 (3.1810)	Violet	506	Yellow- green	105	437 (2.837)
26B	422 (0.0937)	Violet	542	Yellow- green	120	448 (2.931)
29a	493 (1.60)	Blue-green	568 (27)	Red	75	535 (2.31)
29b	483 (1.78)	Green-Blue	550 (28)	Orange	67	522 (2.37)
29c	536 (1.80)	Green	589 (26)	Red	53	560 (2.21)
29d	495 (1.98)	Blue-green	559 (30)	Red	64	542 (2.28)
30a	428 (1.00)	Violet	570 (60)	Yellow- green	142	499 (2.48)
30b	470 (1.07)	Blue	584 (55)	Yellow	114	515 (2.40)
32a	493 (1.25)	Blue-green	566 (60)	Red	73	530 (2.33)
32b	545	Green	626	Purple	81	589

	(1.65)		(54)			(2.10)
32c	530 (0.672)	Green	605 (54)	Purple	75	560 (2.21)
33a	503 (1.20)	Green	584 (55)	Purple	81	546 (2.27)
33b	598 (1.64)	Orange	653 (61)	Green-blue	55	614 (2.01)
33c	543 (1.58)	Green	620 (56)	Purple	77	582 (2.13)

Tables (1) Abbreviations

λ_{max} (nm,), ε_{max} (10^4 $M^{-1}cm^{-1}$,), E_{max} (nm,), (kcal/mol)**,** I (nm, and $E_{0\text{-}0}$ (eV, HOMO-LUMO) calculated point of the experimental absorption (emission) spectra (EtOH).

The spectral behavior of **(29a, d & 30b & 32c & 33a, c)** in aqueous universal buffer solution of different values of pH (2.5, 4.5, 5.5, 7, 8, 9.3, 10.6, 11.9) **[28], Table (2)** showed that they absorbed fundamental blue colour light absorption, λ_{max} = 360-400 nm and near violet light extended to green light λ_{max} = 410-630 nm. Such dyes in aqueous universal buffer solution reveal fundamental violet light absorption at pH=2.5 with batho (hypso)-chromic shifted in fundamental blue light & blue-green light absorption at pH≥7.0 relative to ethanol. The hypsochromic shift of fundamental violet light absorption at pH = 2.5 due to protonation of electrons lone pair on the nitrogen atom which represent electron source atom and so responsible for charge transfer in such solution of low pH value & therefore the interaction is inhibited, & the protonated form does not absorb energy in the visible region. On the other hand, the resulted bathochromic shift as the pH of medium increases due to the fact that protonated compound becomes deprotonated & molecule mesomeric rest interaction becomes high consequently the **CT** interaction within free base is facilitated. The spectral behaviour of **(29a, d)** in aqueous universal buffer solution absorbed fundamental violet extended to blue green light absorption of (**29a**, λ_{max} = 407-499 nm] absorbed fundamental violet light extended to green light for (**29d**, λ_{max} = 422-510 nm]. In acid (pH ≥ 2.5) medium such dyes undergo a hypsochromic colour shift due to protonation of nitrogen electrons lone pair in pyridine ring cases intramolecular charge transfer **(CT)** between heterocyclic donor (oxygen) and heterocyclic acceptor nitrogen atoms does not occur, and long wave length **CT** band disappears. On the other hand, the resulted bathochromic shift as pH of medium increases is due to that protonated compounds become deprotonated and their molecule mesomeric interaction rest becomes high and consequently CT interaction

