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SYNTHESIS, CHEMICAL CONFIRMATION & SPECTRAL BEHAVIOUR OF SOME SELECTED SELF ASSEMBLY [ICT] HETEROCYCLIC FUNCTIONAL & CYANINE DYES[1]

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Abstract

Facile synthetic process of some new N-bridge head poly heterocyclic quaternary salts for synthetic process of their functional & related cyanine dye derivatives of the improved absorption light sensitivity and photosensitization effect. The synthesis of the self assembly **[ICT]** endocyclic moieties based on 1,3-Bis(3-methyl-5-oxo-1-phenyl-4,5-di [H]-1H-pyrazol-4-yl-propan-1,3-dione **(1B) &** 5, 5'-malonyl-bis (pyrimidin-2, 4, 6(1H, 3H, 5H)-trione) **(17).** A special attention has been focused on the spectral behaviour of ethanolic solution of N-bridge head heterocyclic self-assembly **[ICT]** functional & cyanine dye based on in the visible region in order to permit a criterion for their use as photosensitizes & to shed some light upon a possible color-chemical structure relationship. The solvatochromic behavior of such N-bridge head heterocyclic self-assembly **[ICT]** functional & cyanine dye derivatives are observed here in the visible region showing solvatochromism & the colour changes with solvents having different polarities to permits a selection of optimal solvent when these dyes are applied as photosensitizers. The spectral behavior of some selected newly functional dyes in aqueous universal buffer solution & their dissociation (protonation) constants **(pka values)** are described to permit their acid-base properties Mediachromic behavior when these dyes are applied as criteria for their use as photosensitizers.

INTRODUCTION

[1] **This Article was Extracted from *M. A.Ibrahim* M.Sc.Thesis, Award the degree under my supervisor Chemistry Department, Faculty of Science, Aswan University (2018) & for fifth memory of Spirit Late Dr. R.M.BU ELHAMD, Assistant Professor of Organic Chemistry.**

The literature reviews had attracted much attention for the spectral behaviors and in particular, are lacking and represent deficiencies in total picture of heterocyclic functional dyes. Intramolecular (Internal) Charge-Transfer Heterocyclic organic molecules has attracted increasing attention owing to their unique electronic and/or photonic properties **[1-3]** solar cells, etc **[4]** It is of interesting to attempt and throw some light on such synthesis and their physicochemical studies. Heterocyclic moieties as new synthetic entities to functional dyes and as a direct initial intensity in color and increasing of spectral bands of their related photo sensitization effect with the hope to permit an improvement in synthetic routes and to suggest formation mechanistic pathways. The absorption spectra would extend the available range of long wavelength absorbing material depending on nature of heterocyclic residue, their linkage positions, and type of both substituents. The most traditional and promising approach is how to reach the goal and trend in order to systematize such functional dyes according to their quite different physico-chemical features and shed some light upon a possible color-chemical structure relationship in order to permit a criterion for their use as photosensitizes.N-Bridge Self-Assembly of Intramolecular Charge-Transfer Compounds into Functional Molecular Systems **[5a,b]** Head Heterocyclic indolizine and/or quinolizine through the introduction of heterocycles or heteroatoms to the π-conjugated systems or through extending the conjugation of diverse aromatic systems via another aromatic ring. Combining these **[ICT]** compounds featuring different degrees of conjugation with phase transfer methodologies we have self-assembled various organic including the ready processability offer great opportunities for applications in designed molecular sensors based on changes in the efficiency of the **[ICT]** process upon complexation. A moieties in the **[ICT]** of Pyrrolo [2,1,5-cd]indolizine and pyrrolo[2,1,5-de] quinolizine have received considerable attention in the field of synthetic organic chemistry because of their special structural properties, **[6,7].** To date, the self-assembly process for obtaining organic nanomaterials is still highly desirable for the advancement of organic nanoscience and nanotechnology**. [8].** Thus, the choice of materials based on the predication of structure–property relationships shows important significance in this field.

RESULT & DISCUSSION

Our approach of building up of some N-bridge head poly heterocyclic selected self-assembly **[ICT]** functional & cyanine dyes was conducted by the synthesis of 1,3-

Bis(3-methyl-5-oxo-1-phenyl-4,5-di [H]-1H-pyrazol-4-yl-propan-1,3-dione **[1B]** by direct reaction of 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one **(B)** [8] with 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid **(C)** [9-11] in AcOH. Selective quaternization of pyridine by the later **(1B)**, in equimolar amount, using **I_2/ETOH** achieved 1,3-Bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-1,3-dioxo-propan-2-yl-pyridin-1-ium-iodide **(2A)**. The chemical confirmation of **[2A]** was conducted via an alternative pathway via an interaction of 1-(2-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-2-oxo-ethyl-pyridin-1-ium-iodide **(1C)**[12] with 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid **(C)**, in equimolar amount,. Cyclocondensation of **(2A)** was conducted under piperidine catalysis to afford 6,9-dimethyl-7,8-dioxo-4,11-diphenyl-7,7a,8,11-tetra[H]-4H-bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endocyclic-mero-cyanine dye **[3A].** The interaction of diethylmalonate-pyridin-1-ium-iodide **(1A)** [13-15a] & bimolar amounts of 3-methyl-1-phenyl-pyrazolin-5-one in AcOH confirmed the same & mixed melting points for **(2A)** which on heterocyclization using piperidine catalysis achieve the same & mixed melting points for **(3A).** Meanwhile, the interaction of **(1A)** & bimolar amounts of 2-oxo-imidazol-5-one **(D)**, 2-methyl-oxazol-5-one **(E)** and/or barbituric acid **(F)** in AcOH afforded 11-methyl-4-oxo-9-phenyl-3,4,5,9-tetra[H]-1H-imidazo[4,5-b]pyrazolo[3,4-g]pyrido[2,1,6-de]pyrrolo[2,3,4-ij]quinolizin-12-ium-iodide**,**4,11-dimethyl-9-phenyl-1,9-di[H]-oxazolo [5,4-b]pyrazolo[3,4-g]pyrido[2,1,6-de] pyrrolo [2,3,4-ij] quinolizin-12-ium-iodide **&** 1-(1, 3-dioxo-1, 3-bis(2,4,6-trioxohexa [H] pyrimidin-5-yl-propan-2-yl-pyridin-1-ium iodide **(2B-D)** respectively**.** On the other hand, intramolecular heterocyclization of **(2B-D)** under piperidine catalysis afforded self-assembly **[ICT]** 5,7,8,10-tetraoxo-5,6,7,7a,8,9,10,11-octahydro-4H-diimidazo [4,5-b:4',5'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide,5,10-dimethyl-7,8-dioxo-7a,8-di[H]-7H-dioxazolo [5,4-b:4',5'-g]pyrido [2,1,6-de]quinolizin-12-ium-iodide & 5,7,8,9 , 10,12-hexa- oxo-5,6,7,8,8a, 9,10,11,12, 13-deca[H]-4H-pyrido[2,1,6-de]dipyrimido [5,4-b:4', 5'-g] quinolizin-14-ium iodide **(3B-D),** The interaction of **(1B) &** N-ethyl-pyridin-1-ium iodide salt, in equimolar amount, under piperidine catalysis & ethanol afforded 4-(1-hydroxy-1,3-bis-(3-methyl-5-oxo-1-phenyl-4,5-di[H] 1H-pyrazol-4-yl)-3-oxoprop-styryl cyanine dye **(4).** The formation of **(4)** was chemically confirmed by the direct interaction of **(2A) &** N-ethyl-pyridin-1-ium iodide salt, in equimolar amount, under zinc dust/AcOH. The formation criterion of **(4)** is the existance of vapour iodine vapour on warming H_2SO_4 and deeping of colour when treated with ferric chloride

due to the existance β-dicarbonyl enolate. Piperidine catalysis of **[4]** afforded 1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-propan-1,3-dione-2-acyclic mero cyanine dye **(5). Scheme (1A).** N-bridge head heterocycles structurally based on the phenalene ring system possesses distinctive colours **[16, 17].** Thus, the interaction of **(3A)** & hydrazine hydrate, phenyl-hydrazine in acid medium and/or hydroxylamine hydrochloride under basic conditions, in equimolar amount, afforded self-assembly **[ICT]** N-acetyl-3,11-dimethyl-5,9-diphenyl-5,9-di[H]-1H-tripyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide**,**3,11-dimethyl-1,5,9-tri-phenyl-5,9-di[H]-1H-tri-pyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide & 3,11-dimethyl-5,9-diphenyl-5,9-di[H] isoxazolo[3,4,5-ij]bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide **(6a-c)**respectively**.** Meanwhile, the interaction of **(3A)** & urea, in equimolar amount, under acid medium afforded self-assembly 4,12-dimethyl-2-oxo-6,10-diphenyl-1,2,6,10-tetra[H]**[ICT]**dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido[4,5,6-ij] quinolizin-13-ium-iodide **(7).** The methanolic solution of **(3A)** was used as key intermediate for metal enolates on addition of metal divalent **(Ni^{++})** to achieved 4,12-dimethyl-6,10-diphenyl-6,10-di[H]-2H-[1,3]dioxin[4,5,6-ij]bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,13-diium-iodide/chloride-metal complex self-assembly **[ICT], (8a, (X= Ni))** The later metal enolate complex **(8a)** was converted into [1,3] oxathiino/ oxazino[4,5,6-ij]di pyrazolo[4,3-b:3',4'-g] pyrido [2,1,6-de]quinolizin-3,13-diium-iodide/chloride and/or [1,3]oxazino[4,5,6-ij]bis-pyrazolo [4,3-b:3',4'-g]pyrido [2,1,6-de]quinolizin-13-ium) via the effect of % Na_2S or ammonium acetate in aqueous ethanol solution to achieve **[8b,c].** Reaction of 6,9-dimethyl-7,8-dioxo-4,11-diphenyl-7,7a,8,11-tetra[H]-4H-bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endocyclic mero-cyanine dye **(3A)** with hydroxyl amine hydrochloride/ sod.acetate afforded 7-(hydroxyimino)-6,9-dimethyl-8-oxo-4,11-diphenyl-7,7a, 8,11-tetra [H]-4H-bis-Pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide**,** 8-hydroxy-7-(hydroxy-imino)-6,9-dimethyl-4,11-diphe-nyl-7,11-di[H]-4H-bis-pyrazolo[4,3-b:3',4'-g]pyrido [2,1,6-de] quinolizin-12-ium**,**8-(hydroxy amino)-6,9-dimethyl-7-oxo-4,11-diphenyl-7,11-di[H]-4H-bis-pyrazolo[4,3-b:3',4'-g]pyrido [2,1,6-de] quinolizin-12-ium iodide **(9** and/or **10).** Intramolecular heterocyclization of **(9)** using hydrochloric acid in ethanol was conducted to achieve self-assembly **[ICT]** 3,11-dimethyl-5,9-diphenyl-5,9-di[H]-2H-isoxazolo[3,4,5-ij]bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,12-di-ium-chloride/iodide-endocyclic **(11A).** Treatment of **(11A)** with either aqueous solution of

