SYNTHESIS & SPECTRAL BEHAVIOUR OF SELF-ASSEMBLY HETEROCYCLIC [ICT] FUNCTIONAL & OXONIUM ACYCLIC (CYCLIC) MERO CYANINE DYES

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ABSTRACT

1, 3-Bis (3-methyl-1-phenyl-pyrazolin-5-one-4-yl)- & 5, 5'-bis (pyrimidin-2, 4, 6(1H, 3H, 5H)-trione)-β-di-carbonyl precursors **(1A, 5)** were used as key intermediates consequently in the synthesis of Bis-pyrazolo[4,3-b: 3',4'-g]pyrido[2,1,6-de]quinolizin-12-ium iodide & 1,3-bis (2,4,6-tri-oxo-hexa [H] pyrimidin-5-yl)-pyridin-1-ium-iodide-β-di-carbonyl compounds **(1C, 7)** & their self-assembly **[ICT]** functional dyes incorporating based quinolizin-ium, oxonium-cyclic (acyclic) mero**-,(2A-D, 3A,B, 4A-D, 7, 8, 9-11)** and β-di-carbonyl acyclic (cyclic) mero cyanine dyes **(12, !3)**. A special attention had been focused on the spectral behaviour of such dyes to permit possible color-chemical structure relationship & criterion for their use as photosensitizes. The solvatochromic behavior and colour changes with solvents having different polarities of such dyes are observed here to permit a selection of optimal solvent when these dyes are applied as photosensitizers.

Keywords: Synthesis, functional & oxonium acyclic (cyclic) mero cyanine dyes, Spectral & Solvatochromic Behaviours