with free base is facilitated. On comparison of absorption spectra in aqueous universal buffer solution of **(29a, d),** it was obvious that dye **(29d)** has got absorption as it absorb fundamental blue green light absorption for **(29d**, λ_{max} = 422-510 nm, pka=2.4, 7.8) values which bathochromically shifted by ($\Delta\lambda_{max}$ = 11nm) with respect to **(29a**, λ_{max} = 407-499 nm, pka=8.1, 8.9) due to more extended conjugated chromophore in **(29d)** from the electrons lone pair of pyridine ring nitrogen as electron source towards pyridin(quinolin)-[(4)1]-ium salt as electron sink. It was obvious from pka values that dye **(29d)** was possible to be used as a photosensitizer in acidic and basic media, **Table (2 & 3).** The spectral behavior of **(30b, 32c & 33a, c)** in aqueous universal buffer solution showed that such dyes absorbed fundamental violet light absorption light extended to green blue for (**30b,** λ_{max} = 431-489 nm), absorbed fundamental violet light extended to green absorption for (**32c, 33a, 33c,** λ_{max} = 420-550 nm). In acid (pH $\geq$ 2.5) medium such dyes undergo a hypsochromic colour change due to protonation pyridine ring nitrogen atom electrons lone pair. In such cases the intramolecular charge transfer **(CT)** between heterocyclic donor (oxygen) & heterocyclic acceptor nitrogen atoms does not occur & the long wave length **CT** band disappears. On the other hand, the resulted bathochromic shift as pH of medium increases due to protonated compounds become deprotonated & their molecule mesomeric interaction rest becomes high & consequently **CT** interaction with free base is facilitated. On comparison of absorption spectra of **(30b, 32c, 33a, 33c)** in aqueous universal buffer solution, it was obvious that **(33c)** has got absorption fundamental violet light absorption in acidic medium and extended to green in basic media for **(33c,** λ_{max} = 458-545 nm, pka=4.1, 11.9) & might be used as photosensitizers in both acidic & basic medium with bathochromically shifted for **(30b, 32c, 33a**, $\Delta\lambda_{max}$ = 56, 4, 36 nm) with respect to **(30b**, λ_{max} = 431-489 nm, pka=10 **(32c,** λ_{max} = 409-541 nm, pka=6.5, 8.2, 8.7), (**33a**, λ_{max} = 426-509 nm, pka=8.1, 9.1] due to more extended conjugation chromophore in dye **(33c)** from pyridine or pyrazole heterocycle nitrogen atom electrons lone pair in spiro pyrazolo [3,4-b] pyridin-4,9'-xanthen]skeleton supplemented by hyperconjgated from methyl as electron source towards pyridin(quinolin)-[(4)1]-ium salt as electron sink, **Tables (2 & 3).** On comparison of all selected self-assembly **[ICT]** heterocycles & related methine cyanine dyes. It was obvious that **(29d, 32c, 32b, 33a, 33c)** have high fundamental absorption & bathochromically shifted as absorbing fundamental red

light at (λ_{max} = 500-650) in the order **(33c >32c >32b > 30b > 29d >33a)** which absorb fundamental green blue light at (λ_{max} = 430-499) in the order **(29a>30b**. It was concluded that **(29a, d, 30b & 33a, c**) having covalent hydration or appearance of absorption band in low ph. Thus, it was obvious that the acidic-ethanol solution of such dyes gives a permanent colour (deepening in colour) & discharge on basification due to suggested covalent hydration phenomenon. Such phenomenon was occurred in aqueous media, thus heterocyclic moieties changed into corresponding cations & covalent hydrated in acidic media.

Table (2): Absorption (nm) & Extinction Coefficients (10^4 $mol^{-1}cm^{-1}$) of (29a, d, 30b, 32c & 33a, c) in Universal Buffer Solution.

Comp. No.	Universal buffer								Color Abs. range (Trans.)
	2.5	4.5	5.5	7	8	9.3	10.6	11.9	
	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	λ_{max} (ε_{max})	
29a	407 (1.56)	463 (1.73)	464 (1.88)	466 (1.96)	476 (1.96)	480 (1.96)	492 (1.96)	499 (1.96)	Violet to Green-Blue (orange)
29d	422 (1.45)	449 (1.86)	466 (1.91)	486 (1.94)	491 (1.96)	497 (1.99)	501 (2.01)	510 (2.03)	Blue- green (Red)
30b	431 (1.26)	456 (0.93)	464 (0.98)	472 (0.95)	478 (0.98)	480 (0.99)	483 (1.02)	489 (1.c)	Violet to Green-Blue (orange)
32c	409 (0.77)	430 (1.71)	454 (1.59)	505 (1.69)	526 (1.67)	534 (1.69)	539 (1.69)	541 (1.67)	Violet to Green (Purple)
33a	426 (1.33)	459 (1.02)	469 (0.92)	474 (1.07)	485 (1.08)	491 (1.08)	506 (1.06)	509 (1.10)	Violet to Green (Purple)
33c	458 (1.41)	476 (1.42)	523 (1.75)	525 (1.96)	526 (1.91)	539 (1.06)	545 (1.29)	_	Violet to Green (Purple)