Na_2S or NH_4OH achieved the corresponding 3,11-dimethyl-5,9-diphenyl-5,9-di[H]-2H-isothiazolo[3,4,5-ij]bis-pyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de] quinolizin-1,12-di-ium-chloride/iodide-endocyclic **&** 3,11-dimethyl-5,9-diphenyl-5,9-di[H]-1H-tripyrazolo [4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de] quinolizin-12-ium-iodide-endocyclic cyanine dyes **(11B,C)** respectively**.** In a way similar, the interaction of 1,3-bis (3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-propan-1,3-dione **(1B)** & barbituric acid , in equimolar amount, in acetic acid afforded 1,3-bis (3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-propan-1,3-dione-acyclic-mero cyanine dye **(12).** Piperidine catalysis of **(12)**, in equimolar amount, afforded isomeric self-assembly **[ICT]**14,14a-di [H] pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido[3,2,1-ij] quinazolin-1,3,6,8, 9,10, 11,13 (2H,5H,7H, 10aH,12H ,14bH)-octaone, self-assembly **[ICT]** 9-hydroxy-7,10-dimethyl-5,12-diphenyl-pyrazolo[3,4-f] Pyrazolo [4',3':5,6]pyrido[3,2,1-ij]quino-zolin-1,3,8 (2H, 5H,12H)-tri-one & self-assembly **[ICT]** 7,10-dimethyl-5,12-diphenyl-Pyrazolo [3,4-f] pyrazolo [4',3': 5,6] pyrido [3,2,1-ij]quinazolin-1,3,8,9 (2H ,5H ,9aH, 12H)-tetra-one-endo-cyclic mero cyanine dye **(13), Scheme (1B).** Piperidine catalysis for an interaction of **(3A)** & 3-methyl-1-phenyl-pyrazolin-5-one **(A)** ,2-oxo-imidazol-5-one **(D)**, 2-methyl-oxazol-5-one **(E)** and/or barbituric acid **(F)** ,in equimolar amount, afforded self-assembly **[ICT]** endocyclic multi-charge transferred mero cyanine dye 6,9-dimethyl-7-(3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene-8-oxo-4,11-diphenyl-7,7a,8,11-tetra[H]-4H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide**,**7-(2,5-dioxo-imidazolidin-4-yliden-6,9-dimethyl-8-oxo-4,11-diphenyl-7, 7a,8,11-tetra[H]-4H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide**,** 6,9-dimethyl-7-(2-methyl-4-oxooxazol-5(4H)-ylidene-8-oxo-4,11-diphenyl-7,7a, 8,11-tetrahydro-4H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide and/or 6,9-dimethyl-7-oxo-4,11-diphenyl-8-(2,4,6-tri-oxo tetra [H] pyrimidin-5(2H)-ylidene-7,7a,8,11-tetra[H]-4H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide **(14A-D)** respectively**, Scheme (2A).** Piperidine catalysis of **(14B, D)** afforded 5,13-dimethyl-2,4-di-oxo-7,11-diphenyl-3,4,4b 1,7,11, 13b-hexa [H]-2H-bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido [5',4': 5,6] pyrano[2,3,4-ij]quinolizin-15-ium-iodide & 5,13-di-methyl-2,4-dioxo-7,11-diphenyl-2,3,4,4b,1,7,11-hexa[H]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido[5',4':5,6]pyrano[2,3,4-ij]quino-lizin-14,15-diium-iodide/chloride-endocyclic-multi-charge transferred-mero cyanine dyes **(15B, D).** Meanwhile**,** heterocyclization using hydrochloric acid in ethanol for **(14A-D)** afforded self-assembly **[ICT]** 3,4,12-trimethyl-1,6,10-triphenyl-6,10-di[H]-1H-dipyrazolo[4,3-b:

3',4'-g]Pyrazolo [4',3':5,6] pyrano[2,3,4-ij]pyrido[2,1,6-de]quinolizin-13,14-diium-chloride/iodide**,**4,12-dimethyl-2-oxo-6,10-diphenyl-2,3,6,10-tetra [H] imidazo[4',5':5,6] pyrano[2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-14-ium-iodide and/or 4,12-dimethyl-2-oxo-6,10-diphenyl-2,3,6,10-tetra[H]-1H-imidazo[4',5':5,6]pyrano [2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-13,14-diium-chloride/iodide**,** and/or 2,4,12-trimethyl-6,10-diphenyl-6,10-di[H] oxazolo [5',4':5,6] pyrano[2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-13,14-diium-chloride /iodide **(16A-D), Scheme (2A).** Self-assembly **[ICT]** heterocyclic functional & cyanine dyes based on pyrimido[4,5-f] pyrimido[5',4': 5,6] pyrido[3,2,1-ij]quinozolin-octaone was conducted by the synthesis of 5,5'-malonyl-bis (pyrimidin-2,4,6 (1H,3H,5H)-trione) **(17)** via the interaction of diethyl malonate & bimolar amounts of barbituric acid **(F)** in acetic acid. Selective quaternization of pyridine by the later compound **(17)** using I_2/ETOH, in equimolar amount, achieved 1-(1, 3-dioxo-1,3-bis(2,4,6-trioxohexa[H] pyrimidin-5-yl-propan-2-yl-pyridin-1-ium iodide **(18).** The later compound **(18)** was chemically confirmed via the mutual route interaction of N-diethyl malonate-pyridin-1-ium iodide **(1A)** **[13-15]** & bimolar amounts of barbituric **(F)** in acetic acid to give the same & mixed melting points. Replacement of pyridin-1-ium-iodide salt by N-ethyl-pyridin-1-ium-iodide salt in 1-(1,3-dioxo-1,3-bis(2,4,6-trioxo-hexa[H]pyrimidin-5-yl-propan-2-yl-pyridin-1-ium-iodide **(18)** was conducted under zinc dust in acetic acid to afford 1-hydroxy-3-oxo-1,3-bis(2,4,6-trioxo-hexa [H]pyrimidin-5-yl)prop-1-en-2-yl) pyridin-1-ium-iodide styryl cyanine dye **(18)** which was chemically confirmed by the direct interaction of 5,5'-malonyl-bis-pyrimidin-2,4,6(1H,3H,5H)-trione) **(17)** with N-ethyl-pyridin-1-ium-iodide salt, in equimolar amount, under piperidine catalysis & ethanol to give the same and mixed melting points. The formation criterion of **(18)** is the existance of vapour iodine vapour on warming H_2SO_4 and Deeping of colour when treated with ferric chloride due to existance β-dicarbonyl enolate. Excess of piperidine catalysis on **(18)** undergo dehydroiodination to afford 5, 5'(2-(1-ethyl- pyridin-4(1H)-ylidene-malonyl-bis-(pyrimidin-2,4,6 (1H,3H,5H)-trione-acyclic mero cyanine dye **(19).** Condensation of **(17)** with barbituric acid **(F),** in equimolar amount, in acetic acid afforded 5,5'-(2-(2,6-dioxo-tetra[H]pyrimidin-4(1H)-ylidene-malo-nyl-bis-pyrimidin-2,4,6(1H,3H,5H-trione **(20)** which undergoes intramolecular hetero cyclization process under piperidine catalysis & ethanol to achieve self-assembly **[ICT]** pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido[3,2,1-ij]quinazolin-1,3,6,8,9 ,10,11,13 (2H,5H,7H,10aH,12H,14H)-octaone

(21) Scheme (2A). The chemical structure of some selected synthesized compounds was confirmed by other alternative pathways, elemental analysis, visible, IR, ^{1}H-NMR, with the aid of mass spectral analysis **[31a,b,32a,b & 33].** The spectral behaviour of some selected new heterocyclic precursors as self-assembly endocyclic **[ICT]** functional dyes was determined for the first time by studying their visible absorption in 95% EtOH. These precursors were thought to be better photosensitizers when they absorb the visible light at higher wave length (bathochromic and/or red shifted dyes) to initiate their electronic transitions. Consequently, the photosensitization of such precursors decreases when they absorb the light at shorter wave lengths (hypsochromic and/or blue shifted dyes). The absorption spectra of dipyrazolo[4,3-b:3',4'-g] pyrido [2,1,6-de] quinolizin-12-ium-iodide-endocyclic endocyclic **[ICT]** functional mero cyanine dye & di-imidazo[4,5-b: 4',5'-g]pyrido [2,1,6 de]quinolizin-12-ium iodide endocyclic **[ICT]** functional dye**,** dioxazolo[5,4-b:4',5'-g]pyrido[2,1,6-de] quinolizin-12-ium-iodide endo cyclic **[ICT]** functional dye & pyrido[2,1,6-de] dipyrimido[5,4-b:4',5'-g]quinolizin-14-ium iodide endocyclic **[ICT]** functional dye **(3A-D)** in 95% EtOH in the range of λ 393-487nm resulted in absorption bands at λ 393nm, $\boldsymbol{\varepsilon_{max}}$ 3185 cm^2 mol^{-1} for **(3A),** λ 487nm, ε_{max} 15897 cm^2 mol^{-1} for **(3B)** and/or, λ 456nm, $\boldsymbol{\varepsilon_{max}}$ 6218 cm^2 mol^{-1} for **(3C)** λ 462nm, $\boldsymbol{\varepsilon_{max}}$ 6825 cm^2 mol^{-1} for **(3D)** respectively. It was obvious that self-assembly **[ICT]** dyes **(3B-D)** have got of absorption bands bathochromically shifted of **Δ λ (63-94nm)** than those of **(3A)**. This is due to the multi-charge transferred from the di-cyclic NH of di-imidazole or di pyrimidine di-one and/or dioxazolo-oxygen atoms as electron source in two direction towards pyrido [2,1,6 de]quinolizin-12-ium-iodide or the two cyclic carbonyls as electron sinking in self-assembly **[ICT]** or cyclic mero cyanine dye types, **Table (2A).** The absorption spectra of tripyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij] pyrido[2,1,6-de] quinolizin-12-ium-iodide endocyclic **[ICT]** functional dye**,** tri-pyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide endocyclic **[ICT]** functional dye & isoxazolo[3,4,5-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinoli-zin-12-ium-iodide endocyclic **[ICT]** functional dye**,** dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido[4,5,6-ij]quinolizin-13-ium-iodide endo cyclic **[ICT]** functional dye **(6a-c & 7)** in 95% **EtOH** resulted in absorption bands at **λ** 467nm**,** $\boldsymbol{\varepsilon_{max}}$ 6722 cm^2 mol^{-1} for **(6a), λ** 518nm**,** $\boldsymbol{\varepsilon_{max}}$ 5985 cm^2 $mol^{-1}$for **(6b), λ** 459nm**,** $\boldsymbol{\varepsilon_{max}}$ 7319 cm^2 $mol^{-1,}$ for **(6c) , λ** 482nm**,** $\boldsymbol{\varepsilon_{max}}$ 8574 cm^2 mol^{-1} for **(7)** respectively**.** It was obvious that dye **(6b)** have got of absorption bands

bathochromically shifted of **Δ λ (36-58nm)** than those of **(6A, C & 7).** This is due to the incorporating of N-phenyl pyrazole as electron source sublimenting charge transferred towards tripyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido [2,1,6-de] quinolizin-12-ium-iodide as electron sinking in self-assembly **[ICT]** functional dye type than those of N-acetyl or isoxazolo or dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido[4,5,6-ij] quinolizine analogous. On comparison of absorption spectra of tripyrazolo [4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide **&** isoxazolo[3,4,5-ij] dipyrazolo [4,3-b:3',4'-g]pyrido [2,1,6-de] quinolizin-12-ium-iodide endocyclic **[ICT]** functional dye**,** dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] pyrimido [4,5,6-ij] quinolizin-13-ium-iodide endocyclic **[ICT]** functional dye **(6b,c & 7), Table (2A).** The absorption spectra of isoxazolo[3,4,5-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,12-diium-chloride/iodide endo- cyclic **[ICT]** functional dye **(11a),** isothiazolo[3,4,5-ij] dipyrazolo[4,3-b:3',4'-g] pyrido [2,1,6-de]quinolizin-1,12-diium-chloride/iodide endo cyclic **[ICT]** functional dye **(11b) &**tripyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endo cyclic **[ICT]** functional dye **(11c)** in 95% EtOH resulted in absorption bands at λ 499nm, ε_{max} 8931cm^2 mol^{-1} for **11a,** λ 478nm, ε_{max} 7971 cm^2mol^{-1} for **(11b),** λ 469nm, ε_{max} 8092 cm^2 mol^{-1} for **(11c)** respectively**.** It was obvious that the endocyclic **[ICT]** functional dye **(11a)** have got of absorption bands bathochromically shifted of **Δ λ (21-30nm)** than those of (**11b, c).** This is due to the more electron withdrawing character of isoxazolo[3,4,5-ij] dipyrazolo [4,3-b: 3',4'-g] pyrido [2,1,6-de] quinolizin nuclei as electron sink from both N-phenyl-pyrazolo nuclei as electro source in the self-assembly **[ICT]** functional dye **(11a). Table (2A).** On comparison of absorption spectra of isoxazolo [3,4,5-ij] dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]quinolizin-12-ium-iodide **(6c,** λ459nm, ε_{max}7319 cm^2 mol^{-1}**) &** isoxazolo[3,4,5-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,12-diium-chloride/iodide-endo cyclic **[ICT]** functional dye **(11a,** λ 499nm, ε_{max} 8931 cm^2 mol^{-1}**),** it was obvious that the endocyclic **[ICT]** functional dye **(11a)** has got absorption bands hypsochromically (hyperchromically) shifted of **Δ λ** 40 nm **(ε_{max})**, 1612 cm^2mol^{-1} than those of the endocyclic **[ICT]** functional dye **(6c).** This is due to the new charge transferred from both N-phenyl-pyrazolone as electron source towards isoxazolo[3,4,5-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,12-diium-chloride/iodide as electron sink in endocyclic **[ICT]** functional dye **(11a)**. The absorption spectra of pyrazolo[3,4-f] pyrazolo [4',3':5,6] pyrido[3,2,1-ij] quinolizin-2,5,12,12b-tetra[H]1,3,8,9-tetra-one endo cyclic **[ICT]** functional dye **(13)** in 95%