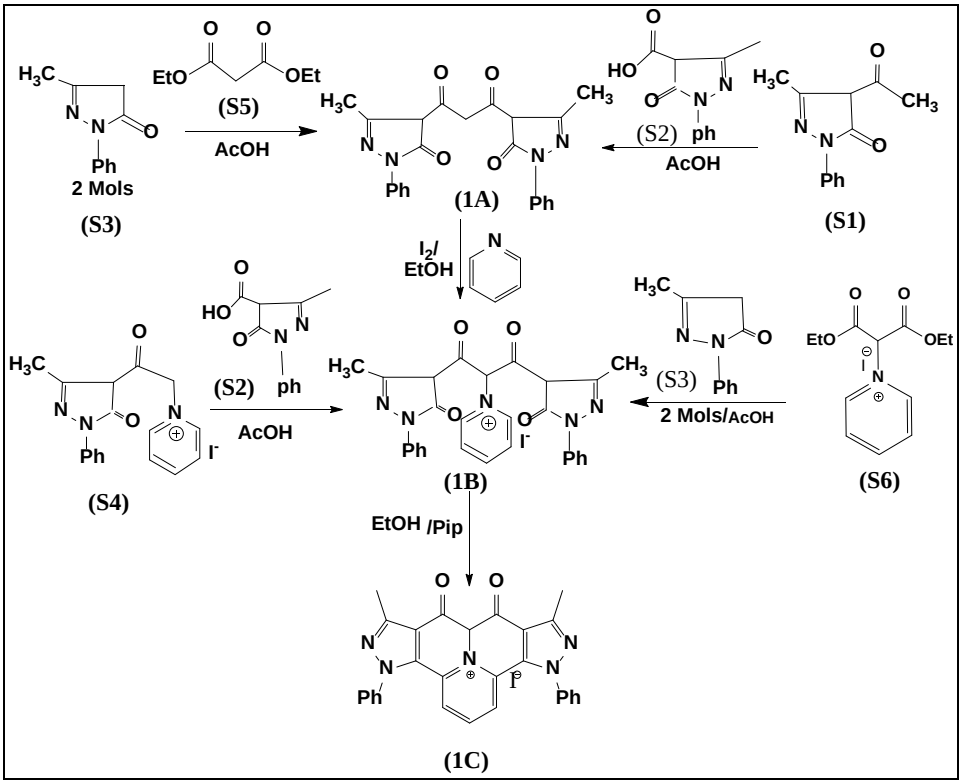
INTRODUCTION

The literature reviews had attracted much attention for Intramolecular Charge-Transfer [ICT] heterocyclic organic molecules owing to their unique electronic and/or photonic properties **[1-3]** solar cells **[4, 5]** It is of interesting to attempt on new synthetic entities for functional dyes and their physicochemical studies. 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 possible color-chemical N-bridge head heterocyclic quinolizine through the introduction of heterocycles to the π-conjugated systems. Combining these [ICT] compounds featuring different degrees of conjugation with phase transfer methodologies. A in the [ICT] of pyrrolo[2,1,5-de] quinolizine & oxonium moieties have received considerable attention in the field of synthetic organic chemistry because of their special structural properties **[5a,b, 6a, 6b,7, 8].**

RESULT & DISCUSSION

An eye opening feat for our approach of building up of some N-bridge head poly heterocyclic selected self-assembly [ICT] functional cyanine dyes based on 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 or 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]di–pyri-mido[5,4-b:4',5'-g]quinolizin-14-ium-iodide and/or pyrimido[4,5-f]pyrimido [5',4': 5,6]

pyrido [3,2,1-ij] quinozolin-octaone was conducted & started 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 (1A) by direct reaction of 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one (S1) **[9]** with 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid **[10-12]** in AcOH. The formation of (1A) was chemically confirmed via an alternative pathway via the direct interaction of bimolar amounts of 3-methyl-1-phenyl-pyrazolin-5-one with diethyl malonate in acetic acid to give the same & mixed melting points. Selective quaternization of pyridine by the later compound (1A), 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 (1B). It was obvious, that chemical confirmation, for the formation of (1B) 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 (S4) **[13]** with 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid, in equimolar amount,. Cyclocondensation of (1B) 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 (1C), It was obvious that, the interaction of diethylmalonate-pyridin-1-ium-iodide (S6) **[14-16]** & bimolar amounts 3-methyl-1-phenyl-pyrazolin-5-one in AcOH confirmed the same & mixed melting points for (1B) which on heterocyclization using piperidine catalysis achieve the same & mixed melting points for (1C).**Scheme (1).**