Table (3): Characteristic Absorbance λ_{max} for (29a,d,30b,32c & 33a,c) in Universal Buffer Solutions

Dye λ_{max} pH	Absorbance					
	29a λ_{445}	**29d** λ_{452}	**30b** λ_{430}	**32c** λ_{470}	**33a** λ_{430}	**33c** λ_{498}
2.5	0.354	1.916	0.342	1.123	1.798	0.426
4.5	0.926	2.458	0.271	1.292	1.862	0.657
5.5	0.65	2.47	0.172	1.185	2.066	-
7	0.828	1.408	0.49	0.858	1.676	0.727
8	0.612	1.831	0.351	1.06	1.825	0.617
9.3	0.738	2.486	0.722	-	2.834	0.739
10.6	0.661	2.619	1.186	0.896	-	0.467
11.9	-		-	0.768	-	-

	8.1	2.4	10.1	6.5	8.1	4.1
pK_a	8.9	7.8		8.2	9.1	11.9
	-	8.8		8.7	-	-

EXPERIMENTAL

Melting points were uncorrected & determined using SMP-10 Melting point apparatus (stuart make). ^{1}HNMR spectra were recorded using a Bruker advance 400 MHZ using DMSO-d6 as solvent & TMS as an internal standard. FTIR spectra were run using Bruker alpha spectrophotometer. Mass spectra were recorded in thermo scientific Exactive (Esims). UV-Vis & fluorescence spectra were recorded using SPECORD S600 & Horiba Fluromax-4 Spectrophotometers. 4-Formyl-3-methyl-1-phenyl-pyrazolin-5-one **(1)** & 3-methyl-1-phenyl-pyrazolin-5-imine-4-keto methylene-N-pyridin (quinolin)-4-ium iodide) **(27a, b)** were prepared in a way that described in prospective references **[22; 23, 29, 30].**

Synthesis of 4-(3, 5-Dimethyl-1, 7-Diphenyl-1,4,7,8-Tetra[H]Bis-Pyrazolo[3, 4-b:4', 3'-e] Pyridin-4-yl)-[Pyrido[2, 3-d:6, 5-d']Bis-Pyrimidine] (25, 26)A

An ethanolic solution of 3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazolin-4-carboxaldehyde (1m mol) & 3-methyl-1-phenyl-1H-pyrazolin-5-one (2 m mol) and/or barbituric acid in presence aqueous solution of oxalic acid was refluxed overnight at 115 °C. The reaction mixture was allowed to cool, quenched by adding 50ml of distilled water & extracted by chloroform. The organic layer condensed & crystallized from petroleum ether to give **(25, 26) A. (25A):** m.p. 135, Yield, 71, colour, red, Mol. Formula,.$C_{31}H_{27}N_7O$, M. Wt. (514), elemental analysis Calc. (Found) %, C, 72.50 (71.01), H, 5.30 (5.27), N, 19.09 (19.12), **(25B):** m.p. 145, Yield, 42, colour, reddish brown, Mol. Formula. $C_{31}H_{25}N_7O$, M. Wt. (512), elemental analysis Calc. (Found) %, C, 72.78 (72.79), H, 4.93 (4.92), N, 19.17 (19.20)

Synthesis of 4-(3, 5-Dimethyl-1, 7-Diphenyl-Bis-Pyrazolo [3, 4-b: 4', 3'-e] pyridin-4(1H, 7H, 8H)-pyrido [2, 3-d:6, 5-d'] Dipyrimidine Self-Assembly Endo Cyclic [ICT] Functional Mero Cyanine Dyes (25, 26)B