EtOH exhibit absorption bands at λ 492nm, ε_{max} 8564 cm^2 mol^{-1}**.** On comparison of absorption spectra of **(13) &** dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endocyclic endo- cyclic **[ICT]** functional mero cyanine dye **(3A),** It was obvious that the endocyclic **[ICT]** functional dye **(13)** have got of absorption bands hypsochromically shifted of **Δ λ (99nm)** than those of (**3A**)**.** This is due to the multi-charge transferred in pyrimido[4,5-f]pyrimido[5',4':5,6] pyrido [3,2,1-ij] quinozoline self-assembly **[ICT]** functional dye **(13)** than those of **(3A), Table (2A),**. The absorption spectra of 1-hydroxy-1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]1H-pyrazol-4-yl-3-oxo-prop-styryl cyanine dye **(41)** in 95% EtOH resulted in absorption bands at λ 419nm, ε_{max} 5186 cm^2 mol^{-1}. On comparison between the absorption spectra of **(4 & 5),** it was obvious that dye **(5)** has got absorption bands bathochromically shifted of **Δ λ (67 nm)** than those of dye **(4).** This is due to the conjugated releasing electrons of N-ethyl-pyridine as electron source than those of pyridinium-ethyl iodide does as electron source towards β-acyclic dicarbonyl as electron sink in both **(5 & 4)**,**Table (2A).** The absorption spectra of [1,3]dioxin[4,5,6-ij]bis-pyrazolo [4,3-b: 3',4'-g]pyrido[2,1,6-de] quinolizin-1,13-diium-iodide/ chloride-metal enolate complex self-assembly **[ICT],(8a,** (X= Ni**)),** [1,3] oxathiino/ oxazino[4,5,6-ij]di pyrazolo[4,3-b: 3',4'-g] pyrido [2,1,6-de]quinolizin-3,13-diium-iodide/chloride and/or [1,3] oxazino[4,5,6-ij]bis-pyrazolo[4,3-b:3',4'-g]pyrido [2,1,6-de] quino-lizin-13-ium) **(8b,c)** in 95% EtOH resulted in absorption bands at λ 508nm, ε_{max} 7631cm^2 mol^{-1} for **(8a),** λ 515nm, ε_{max} 6254 cm^2mol^{-1} for **(8b),** λ 519nm, ε_{max} 5631 cm^2 mol^{-1} for **(8c)** respectively**.** It was obvious that dyes **(8b, c)** have got absorption bands bathochromically shifted of **Δ λ (7-11nm)** than those of (**8a**)**.** This is due to the more electron donating character of [1,3] oxathiino or [1,3] oxazino nuclei as electron source sublimenting charge transferred towards bis-pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-1,13-diium-iodide/ chloride as electron sinking in self-assembly **[ICT]** functional dye type than those of [1,3]dioxin analogous does, **Table (2A).** The absorption spectra of di[H]-1H-pyrazol-4-yl-propan-1,3-dione acyclic mero cyanine dye **(12)** in 95% EtOH resulted in absorption bands at λ 456nm, ε_{max} 7631cm^2 mol^{-1}**.** It was obvious that dyes **(12)** have got of absorption bands hypsochromically shifted of **Δ λ (30nm)** than those of di[H]-1H-pyrazol-4-yl) propane-1,3-dione-2-acyclic mero cyanine dye (**5**)**.** This is due to the conjugated releasing electrons of N-ethyl-pyridine as electron source than those of the incorporating of two cyclic carbonyl in pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido [3,2,1-ij] quinozoline

(12) towards β-acyclic dicarbonyl as electron sink in both **(5 & 12), Table (2A).** The absorption spectra of dipyrazolo[4,3-b:3',4'-g]pyrido [2,1,6-de] quinolizin-12-ium iodide & dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]quinolizin-12-ium-iodide, dipyrazolo [4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide & dipyrazolo [4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endocyclic-multi-charge transferred mero cyanine dyes **(14A-D)** in 95% EtOH resulted in absorption bands bathochromically shifted at λ 467nm, ε_{max} 8131cm^2 mol^{-1}, for **(14A),** λ 456nm, ε_{max} 8154 cm^2mol^{-1} for **(14B),** λ 469nm, ε_{max} 5839 cm^2 mol^{-1} for **(14C),** λ 398nm, ε_{max} 3575 cm^2mol^{-1} for **(14D)** respectively. It was obvious that the dyes **(14A-D)** have got of absorption bands hypsochromically shifted of Δ λ **(5-74nm)** than those of **(3A).** This is due to the inserting of either pyrazolin-5-one, imidazolin-5-one, 2-methyl-oxazol-5-one and/or pyrimidin-tri-one causes multi-charge transferred from N-phenyl-pyrazole as electron source towards cyclic carbonyl or pyrido [3,2,1-ij] quinozolin-ium-iodide as electron sink in self-assembly **[ICT]** functional dyes. The absorption spectra of imidazo[4',5':5,6]pyrano[2,3,4-ij] dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]quinolizin-14-ium-iodide-endocyclic-multi-Charge transferred mero cyanine dye & dipyrazolo [4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido[5',4':5,6]pyrano[2,3,4-ij]quinolizin-15-ium-endocyclic -multi-Charge transferred mero cyanine dyes **(15B, D)** in 95% EtOH resulted in absorption bands at λ477nm, ε_{max} 8521 cm^2 mol^{-1}, for **(15B),** λ 492nm, ε_{max} 6582 cm^2mol^{-1} for **(15D)** respectively. It was obvious that the dye (53B, D) have got of absorption bands bathochromically shifted of Δ λ (21-29nm) than those of **(14B, D).** This is due to the building up pyrano [2,3-d]imidazol-2(1H)-one or pyrimidin-2,4(3H)-di-one in conjunction with pyrido[2,1,6-de]quinolizin-ium-iodide causes creation of new charge transferred from N-phenyl-pyrazolo as electron source towards oxonium chloride or pyridinium-iodide as electron sink, The absorption spectra of dipyrazolo[4,3-b:3',4'-g]pyrazolo [4',3':5,6]pyrano[2,3,4-ij] pyrido [2,1,6-de]quinolizin-13,14-diium-chloride iodide & imidazo[4',5':5,6] pyrano [2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-13,14-diium-chloride iodide, oxazolo[5',4':5,6] pyrano [2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-13,14-diium-chloride/iodide & dipyrazolo [4,3-b:3',4'-g]pyrido[2,1,6-de] pyrimido [5',4': 5,6]pyrano [2,3,4-ij]quinolizin-14,15-diium-iodide/chloride endocyclic or multi-charge transferred mero cyanine dyes **(16A-D)** in 95% EtOH resulted in absorption bands at Λ 489 nm, ε_{max} 8574 cm^2 mol^{-1}, for **(16A),** λ 475nm, ε_{max} 2599 cm^2mol^{-1} for (54B), λ 482nm, ε_{max} 7586 cm^2 mol^{-1} for **(16C),** λ 463 nm, ε_{max} 6258 cm^2

mol^{-1} for (54D) respectively. It was obvious that the dyes **(16A-D)** have got of absorption bands bathochromically shifted of Δ λ (13-65nm) than those of **(14A-D).** This is due to the building up pyrano[2,3-c]pyrazol-7-ium [imidazol-4-ium(oxazol-4-ium)- & pyrimidin-8-ium] chloride in conjunction with pyrido[2,1,6-de]quinolizin-ium-iodide causes creation of new charge transferred from N-phenyl-pyrazolo as electron source towards oxonium chloride or pyridinium-iodide as electron sink. The absorption spectra of pyrimido[4,5-f]pyrimido[5',4':5,6]pyrido [3,2,1-ij] quinazolin-octaone endocyclic **[ICT]** functional dye **(21)** in 95% ethanol exhibit absorption bands at λ 389nm, ε_{max} 8957 cm^2 mol^{-1}, λ 454nm, 9524 cm^2 mol^{-1}. On comparison of absorption spectra of **(13 & 21),** it was obvious that the former dye **(13,** λ 492nm, ε_{max} 8564 cm^2 mol^{-1}) has got absorption bands bathochromically shifted of Δ λ (38nm) than those of (59, λ 389nm, 454nm, ε_{max} 8957,9524 cm^2 mol^{-1}). This is due to the sublimenting of more electron donating character of biphenyl-pyrazolo[3,4-f] Pyrazolo [4',3':5,6] pyrido[3,2,1-ij]quinolizine than those of pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido[3,2,1-ij] quinolizine does, The spectral behaviour of some selected new cyanine dyes was determined by studying their visible absorption in 95% EtOH. These dyes were thought to be better photosensitizers when they absorb the visible light to initiate their electronic transitions at higher wave length (bathochromic and/or red shifted dyes). Consequently, the photosensitization of such dyes decreases when they absorb the light at shorter wave lengths (hypsochromic and/or blue shifted dyes). Cyanine dyes had been useful in studying the colour of organic substances **[15b]** and there are several fundamental principles exist that correlate origin of colour to chemical structures of the solute and nature of the solvents **[16, 17].** Moreover, these classes of heterocyclic compounds are useful in various industrial fields **[18,19]**. This encouraged us and directed our attention to study the solvatochromic behavior of some selected cyanine dyes incorporating new hetercyclic have been studied to investigate the best conditions when these new dyes are applied as photosensitizers. The absorption spectra of the cited dyes, in the wavelength range 350-700 nm have been studied in pure organic solvents of different dielectric constants **[DMF (36.70), EtOH (24.3) & C_6H_6 (2.22)]** are recorded **[20,21].** This is constructed with the intention to illustrate the solvatochromic behavior of such dyes (λ_{max} and ε_{max}) values of the interamolecular and intermolecular charge transfer bands and given in **Tables (3, 4).** It is clear from data that λ_{max} of the interamolecular charge transfer absorption bands exhibits a marked

red shift (bathochromic) on transfer from nonpolar to polar solvents (positive solvatochromism), and some exhibits a blue shift (hypsochromic) of absorption bands with increasing solvent polarity (negative solvatochromism). The unexpected blue shift observed in the λ_{max} of these cyanine dyes in ethanol & water may be due to strong electrostatic interaction [H-bonding] of solvent that cause hypsochromic shift of λ_{max}. Specific solvation of dyes occurs as a result of electrostatic interaction of the distributed cationic charges with the dipoles of solvated molecules. The main contribution to specific solvation of cationic dye is by nucleophilic solvated forms of dyes **(S.S.F.D),** the greater the charge on the cation and the nucleophilicty B is a given solvents, the more the dye is subject to specific solvation **[18,22].** The absorption spectra of **(19 & 21)** have been studied in organic solvents of different polarities **(EtOH, Dioxan, C_6H_6 & DMF)** and (λ_{max} and ε_{max}) values of the interamolecular and intermolecular charge transfer bands and given in **Table (1) fig.(2).**. The absorption spectra of dyes in ethanol are characterized by the presence of one or two essential bands which reflects the presence of intermolecular charge transfer. This intermolecular charge transfer had arisen from transferring the electron lone pair of the nitrogen atom of the heterocyclic ring system towards the positively charged residue along the conjugated chain between both. The relevant data in **Table (1)** as well as the representing graphs disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, and C_6H_6. The bathochromic shift occurred in DMF relative to EtOH is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former. The hypsochromic shifts appeared in EtOH relative to, C_6H_6 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center. The solute-solvent interactions in cases of C_6H_6 generated aresidual negative charge on the nitrogen atoms of heterocyclic ring system which intern facilitated the electronic charge transfer to positively charged center and this explain the bathochromic shifts in these solvents relative to ethanol. **[23a,b]**, in a supplementary, electronic transitions can be localized on the “antenna” or “acceptor” fragments, as they are of the **[ICT]** type **[20 & 24],** the dyes demonstrate a complex spectral behaviour that is highly dependent on the solvent properties. Thus, the positions of the absorption bands undergo bathochromic shifts

when in media of higher polarizability **[25],** because polarisable solvent molecules apparently stabilize cations. At the same time, the influence of the nucleophilicity of polar solvents is abnormally weak owing to the formation of π-complexes between the aromatic molecules & organic cations **[20, 24].** Comparison of values in nucleophilic polar and nonpolar solvents shows that the solvent molecules form nucleophilic complexes with the positively. The larger the positive charge on the fragment, the stronger the nucleophilic complex. Interfragmental charge transfer following excitation results in a decrease of positive charge on fragment owing to the partial delocalisation of the charge on the C fragment. When the value of is high, the **[ICT]** upon excitation leads to a substantial decrease in the positive charge on the fragment and, consequently, to a weakening of the stability of nucleophilic complexes with the solvent molecules. In this case, the increase in the medium's nucleophilicity can result in a significant lowering of the ground state energy. Thus, in a solvent of higher nucleophilicity, the energy between the ground and excited state in molecule increases: This explains the hypsochromic shift of the long-wavelength band. Another phenomenon, also due to **[ICT]** following excitation, is the equalisation of the positive charge between in the opposite case, the dependence. If these effects are of similar intensity, the behaviour of the long-wavelength band can be described. In the case of derivatives with low, there are no dramatic changes in the positive charge on the BP fragment upon excitation. That is why the weakening stability of nucleophile complexes and depolarisation following excitation are less intensive.As a result, the dependencies between are weaker. The data listed in **Table (1) fig. (3)** Show that solvatochromic effects are substantially weaker. This can be explained by the lower positive charge on the fragment in the relaxed excited state. The positions of the absorption band maxima of (5) do not depend on the solvent properties; the band maxima undergo bathochromic shifts with increasing medium polarity. Moreover, the increase in nucleophilicity resulted in the opposite spectral effects. The absorption spectra of the selected dyes in aqueous universal buffer solutions of varying pH values **(2.5, 5.5,7,9.3 & 11.9)** showed bathochromic shifts with intensification of the absorption bands at high pH values (alkaline media) especially in **n-π*** and **C.T**. bands. Otherwise, hypsochromic shifts with quenching the intensity of the absorption bands at low pH values (acidic media) were recorded. Increasing **pH** values of the medium intensified the electronic charge transfer due to deprotonation which intern support the lone pairs of electrons of the heterocyclic ring

system and increase its mobility. In the other hand, decreasing pH values of the medium interrupted the charge transfer due to protonation and intermolecular hydrogen bonding which intern preclude the availability of the lone pairs of the heterocyclic ring system. The spectrophotometric determination of dissociation/ protonation constants **(pka)** values of such dyes **(7 & 10)** can be utilized through the variation of the absorbance with pH values **[26].** Thus, the absorbance pH curves are typical dissociation constant **(pka)** of dyes was determined from the variation of absorbance with pH using the spectrophotometric half-light limiting absorbance and collector methods **[27-29].** On plotting the absorbance at fixed wave number versus pH values, S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to the left corresponded to the acidic form of the dye, while the upper portion to the right corresponded to the basic form. Since the pka value was defined as the pH value for which one half of dye is in the basic form and the other half in the acidic form. This pka value was determined by the intersection of S-curve with horizontal line midway between the left and right segments **[30].** In point view of the determination of pka values, the results showed that the pka values of dyes under investigation **(7 & 10)** was represented which indicated that they have more basic character than dye it was suggested that the dye **(3B)** is more sensitive as photosensitizers in acidic medium, **Table (2),fig.(3)**

EXPERIMENTAL

All melting points are uncorrected Elemental analysis was carried out at the Micro analytical center (Cairo-University). The IR (νKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo and Aswan University). ^{1}H–NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on an Hp Ms 6988 spectrometer (Cairo and Sohag University). The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-750 nm) on Thermo Nicolite evolution 100 spectrophotometer, water company, Aswan..4-Acetyl-3-methyl-1-phenyl-pyrazolin-5-one **(B)** & 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid were prepared in accordance with respective references **[8-11].** 1-(2-(3-Methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-2-oxo-ethyl-pyridin-1-ium-iodide **(1C)** was prepared in way described in perspective reference **[12]**

Synthesis of 1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-propan-1,3-dione (1B)

(A):3-Methyl-4-acetyl-1-phenyl pyrazol-5- one **(B,** 0.01 mol.) & 3-methyl-1-phenyl-pyrazol-5-one 4-carboxylic-acid **(C,** 0.01mol.) in acetic acid was refluxed for 4 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized to give **(1B), (B):** N-acetyl- pyridin-3-methyl-1-phenyl- pyrazol -5- one **(1C,** 0.01mol.) and 3-methyl-1-phenyl- pyrazol-5-one 4-carboxylic-acid **(C,** 0.01mol.) in acetic acid was refluxed for 5hrs, the reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized to give **(1B), Table (3). (C):** 3-methyl-1-phenyl-pyrazol -5-one (0.01mole) and N-pyridinium -malonate (0.01mole) in acetic acid was refluxed for 3 hrs. The reaction mixture was filtrated while hot from unreacted materials. The filtrate was concentrated, cooled and. The precipitated products after dilution with water were separated, filtrated and crystallized to give **(1B), Table (3).** IR (γ ^{KBr} cm^{-1}) of **(1B)** 3864.65,3833, 3761.47cm^{-1}(γ CH Stretch. & γCH_3, γ CH_2 3433, 3065 cm^{-1} (γ Ar.), 2922, 2861, 2364. 1955, 1880, 1752cm^{-1} (γ acyclic β-di-C=O). 1602,1552-1570 cm^{-1}(acyclic β-dicarbonyl), 1494cm^{-1} (γ C=N), 1444, 1313, 1162, 1097, 1029, 904, 835, 754, 691cm^{-1} (γ mono sub. Ar.), 656, 617, 504, 459, **[31a,b],** ^{1}HNMR of **(1B)** δ,3.61,S,2H,pyrazolone-H, δ,7.19-7.94, m,10H,2-Phenyl, δ,S,1.84,6H, 2CH_3. **[32a, b].** Mass spectra of **(1B)** confirmed a molecular formula ($C_{23}H_{20}N_4O_4$) agree with a molecular ion at m/z = Molecular Weight: M^+=416.43 and base peaks (100%) at m/z= 358, characteristic for, [M+-CH_3+$C_3H_2O_2$], **[33].**

Synthesis of 1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-1,3-dioxo-propan-, 1,3-bis(2,5-dioxoimidazolidin-4-yl)-1,3-dioxo-propan-2-yl), 1,3-bis (2-methyl-4-oxo-4,5-di[H]oxazol-5-yl)-1,3-dioxo-propan & 1,3-dioxo-1,3-bis (2,4,6-trioxo hexa [H] pyrimidin-5-yl)propan-2-yl)-pyridin-1-ium iodide (2A-D)

A-An Ethanolic solution of **(1B)** (0.01mole) and (0.01mole) of pyridine and (0.01 mol.) from Iodine were refluxed for 4 hrs. The reaction mixture was filtrated hot from unreacted materials. The filtrate was concentrated, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized to give **(2A),**
B-An Ethanolic solution of 2-oxo-imidazol-5-one, 2-methyl-oxazol-5-one and/or

barbituric acid (0.02mol.) and diethyl malonate (0.01mol.) in acetic acid was refluxed for 3 hrs. The reaction mixture was filtrated hot from unreacted materials. The filtrate was concentrated, cooled and. The precipitated products after dilution with water were separated, filtrated and crystallized to give **(2B-D), Table (3).**

Synthesis of di pyrazolo[4,3-b:3',4'-g]pyrido/diimidazo[4,5-b:4',5'-g]pyrido -mero, [2,1,6-de]quinolizin-12-ium-iodide, dioxazolo [5,4-b:4',5'-g]pyrido [2,1, 6-de]quinolizin-12-ium-iodide & pyrido [2,1,6-de]dipyrimido [5,4-b:4',5'-g] quinolizin-14-ium iodide (3A-D)

An Ethanolic solution of **(2A-D)** in few drops of piperidine was refluxed for 3 hrs. The reaction mixture was filtrated from unreacted materials, filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(3A-D), Table (4A),fig,(1)** IR ($\upsilon^{KBr}cm^{-1}$) of **(3A).** 1465-1610 cm^{-1}(γ C=N & υ C=N cyclic), 688-839cm^{-1} (γ mono-sub-Ar.), 2890 cm^{-1}(γ Ylide anion), 688.46-839cm^{-1},(γ mono-sub-Ar.),3610-3645cm^{-1}O–H str. 1277, 1358,1452cm^{-1} (γ2CH_3). ,1570 cm^{-1} (γ cyclic β-dicarbonyl), 1685-1666cm^{-1} (γ, α, β-unsat. ketones), 688.46-839.85cm^{-1} (γ mono-sub-Ar.),2890 cm^{-1}(γ Ylide anion),688-839cm^{-1},(γ mono-sub-Ar.),1277, 1358, 1452cm^{-1} (γ2CH_3) Pyridine, (1645-1590) cm^{-1}, 1585-1560cm^{-1}, 1540-1471cm^{-1}, 1440-1410cm^{-1} 3037-3144cm^{-l} (γ pyridinium quaternary), 3120 cm^{-l}, (γ N-H str., pyridinium ion), 3150-3000 cm-1 (γ str. C-H. pyridinium iodide) ,1650-1400 cm^{-1} (γ C=C & C=N), 1650-1625 cm^{-1} (γ C=N or C=C-C=N conj. pyridinium salts), 1631-1625 cm^{-1} (γ quatern pyridine), 1594 &1580 cm^{-1} (γ disappearing Ar. C-C in quaternary salts), 1482cm^{-1} (γ conj. C=C & C =N).1465-1430 cm^{-1} (γ Hyperconj. quaternary salts),. 1631-625cm^{-1} (γ pyridinium ion C=N, γ pyridine quaternization amino-aldehyde character).1594 and 1580 cm^{-1} (γ Ar. C-C), **[31a,b],** IR (νKBr cm^{-1}) of **(3B)** 3084cm^{-1}(υ pyridinium iodide),2882 cm^{-1}(υ ylide iodide),1585-1596 cm^{-1}(υ C=O coupled C=N),3591 cm^{-1}(υ enolized OH),2931-2908 cm^{-1} (υ heterocyclic Q salt).1735 cm^{-1} (υ cyclic β-carbonyl) 1435-1432 cm^{-1}(υ α,βunsaturated C=O), [31a,b], ^{1}HNMR (DMSO, 300MHZ Spectra of (3A) multiplet signals at δ,7.45-7.62, m. 10H, 2Ph, at δ, 2.47,S,6H,2CH_3. δ,3.2, S,6H, 2CH_3, δ,8.33, d,2H, pyridinium, δ, 8.86, d,1H, pyridinium, [32a,b]. Synthesis of 1-Hydroxy-1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]1H-pyrazol-4-yl)-3-oxoprop-styryl cyanine dye **(4).**