Fusion of **(25, 26)A** in piperidine catalyst (2-3 drops) for 30min. then 10ml of ethanol added & refluxed for 3 hours. The reaction mixture allowed to cool & quenched by water then extracted by ethyl acetate. The organic layer concentrated & crystallized by hexane. **(26A):** m.p. 130, Yield, 62, colour, pale brown, Mol. Formula. $C_{19}H_{15}N_7O_5$, M. Wt. (421), elemental analysis Calc. (Found) %, C, 54.16 (54.13), H,

3.59 (3.62), N, 23.27 (23.21). **(26B):** m.p. 165, Yield, 59, colour, red, Mol. Formula. $C_{19}H_{13}N_7O_5$, M. Wt. (419), elemental analysis Calc. (Found) %, C, 54.42 (54.43), H, 3.12 (3.09), N, 23.38 (23.41)

Synthesis of 3, 6-Dimethyl-4-Oxo-1-Phenyl-4,7-Di[H]-1H-Pyr-azolo [3,4-b]Pyridin- Zero-5(4)-Methine Cyanine (28a, b)

A mixture of **(27a, b,** 1 m mol) & excess of acetic anhydride was irradiated in microwave oven for 9 minutes at 200 watts under solvent-free conditions. After reaction completion, the reaction mixture was allowed to cool & poured on crushed ice & then solid thus was separated collected by filtration &recrystallized from ethanol. **(28a):** m.p. 165, Yield,59, colour brown, Mol. Formula.$C_{21}H_{21}IN_4O$, M. Wt. (472), elemental analysis Calc. (Found) %, C, 53.40 (53.67), H, 4.48 (4.50), N, 11.86 (11.81), **(28b):** m.p. 120, Yield,45, colour, pale brown, Mol. Formula. $C_{25}H_{23}IN_4O$, M. Wt. (522), elemental analysis Calc.(Found) %, C, 57.48 (57.44), H, 4.44 (4.39), N, 10.73 (10.91)

Synthesis of 3-Methyl-1-Phenyl-1H-pyrazolo [3, 4-b] pyridin-(7H)-5-Zero[4(1)] Methine-4-Mono[2(4)]Methine Cyanine Dyes (29a-d)

A mixture of **(28a, b,** 1mmol) and 2-methyl-pyridin(quinolin)-2(4)-ium-ethiodide salts (1mmol) was irradiated in microwave oven for 8 minutes at 200 watt under solvent-free conditions. After reaction completion, the mixture was allowed to cool & poured on crushed ice, and then solid was separated, collected by filtration & recrystallized from ethanol, **Table (4).**

Table (4): Characterization Data for (29a-d).

Comp No.	Nature of Product				%Calcd (Found)		
	M.p. °C	Yield %	Colour	Mol. Formula (Mol.wt)	C	H	N
29a	175	85	Red violet	$C_{33}H_{33}I_2N_5$ (753)	52.6 (52.48)	4.41 (4.38)	9.29 (9.22)
29b	100	79	Reddish	$C_{33}H_{33}I_2N_5$ (753)	52.6 (52.59)	4.41 (4.39)	9.29 (9.33)
29c	170	93	Violet	$C_{37}H_{35}I_2N_5$ (803)	55.31 (55.31)	4.39 (4.30)	8.72 (8.75)
29d	115	85	Red	$C_{33}H_{33}I_2N_5$ (753)	52.6 (52.55)	4.41 (4.40)	9.29 (9.32)

Synthesis of 3', 6'-Dihydroxy-3, 6-Dimethyl-1-Phenyl-1, 7-Di[H] Spiro [Pyrazolo [3, 4-b] Pyridin-4, 9'-Xanthen]-Zero-5[4(1)] Methine Cyanine (30a, b)

A mixture of **(28a, b,** 1mmol), resorcinol (2 mmol) and 8M sulfuric acid (3 drops) were added and heated in sand bath to 180°C for 30 minutes, the solution cooled to room temperature and poured on crushed ice and the solid thus separated was collected by filtration and recrystallized from acetone, **Table (5).**

Synthesis of 3', 6'-Dihydroxy-3, 6-Dimethyl-1-Phenyl-1, 7-di [H] Spiro[Pyrazolo[3,4-b]Pyridine-4,9'-Xanthen]-2-ium-Ethiodide-Zero-5[4(1)] Methine Cyanine (31a, b)