A-An Ethanolic solution of **(1B,** 0.01 mol.) and pyridin-ium-ethiodide salts (0.01mol.) in few drops of piperidine was refluxed for 4 hrs, reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(4), (B):** An Ethanolic solution of **(2A,** 0.01mol.**)** and pyridin-ium-ethiodide (0.01mole) in Zn dust/ acetic acid and were refluxed for 4 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(4), Table (4A)** IR ($\nu^{KBr}cm^{-1}$) of **(4)** 684,832 cm^{-1} (υ mono sub.ph), 1364-1455cm^{-1} (υ$2CH_3$)1713,1775 cm^{-1} (υ C=O)1447,1455 cm^{-1} (υ C=N) 2875, 2886cm^{-1} (υ heterocyclic Q. salts)1713 cm^{-1} (υ acyclic c=o) 3147,3017cm^{-1} (υ exocyclic pyridinium)**, [31a,b].**

Synthesis of 1, 3-bis (3-Methyl-5-oxo-1-phenyl-4, 5-di [H]-1H-pyrazol-4-yl) propan-1, 3-dione-2-acyclic mero cyanine dye (5)

An Ethanolic solution of (**4,** 0.01mol.) in few drops of piperidine was refluxed for 4 hrs; the reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(5), Table (4A).**

Synthesis of tripyrazolo[4,3-b:3',4'-g: 3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide, tripyrazolo[4,3-b:3',4'-g:3'',4'',5''-ij]pyrido[2,1,6-de] quinolizin-12-ium-iodide & isoxazolo[3,4,5-ij] dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] quinolizin-12-ium-iodide (6a-c)

A-An Ethanolic solution of **(3A,** 0.01 mol.) with hydrazine hydrate (0.01mol.) in few drops of acetic acid was refluxed for 4 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to half of its volume, cooled. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(6a), B-**An Ethanolic solution of **(3A,** 0.01mol) in few drops of piperidine with (phenyl hydrazine or hydroxylamine hydrochloride (0.01mole) was refluxed for 3-5hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to half of its volume, cooled and acidified with acetic acid to

neutralize the excess from piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(6b, c), Table (4A)** IR (νKBr cm^{-1}) of **(6b)** 1586cm^{-1} (γ C=N), 3060 cm^{-1} (γ Ar), 691 cm-1 (γ mono Sub. Ar.) 3428-32 cm^{-1} (γ heterocyclic quaternary salt) & ylide iodides), 3060 cm^{-1} (γ Ar.), 1364-1433 cm^{-1} (γ $2CH_3$), 1596 cm^{-1} (γ conj. C=C), 3424-3437 cm^{-1} (γ cyclic NH secondary), **[31a, b].**

Synthesis of dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]pyrimido [4,5,6-ij] quinolizin-13-ium iodide (7).

An Ethanolic solution of **(3A,** 0.01mol) and urea (0.01mole) and few drops of conc. HCL were refluxed for 3 hrs. The filtrate was concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated filtrated, crystallized from ethanol to give **(7), Table (4A)** IR (ν^{KBr} cm^{-1}) of **(7)** 1716 cm^{-1} (γ C=O), 1585 cm^{-1} (γ C=N), 3061cm^{-1} (γ Ar), 691-827cm^{-1} (γ mono Sub. Ar.), 3428-32 cm^{-1} (γ heterocyclic quaternary salt) & ylide iodide), 3060 cm^{-1} (γ Ar.), 1364-1499 cm^{-1} (γ $2CH_3$) 1595 cm^{-1} (γ conj. C=C), 3365cm^{-1} (γ cyclic NH secondary), & 2878cm^{-1}(γ ylide iodides), **[31a, b].**

Synthesis of [1,3]dioxino, [1,3]oxathiino [4,5,6-ij] & dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]quinolizin-1,13-diium)iodide/chloride, [4,3-b:3',4'-g] pyrido[2,1,6-de] quinolizin-13-ium) chloride /iodide) metal enolate complexes (X= Ni) [8a-c]

A-A concentrated aqueous solution of metal (II) Chloride (0.01mol) was added under stirring to a methanolic solution 20 ml **(3A,** 0.01mol). Stirring was continued for 1.5-2h. The precipitated complex was filtered, washed with water, recrystallized from hot chloroform and dried under vacuum. The precipitates complexes had a colour to give **(8a)** The complexes were well soluble in DMSO and DMF, **Table (4), B-**An Ethanolic solution of **(8a)** with 1%sod.sulfide solution (Na_2S) was refluxed for 4 hrs; the reaction mixture was filtrated from unreacted materials, cooled and precipitated by addition of cold water. The precipitated filtrated, crystallized from ethanol to give **(8b), C-**An Ethanolic solution of **(8a)** with ammonium acetate (0.01 miles) was refluxed for 5 hrs.; the reaction mixture was filtrated from unreacted materials, cooled and precipitated by addition of cold water. The precipitated filtrated, recrystallized from ethanol to give **(8c), Table (4A),** IR (□KBr cm-1) of **(8a, c)** 1716cm^{-1} (γ C=O), 1596-1612 cm-1 (γ C=N), 3064-8 cm-1 (γ Ar), 685-829 cm^{-1} (γ mono Sub. Ar.), 2922-

39 cm-1 (γ heterocyclic quaternary salt) & ylide iodides), 3064-8 cm^{-1} (γ Ar.),1365-1482 cm-1(γ $2CH_3$), defined absorption band at 1596 cm-1(γ conj. C=C), 2891-2939 cm^{-1} (γ ylide chloride/iodide), & 669-691cm^{-1} (γ M-O of metal complex), (1640 cm-1), assignable to str. of an enolized acetyl carbonyl group IR spectra of all complexes, the broad free ligand band in (2500-3300 cm^{-1}) had disappeared, indicating the replacement of an Enol-H by a metal ion during complexation. The absence of the free ligand band at (1270 cm^{-1}) due to C–O–H bending also supports the replacement of the Enol-H by a metal ion. However, the band due to the H-bonded acetyl carbonyl group disappeared & instead a new band appeared at (1570 cm^{-1}) in the spectra of all complexes, supporting the involvement of the enolized carbonyl in the bonding with the metal ion, **[31a,b].**

Synthesis of 7-(hydroxyimino)-6,9-dimethyl-8-oxo-4,11-diphe-nyl-7,7a,8,11-[H]4H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] quinolizin-12-ium-iodide & 8-(hydroxyamino)-6,9-dimethyl-7-oxo-4,11-diphenyl-7,11-di[H]-4H-dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de] quinolizin-12-ium iodide (9 & 10)

A-An Ethanolic solution of **(3A, 0**.01mol.) and hydroxylamine hydrochloride (2 moles) with sodium acetate (3mols.) were refluxed for 5 hrs. The reaction mixture was filtrated while hot from unreacted materials. The filtrate was concentrated, cooled and precipitated by addition of cold water and crystallized from ethanol to give **(9). B-** An Ethanolic solution of **(9)** in few drops of piperidine was refluxed for 3 hrs. The reaction mixture was filtrated while hot from unreacted materials. The filtrate was concentrated, cooled and precipitated by addition of cold water and crystallized from ethanol to give **(10). Table (3),** IR **(υ $^{KBr}cm^{-1}$)** of **(9)** 1685-1666cm^{-1},=NOH oxime, 1465-1610 cm^{-1}(γ C=N & υ C=N cyclic), 688-839cm^{-1} (γ mono-sub-Ar.), 2890 cm^{-1}(γ Ylide anion),688.46-839cm^{-1},(γ mono-sub-Ar.),3610-3645cm^{-1}O–H str. 1277,1358,1452cm^{-1} (γ$2CH_3$) for **(9)** & 2500-3200cm^{-1} broad, (υ C-CH_3), 1720cm^{-1} (υ C=O) for **(9)** Pyridine, 1645-1590cm^{-1},1585-1560 cm^{-1}, 1540-1471cm^{-1},(1440-1410) cm^{-1}. 3037-3144cm^{-l} (γ pyridinium quaternary), 3120 cm^{-l}, (γ N-H str., pyridinium ion), 3150-3000 cm^{-}1 (γ str. C-H. pyridinium iodide) ,1650-1400 cm^{-1} (γ C=C & C=N), 1650-1625 cm^{-1} (γ C=N or C=C-C=N conj. pyridinium salts), 1631-1625 cm^{-1} (γ quatern pyridine), 1594 &1580 cm^{-1} (γ disappearing Ar. C-C in quaternary salts), 1482cm^{-1} (γ conj. C=C & C=N).1465-1430 cm^{-1} (γ Hyperconj. quaternary salts),. 1631-625cm^{-1} (γ C=N of pyridinium ion, γ amino-aldehyde character for pyridine

quaternization ring).1594 & 1580 cm^{-1} (γ Ar. C-C), 1482 cm^{-1} (γ conj. C=C & C =N) **[31a,b].**

Synthesis of isoxazolo(isothiazolo)[3,4,5-ij]dipyrazolo[4,3-b: 3',4'-g]pyrido [2,1,6-de]quinolizin-1,12-diium-chloride/iodide & tripyrazolo[4,3-b:3',4'-g: 3'',4'',5''-ij]pyrido[2,1,6-de]quinolizin-12-ium-iodide-endocyclic cyanine dyes (11a-c)

A-An Ethanolic solution of **(9)** in few drops of conic HCL was refluxed for 3 hrs The reaction mixture was filtrated while hot from unreacted materials. The filtrate was concentrated, cooled and precipitated by addition of cold water and crystallized from ethanol to give **(11A). B-**An Ethanolic solution of **(11A)** and 1% sod. Sulfide solution was refluxed for 4 hrs. ; the reaction mixture was filtrated from unreacted materials, cooled and precipitated by addition of cold water. The precipitated was filtrated, crystallized from ethanol to give **(11B),** C-An Ethanolic solution of **(11A)** with ammonium acetate (0.01moles) was refluxed for 4 hrs., the reaction mixture was filtrated from unreacted materials, cooled and precipitated by addition of cold water. The precipitated filtrated, and recrystallized from ethanol to give **(11C), Table (4B)** IR (υ ^{KBr} cm^{-1}) of **(11A)** 3344cm^{-1} (γ NH), 1465-1610 cm^{-1}(γ C=N & υ cyclic C=N), 2890 cm^{-1} (γ Ylide iodide or chloride anions), 1277, 1358, 1452cm^{-1} (γ2CH_3), 3344cm^{-1} (γ NH), 1465-1610 cm^{-1}(γ C=N & υ cyclic C=N), 2890 cm^{-1} (γ Ylide iodide or chloride anions), 1277, 1358, 1452cm^{-1} (γ2CH_3), Pyridine, 1645-1590cm^{-1}, 1585-1560cm^{-1}, 1540-1471cm^{-1}, 1440-1410cm^{-1} 688-839cm^{-1} (γ mono-sub-Ar.), 3037-3144cm^{-l} (γ 2 bands pyridinium quaternary), 3120 cm^{-l}, (γ N-H str., pyridinium ion) 3150-3000 cm^{-}1(γ str. C-H. pyridinium iodide) ,1650-1400 cm^{-1} (γ C=C & C=N), 1650-1625 cm^{-1} (γ C=N or C=C-C=N conj. pyridinium salts), 1631-1625 cm^{-1} (γ quatern pyridine), 1594 &1580 cm^{-1} (γ disappearing Ar. C-C in quaternary salts), 1482cm^{-1} (γ conj. C=C & C =N).1465-1430 cm^{-1} (γ Hyperconj. quaternary salts), 1129-092 cm^{-1} (γ exocyclic N-C str. pyridinium salts). 1631-625cm^{-1} (γ C=N of heterocyclic quaternary nitrogen atom or ring vibrations of pyridinium ion, γ amino-aldehyde character for pyridine quaternization ring).1594 and 1580 cm^{-1} Ar. C-C vibrations disappear completely. Pyridine, 1482 cm^{-1} (γ conj. C=C & C =N) **[31a,b].**

Synthesis of 1, 3-Bis (3-methyl-5-oxo-1-phenyl-4, 5-di [H]-1H-pyrazol-4-yl) propan-1, 3-dione -Acyclic Mero Cyanine Dye (12)

An Ethanolic solution of **(39,** 0.01mole) with Barbituric acid (0.01mole) was refluxed for 4 hrs. the reaction mixture was filtrated while hot from unreacted materials. The

filtrate concentrated, cooled and precipitated by addition of cold water, filtrated and crystallized from ethanol to give **(12), Table (4B)**

Synthesis of Pyrimido[4,5-f]pyrimido[5',4':5,6]pyrido[3,2,1-ij] quinazolin-1,3,6,8,9,10,11,13(2H,5H,7H,10aH,12H,14bH)-octaone (13)

An Ethanolic solution of **(12,** 0.01mol) in few drops of piperidine was refluxed for 3-5 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol **(13), Table (4B), fig,(1).**

Synthesis of Dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide, dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quino-lizin-12-ium-iodide, dipyrazolo [4,3-b:3',4'-g]pyrido[2,1,6-de] quinolizin-12-ium-iodide & dipyrazolo[4,3-b:3',4'-g] pyrido [2,1,6-de]quinolizin-12-ium-iodide-endocyclic multi-charge transferred mero cyanine dyes (14A-D)

An Ethanolic solution of **(3A) & 3**-methyl-1-phenyl-pyrazolin-5-one, 2-oxo-imidazol-5-one, 2-methyl-oxazol-5-one and/or barbituric acid (0.01mol.) in few drops of piperidine was refluxed for 3-5 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated and crystallized from ethanol to give **(14A-D), Table (4B), fig,(1).**

Synthesis of imidazo [4',5': 5,6]pyrano[2,3,4-ij]dipyrazolo[4,3-b:3',4'-g] pyrido[2,1,6-de]quinolizin-14-ium-iodide & dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] pyrimido[5',4':5,6]pyrano[2,3,4-ij]quinolizin-15-ium-iodide-endocyclic multi-charge transferred mero cyanine dye (15B,D).

An Ethanolic solution of **(14B, D, 0.01mol)** in few drops of piperidine was refluxed for 3-5 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(15B, D) Table (4B).**

Synthesis of dipyrazolo[4,3-b:3',4'-g]pyrazolo[4',3':5,6]pyrano [2,3,4-ij]Pyrido [2,1,6-de]quinolizin-13,14-diium-imidazo[4',5': 5,6]pyrano[2,3,4-ij]dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] quinolizin-13,14-diium-chloride/iodide, oxazolo [5',4':5,6]pyrano [2,3,4-ij]dipyrazolo[4,3-b:3',4'-

g]pyrido[2,1,6-de]quinolizin-13, 14-diium-chloride/iodide,dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrimido [5',4':5,6]pyrano[2,3,4-ij]quinolizin-14,15-diium-iodide/chloride-endo cyclic multi-charge transferred mero cyanine dyes (16A-D).

An Ethanolic solution of **(14A-D, 0.01mol)** in few drops of conc HCl was refluxed for 3-5 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated to one third of its volume, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(16A-D), Table (4B).**

Synthesis of 5, 5'-malonyl-bis (pyrimidin-2, 4, 6(1H, 3H, 5H)-trione) (17)

A mixture of Barbituric acid **(0.02mol)** & diethyl malonate (0.01mol.) in acetic acid was refluxed for 3 hours. The reaction mixture was filtrated from unreacted materials, concentrated and cooled; the solid product was collected and crystallized from ethanol to give **(55), Table (4B),** Mass spectra of **(17)** confirmed a molecular formula ($C_{11}H_8N_4O_8$) agree with a molecular ion at m/z = Molecular Weight: M^+=324.20 and base peaks (100%) at m/z= 127, [barbituric acid], **[33].**

Synthesis of 1-hydroxy-3-oxo-1,3-bis(2,4,6-trioxohexa[H] pyrimidin-5-yl-prop-1-en-2-yl)styryl cyanine (18)

(A): An Ethanolic solution of **(17,** 0.01 mol.**)** and pyridin-ium-ethiodide salts (0.01mol.) in few drops of piperidine was refluxed for 4 hrs, reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(18), (B):** An Ethanolic solution of **(2D,** 0.01mole) and pyridin-ium-ethiodide (0.01mol.) in Zn dust/ acetic acid and were refluxed for 4 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(18), Table (4B).**

Synthesis of 5, 5'-(2-(1-ethylpyridin-4(1H)-ylidene-malonyl-bis (pyrimidin-2, 4, 6 1, 3, 5-tri-[H]-trione)mero cyanine dye (19)

An Ethanolic solution of **(18,** 0.01mole) in few drops of piperidine was refluxed for 4hrs; the reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid to

neutralize the excess of piperidine. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give **(19), Table (4B)**

Synthesis of 5,5'-(2-(2,6-dioxotetra[H]pyrimidin-4(1H)-ylidene-malonyl-bis (pyrimidin-1, 3, 5-tri-[H]-2,4,6-trione)pyrimido [4,5-f]pyrimido [5',4':5,6] pyrido [3,2,1-ij]quinazolin-2,5,7,10a,12, 14-hexa[H]-1,3,6,8,9,10,11,13-octaone (20 & 21)

A-An Ethanolic solution of **(18, 0.01mol.)** and barbituric acid (0.01mole) in few drops of piperidine was refluxed for 4 hrs. The reaction mixture was filtrated hot from unreacted materials. The filtrate was concentrated, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized to give **(20), B-**An Ethanolic solution of **(20,** 0.01mole**)** in few drops of piperidine was refluxed for 1 hrs, the reaction mixture was filtrated hot from unreacted materials. The filtrate was concentrated, cooled and the precipitated products after dilution with water were separated, filtrated, crystallized to give **(21), Table (4B), fig, (1).** IR (υ^{KBr} cm^{-1}) **(21)** showed, in addition to, the general absorption bands at 3344cm^{-1} **(γ NH),** 1465-1610 cm^{-1}(γ C=N & υ cyclic C=N), 2890 cm^{-1} (γ Ylide iodide or chloride anions), 2500-3200cm^{-1} broad, (γ C-CH_3), 1720cm^{-1} (υ C=O), 1600-1545cm^{-1},1575-1540cm^{-1},1510-1410cm^{-1},14711-1330cm^{-1}(γ3-pyrimidine nuclei),1065-1173cm^{-1}(γ C-N-C cyclic), 1685-1666)cm^{-1}, (γ α, β-unsaturated ketones), Pyrimidines ,(1010-900),(850-780),(860-830)cm^{-1}, (1600-1545), (1575-1540), (1510-1410), 1471-1330 cm^{-1} (γ3-pyrimidine nuclei) **[31a,b].**

Solvatochromic and Acid-Base Properties:

The organic solvents were used of spectroscopic grade of purified. The absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1cm cell. The stock solution of dye was of the order 10^{-3} M. Solution of low molarities used in spectral measurements was obtained by accurate dilution.

Preparation of dyes solution:

1- For studying the effect of pure solvents in visible range. Accurate volumes of the stock solution of dyes were diluted to appropriate volume in order to obtain the required concentrations. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect of time. **2-** For studying the spectral behaviour in aqueous universal buffer solutions, an accurate volume of the stock solution was added to 5 ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water.

Preparation of Universal Buffer Solution:

A modified of buffer series solutions with pH values ranging from **(2.09-11.98)** was prepared in a way described in respective reference **[34]**. The pH's of buffer solutions were checked using Orion pH-meter model **(60, A),** accurate to 0.005 pH units, at 25°C.