A mixture of **(30a, b, 1mmol)** and ethyl iodide (1m mol) were heating at 60 °C in water bath for 30 minutes then 20 ml of ethanol were added, and the mixture refluxed for 2-3 hours, the solution cooled to room temperature and ethanol evaporated under pressure then the compound precipitated by petroleum ether and recrystallized from ethanol to form the pure crystals, **Table (5).**

Synthesis of 3', 6'-Dihydroxy-3, 6-Dimethyl-1-Phenyl-1, 7-di[H] Spiro [Pyrazolo [3, 4-b]Pyridin-4, 9'-Xanthen]-N-Ethyl-Pyridin (Quinolin)-Zero(Mono)-5(4)[15(4(1))]Methine Cyanine Dyes (32, 33) a-c

A mixture of **(31a, b,** 1 mmol) and pyridin (quinolin)-4(1)-ium-ethiodide salts (1 mmol) were stirred in 30 ml of ethanol for 10 minutes then 2-3 drops of piperidine added. The reaction mixture refluxed for 6 hours at 110°C. After the reaction completion, the product quenched by water and extracted by chloroform. The combined organic layers dried over anhydrous Na_2SO_4, and filtered. After removing the solvent by rotavapor, the compound crystallized by hexane and recrystallized from ethanol, **Table (5).**

Table (5): Characterization Data for (30, 31) a, b & (32, 33) a-c

Comp No.	Nature of Product			Mol. Formula (Mol.wt)	%Calcd (Found)		
	M.p. °C	Yield %	Colour		C	H	N
30a	160	61	Red brown	$C_{33}H_{29}IN_4O_3$ (656)	60.37 (60.33)	4.45 (4.42)	8.53 (8.51)
30b	165	78	Red	$C_{37}H_{31}IN_4O_3$ (707)	62.89 (62.82)	4.42 (4.40)	7.93 (7.92)
31a	164	53	red	$C_{35}H_{34}I_2N_4O_3$ (812)	51.74 (51.70)	4.22 (4.20)	6.90 (6.94)
31b	172	67	violet	$C_{39}H_{36}I_2N_4O_3$ (862)	54.31 (54.34)	4.21 (4.25)	6.50 (6.94)
32a	175	53	red	$C_{43}H_{45}I_2N_5O_3$ (933)	55.32 (55.34)	4.86 (4.845)	7.50 (7.64)
32b	235	60	violet	$C_{47}H_{47}I_2N_5O_3$ (983)	57.38 (57.40)	4.82 (4.72)	7.12 (7.26)
32c	228	59	violet	$C_{47}H_{47}I_2N_5O_3$ (983)	57.38 (57.33)	4.82 (4.81)	7.12 (7.16)
33a	254	61	violet	$C_{43}H_{45}I_2N_5O_3$ (933)	55.32 (55.32)	4.86 (4.845)	7.50 (7.52)
33b	269	64	violet	$C_{47}H_{47}I_2N_5O_3$ (983)	57.38 (57.40)	4.82 (4.72)	7.12 (7.10)
33c	275	56	violet	$C_{47}H_{47}I_2N_5O_3$ (983)	57.38 (57.43)	4.82 (4.87)	7.12 (7.15)

ACID-BASE PROPERTIES

The organic solvents were used of spectroscopic grade which purified according to the recommended methods **[36].** The absorption spectra of dyes in organic solvents were recorded within wavelength (350-700 nm) on UV/Visible recording using 1cm cell in spectrophotometer. The stock solution of dye was of order 10^{-3} $mol^{-1}dm^{-3}$ solutions of low molarities used in spectral measurements were obtained by accurate dilution

PHYSICO-CHEMICAL WORKING SOLUTIONS STUDIES

A-For studying the effect of pure solvents in visible range, an accurate volume of stock solution of dyes were diluted to appropriate volume in order to obtain required concentration. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect spectral of time. **B-** For studying the behaviour in aqueous universal buffer solutions, an accurate volume of stock solution was added to 5 ml of buffer solution in 10 ml measuring flask. The pH of

solution was checked then absorption spectra of dyes in different pH solutions were recorded using 1cm quartz cell within a wavelength range (350-700 nm)

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