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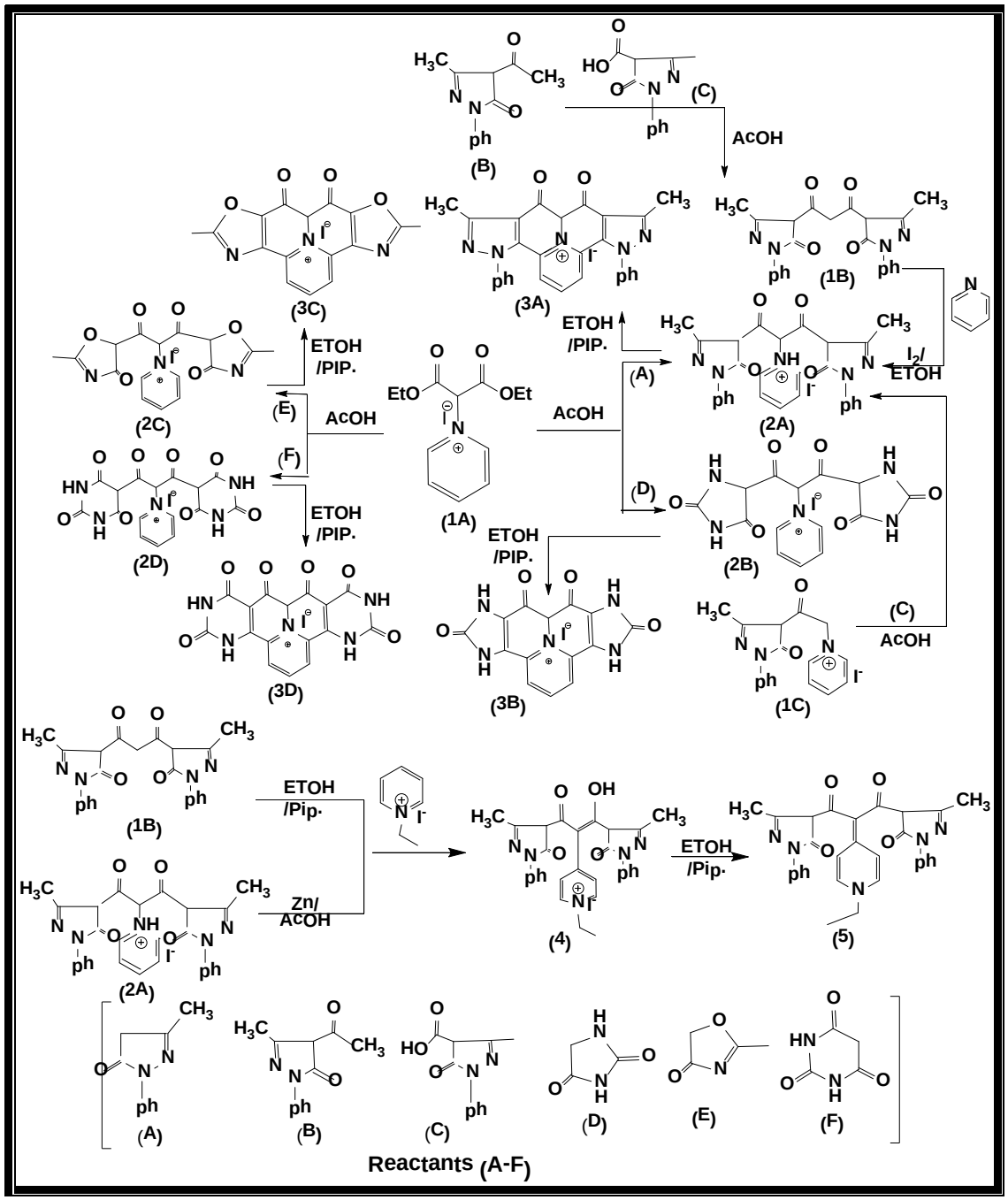
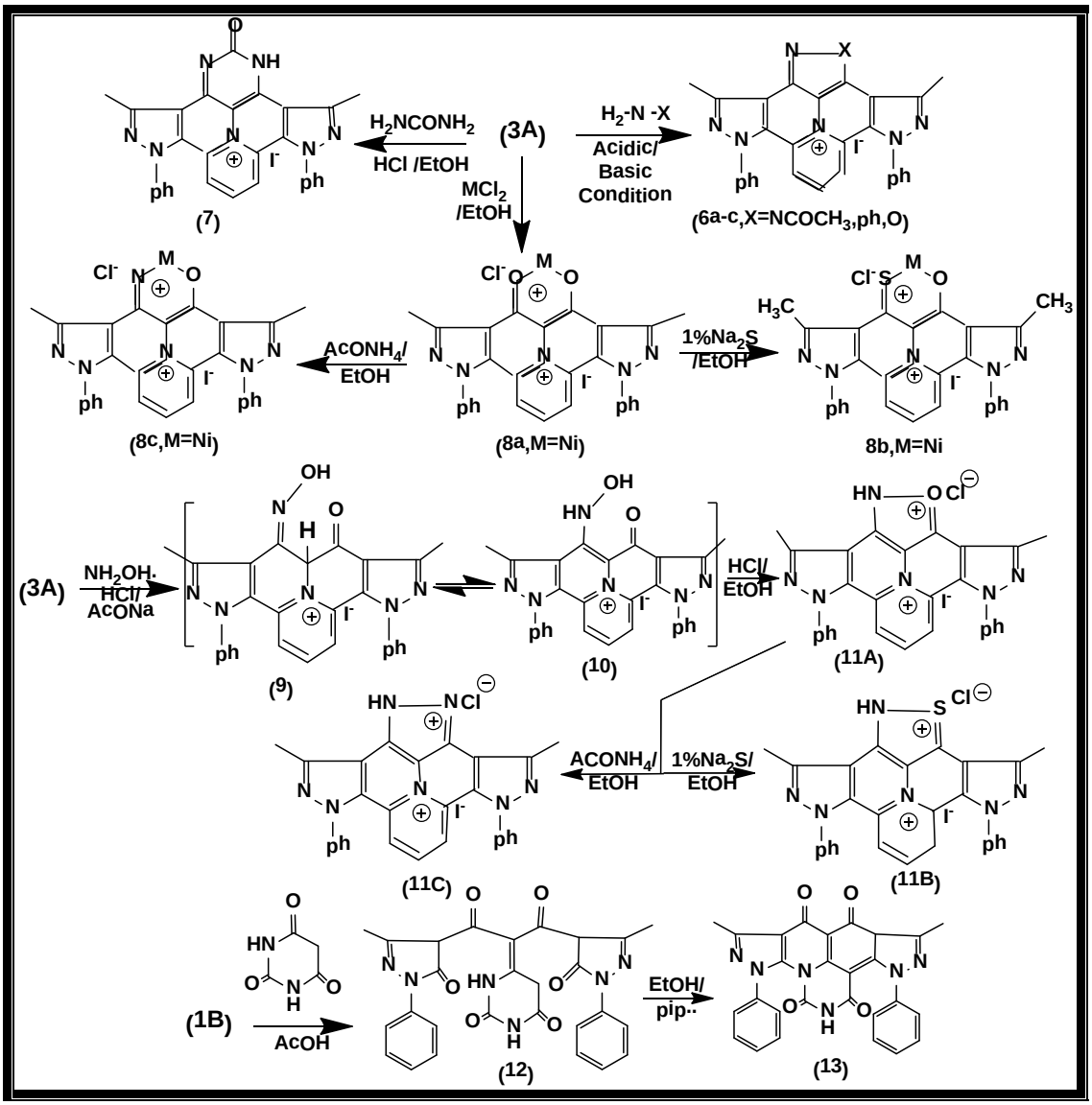
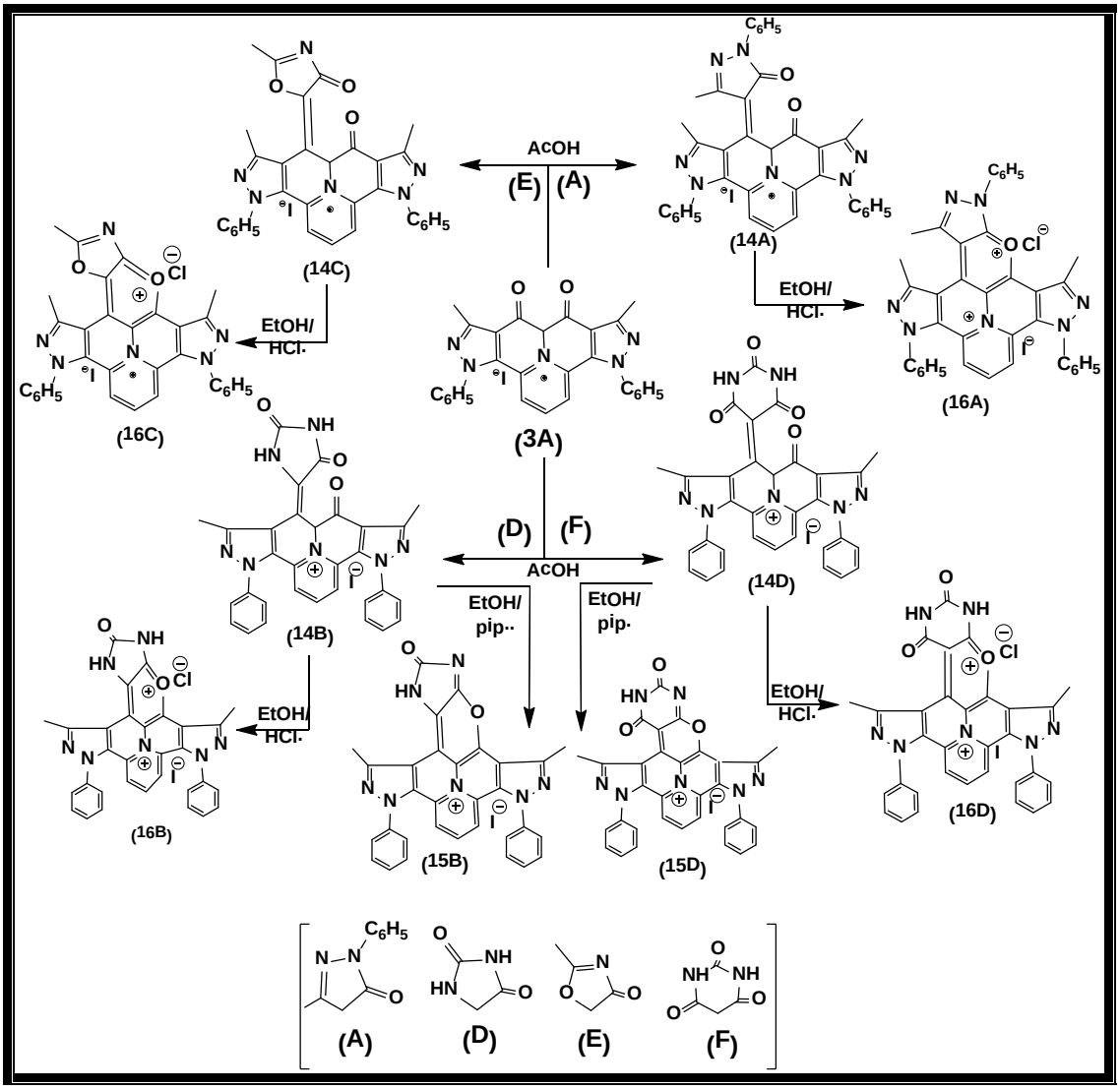


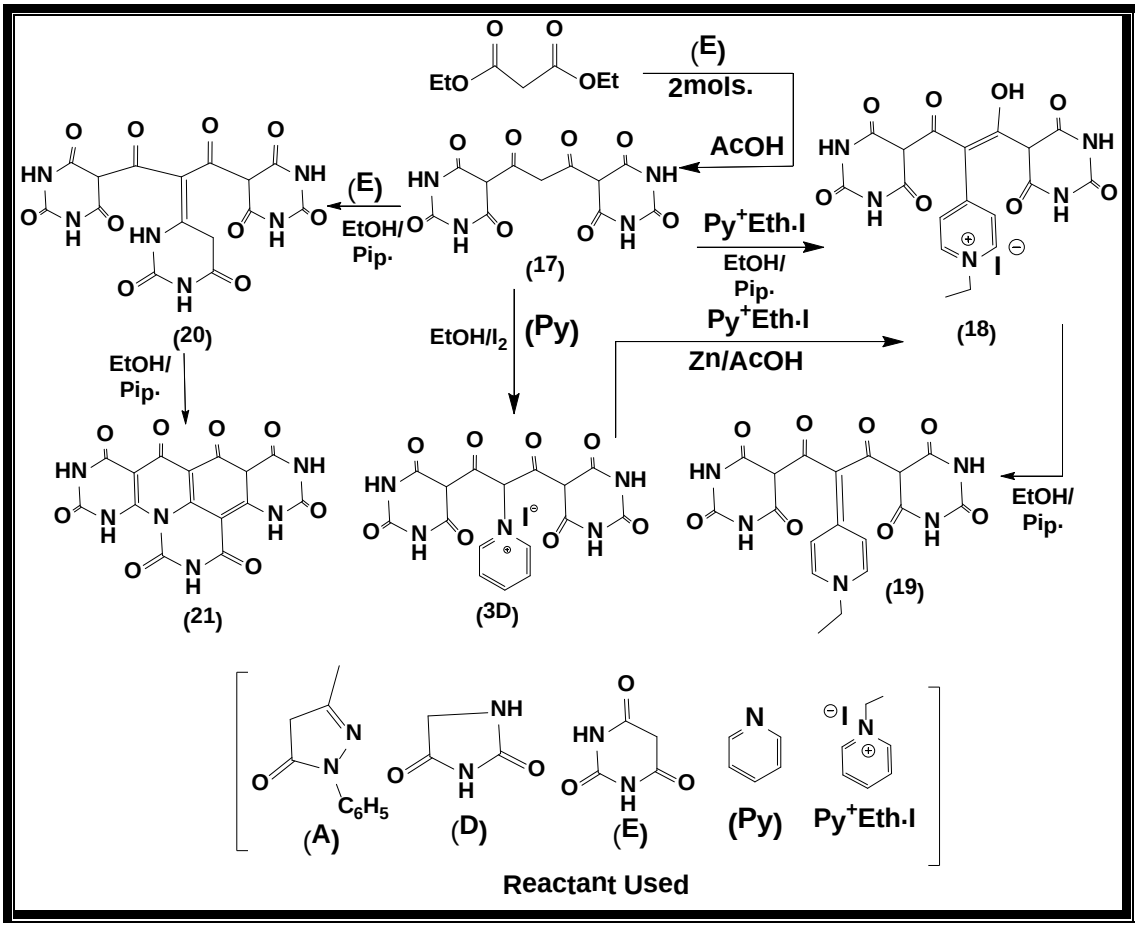
Scheme (1A)


(7)
H2NCONH2
HCl /EtOH
(3A)
H2-N -X
Acidic/
Basic
Condition
(6a-c,X=NCOCH3,ph,O)
MCl2
/EtOH
(8c,M=Ni)
AcONH4/
EtOH
(8a,M=Ni)
1%Na2S
/EtOH
8b,M=Ni
(3A)
NH2OH.
HCl/
AcONa
(9)
(10)
HCl/
EtOH
(11A)
ACONH4/
EtOH
1%Na2S/
EtOH
(11C)
(11B)
(1B)
AcOH
(12)
EtOH/
pip..
(13)

Scheme (1B)


AcOH
(E) (A)
(14C)
(14A)
EtOH/ HCl.
(16C)
(3A)
(16A)
(D) (F)
AcOH
(14D)
(14B)
EtOH/ pip..
EtOH/ pip.
EtOH/ HCl.
(16B)
(15B)
(15D)
(16D)
(A)
(D)
(E)
(F)

Scheme (2A)



Scheme (2B)

Table (1): Values of λ_{max} (nm) (ε_{max}) ($mol^{-1}\,cm^{-1}$) of (19 & 21) in pure organic solvents.

Comp. No.	Colour in pure organic solvents & $\lambda_{max}(\varepsilon_{max})$							
	EtOH		Dioxan		C_6H_6		DMF	
	Colour	λ_{max} (ε_{max})	Colour	λ_{max} (ε_{max})	Colour	λ_{max} (ε_{max})	Colour	λ_{max} (ε_{max})
19	Pink	518 (7922)	yellow	435 (8173)	Orange	496 (7266)	Pink	494 (4517)
21	red	509 (7266)	Orange	398 (2670)	orange	477 (6142)	red	509 (7266)

Table (2): Values of λ_{max} (nm) & (ε_{max}) ($mol^{-1}\,cm^{-1}$) of (3B) in aq.universal buffer solution.

Comp No.	Colour in Universal buffer & λ_{max} (ε_{max})										pKa
	2.5		5.5		7		9.3		11.9		
	Colour	λmax (εmax)	Colour	λmax (εmax)	Colour	λmax (εmax)	Colour	λmax (εmax)	Colour	λmax (εmax)	
3b λ_{max}. 432 nm	Pink	409 (9544)	Pink	418 (9432)	Pink	416 (10930)	Orange	428 (9641)	Orange	433 (8054)	6.5
	0.17		0.15		0.18		0.16		0.07		

Table (3): Characterization data for (1B, 2A-D, 9, 10)

Comp No.	Nature of Products			Mol. Formula (Mol. Wt.)	% Calcd. (Found)		
	M.p° C	Yield %	Color		C	H	N
1B	140	74	Reddish brown	$C_{23}H_{20}N_4O_4$ 416	66.34 66.37	4.84 4.88	13.45 13.46
2A	178	71	Brown	$C_{28}H_{24}IN_5O_4$ 621.	54.12 54.17	3.89 3.92	11.27 11.25
2B	165	67	Pale brown	$C_{14}H_{12}IN_5O_6$ (473)	35.54 35.57	2.56 2.59	14.80 14.76
2c	188	66	Pale yellow	$C_{16}H_{14}IN_3O_6$ (471)	40.78 40.71	2.99 2.93	8.92 8.99
9	185	77	Pale brown	$C_{28}H_{21}IN_6O_2$ (600)	56.01 56.07	3.53 3.57	14 14.02
10	205	73	orange	$C_{28}H_{21}IN_6O_2$, 600	56.01 56.04	3.53 3.51	14 14.03

Table (4A): Characterization data for (3A-D, 4, 5, 6a-c, 7, 8a-c)

Comp. No.	Nature of Products			Mol. Formula (Mol. Wt.)	% Calcd. (Found)			Absorption spectra in 95% EtOH Conc. ($1x10^{-4}$g/mol.)	
	M.p. °C	Yield %	Color		C	H	N	λ_{max} (nm)	ε_{max} (cm^2mol^-)
3A	195	66	Red	$C_{28}H_{20I}N_5O_2$ 585	57.45 57.47	3.44 3.41	11.96 11.95	393	3185

3B	205	67	Violet	$C_{14}H_8IN_5O_4$ (437)	38.47 38.44	1.84 1.86	16.02 16.07	487	15897
3C	195	66	Red	$C_{16}H_{10}IN_3O_4$ (435)	44.16 44.11	2.32 2.35	9.66 9.71	456	6218
4	195	73	Brown	$C_{30}H_{28}IN_5O_4$ 649	57.45 57.41	3.44 3.47	11.96 11.98	519	5186
5	197	71	Orange	$C_{30}H_{27}N_5O_4$ 521	69.08 69.12	5.22 5.26	13.43 13.47	486	3582
3D	182	79	Orange	$C_{16}H_8IN_5O_6$ (493)	38.97 38.99	1.64 1.67	14.20 14.27	452	6825
6a	185	73	Yellow	$C_{30}H_{22}IN_7O$ (623)	57.80 57.83	3.56 3.52	15.73 15.71	467	6722
6b	215	77	orange	$C_{34}H_{24}IN_7$ (657)	62.11 62.15	3.68 3.65	14.91 14.88	518	5985
6c	205	63	Deep orange	$C_{28}H_{19}IN_6O$ (582)	57.74 57.71	3.29 3.24	14.43 14.47	459	7319
7	195	66	Violet	$C_{29}H_{20}IN_7O$ (609)	57.15 57.19	3.31 3.28	16.09 16.05	482	8574
8a	225	72	Pale brown	$C_{28}H_{19}ClIN_5O_2Ni$ (673)	49.68 49.88	2.81 2.88	10.42 10.44	508	7631
8b	215	78	Orange	$C_{28}H_{19}ClIN_5OSNi$ (689)	48.70 48.74	2.75 2.79	10.14 10.18	515	6254
8c	200	69	Brown	$C_{28}H_{19}ClIN_6ONi$ (675)	49.71 49.77	2.81 2.86	12.42 12.48	519	5631

Table (4B): Characterization data for (11A-C, 12 & 13, 16A-D, 17, 18, 19, 20 & 21)

11A	190	71	violet	$C_{28}H_{20}ClIN_6O$ (618)	54.34 54.31	3.26 3.22	13.58 13.55	499	8931
11B	210	78	Red	$C_{28}H_{20}ClIN_6S$ 634	52.97 52.92	3.18 3.19	13.24 13.26	478	7971
11C	225	75	Deep orange	$C_{28}H_{20}ClIN_7$ 616	54.52 54.5	3.27 3.29	15.89 15.86	469	8092
12	178	77	Orange	$C_{28}H_{26}N_6O_6$ (542)	61.99 61.94	4.83 4.86	15.49 15.45	456	7631
13	220	71	Pale brown	$C_{15}H_8N_6O_8$ (400)	45.01 45.05	2.01 2.04	21.00 21.04	492	8564
16A	215	78	Pale brown	$C_{33}H_{25}ClIN_7O$ (697)	56.79 56.28	3.61 3.66	14.05 14.00	489	2599
16B	245	83	Reddish violet	$C_{31}H_{21}ClIN_7O_2$ (685)	54.28 54.31	3.09 3.11	14.19 14.32	475	7586

16C	205	81	Orange	$C_{32}H_{22}ClIN_6O_2$ (684)	56.12 56.17	3.24 3.27	12.17 12.29	482	3575
16D	222	79	Orange	$C_{32}H_{21}ClIN_7O_3$ (713)	53.84 53.88	2.96 2.99	13.73 13.77	398	4698
17	210	75	Pale red	$C_{11}H_8N_4O_8$ (324)	40.75 40.71	2.49 2.45	17.28 17.25	462	6587
18	225	71	Deep orang	$C_{18}H_{16}IN_5O_8$ 557	38.80	2.89	12.57	428	8054
19	238	73	Pale black	$C_{18}H_15N_5O_8$ 429	50.35 50.38	3.52 3.55	16.31 16.37	469	4974
58	195	77	Orange	$C_{15}H_{10}N_6O_{10}$ 434	41.49 41.15	2.32 3.35	19.53 19.39	460	5897
59	222	79	Reddish violet	$C_{15}H_6N_6O_8$ 398	45.24 45.27	1.52 1.58	21.10 21.15	454	8957

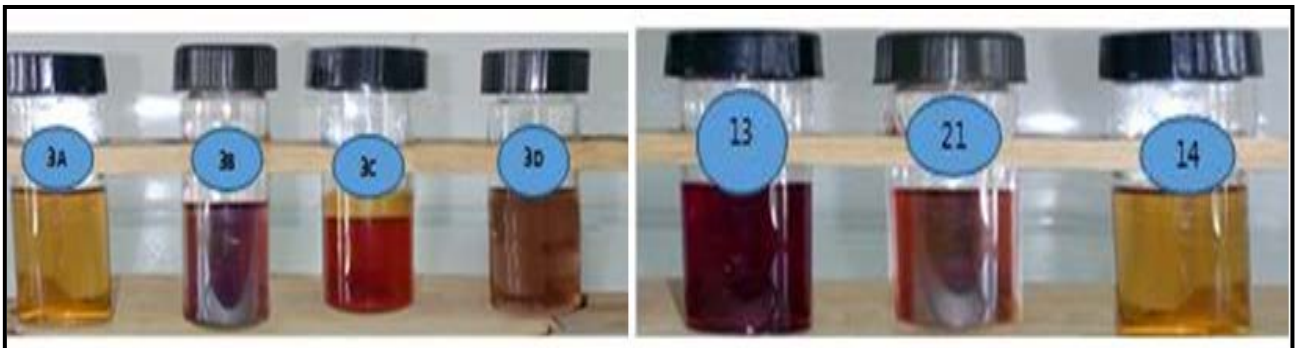


Fig (1): photo colour for compounds (3A-D, 13, 21, and 14)

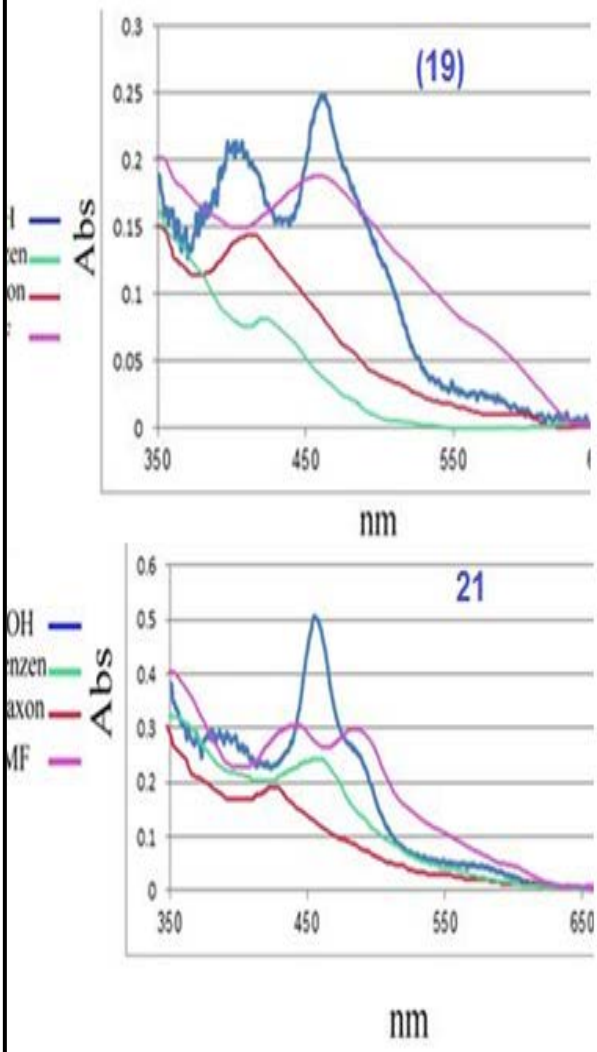


Fig (2): Solvatochromic behaviour of (19, and 21) in organic Solvent

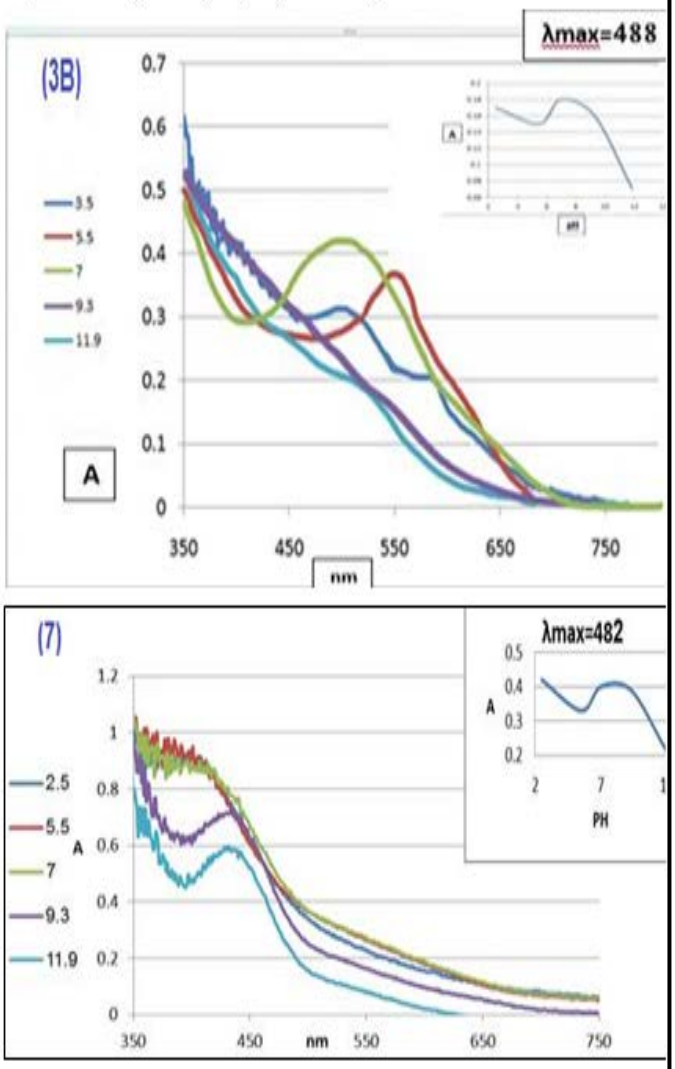


Fig (3): Absorption spectra in Aqueous universal buffer solutions S-curve determination of (3B, and 7)