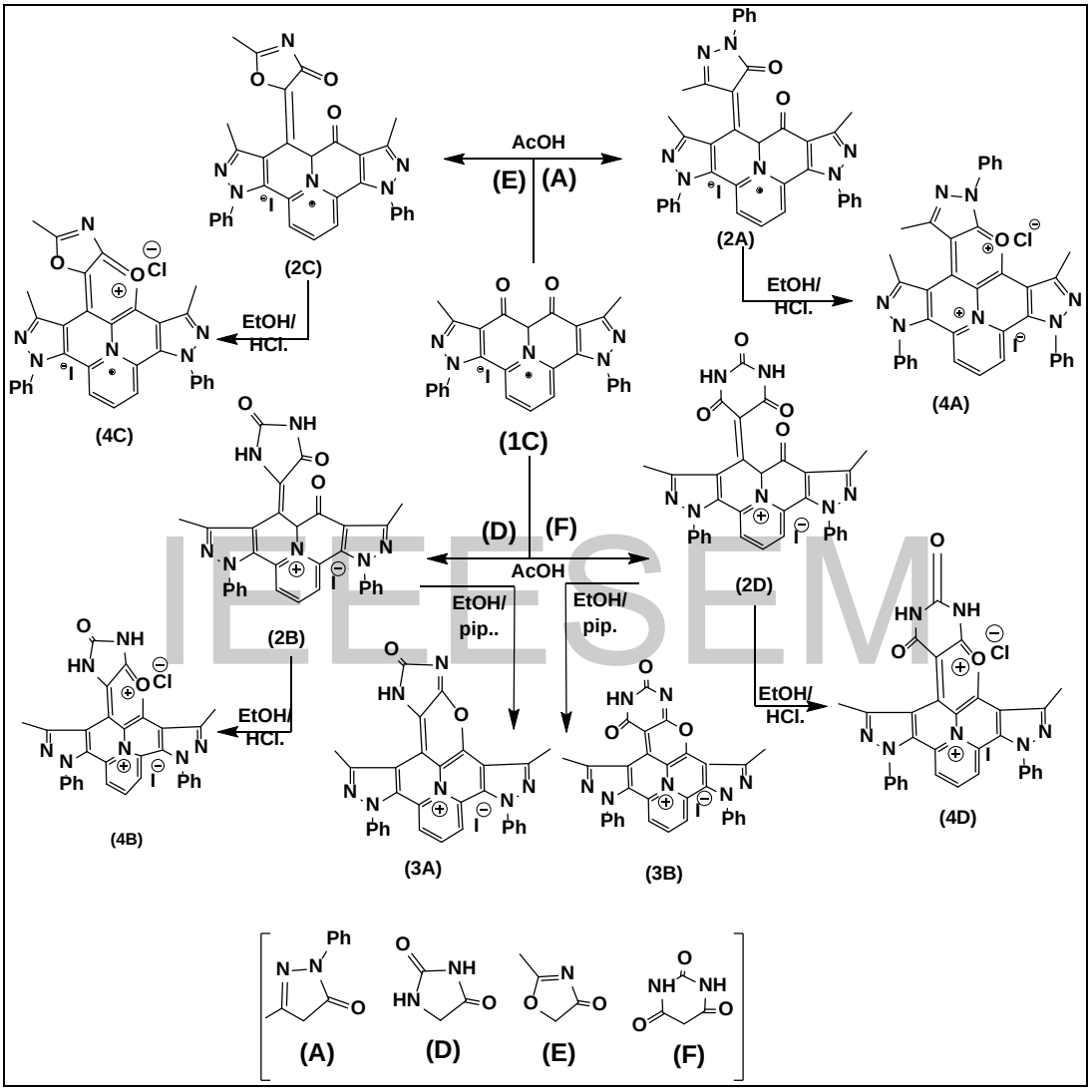


Scheme (1)

The structure of (1A) was confirmed by elemental & spectral data. IR (γ ^{KBr} cm^{-1}) of (1A) showed in addition of general peak picking absorption bands at 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. **[17,18].** ^{1}HNMR of 1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)propan-1,3-dione (1A) δ,3.61, S,2H,pyrazolone-H,δ,7.19-7.94, m,10H,2-Phenyl, δ,S,1.84,6H, 2CH_3 **[19, 20].** The mass spectra of **(1A)** 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+$C_3H_2O_2$] **[21].**The structure of (1C) was confirmed by elemental & spectral data. IR spectra strongly support the existence of heterocyclization of (1C). IR (υ KBrcm-1NH),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) characteristic strong band at1435-1432cm-1(υα,βunsaturated C=O) **[17,18].**

Piperidine catalysis for the interaction of 6,9-dimethyl-7,8-dioxo-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 (1C), in equimolar amount, afforded 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 (2A), 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 (2B), 6,9-dimethyl-7-(2-methyl-4-oxooxazol-5(4H)-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 (2C) and/or 6,9-dimethyl-7-oxo-4,11-diphenyl-8-(2,4,6-tri-oxo-tetra[H]pyrimidin-5(2H)-7,7a,8,11-tetra[H]-4H-dipyrazolo [4,3-b:3',4'-g]pyrido [2,1,6-de]quinolizin-12-ium-iodide (2D) cyclic Mero cyanine dyes respectively, as self-assembly [ICT] endocyclic multi-charge transferred mero cyanine dye (2A-D), Scheme (2). Either piperidine catalysis in ethanol for (2A, D) afforded 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 cyclic mero cyanine dyes (3A, B) . Meanwhile, acid catalysis using hydrochloric acid of (2A-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 (4A), 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 (4B), and/or 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 (4C) & ,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]quinolizin-14,15-diium-iodide/ chloride-endocyclic-multi-charge transferred-oxonium-mero cyanine dyes (4D). The formation of (4A-D) was chemically confirmed by their treatment with aqueous solution of KI followed by the intense liberation clawed of iodine on conc.H_2SO_4 warming. This is a criterion for replacement of ium-chloride by iodide analogous, **Scheme (2).**

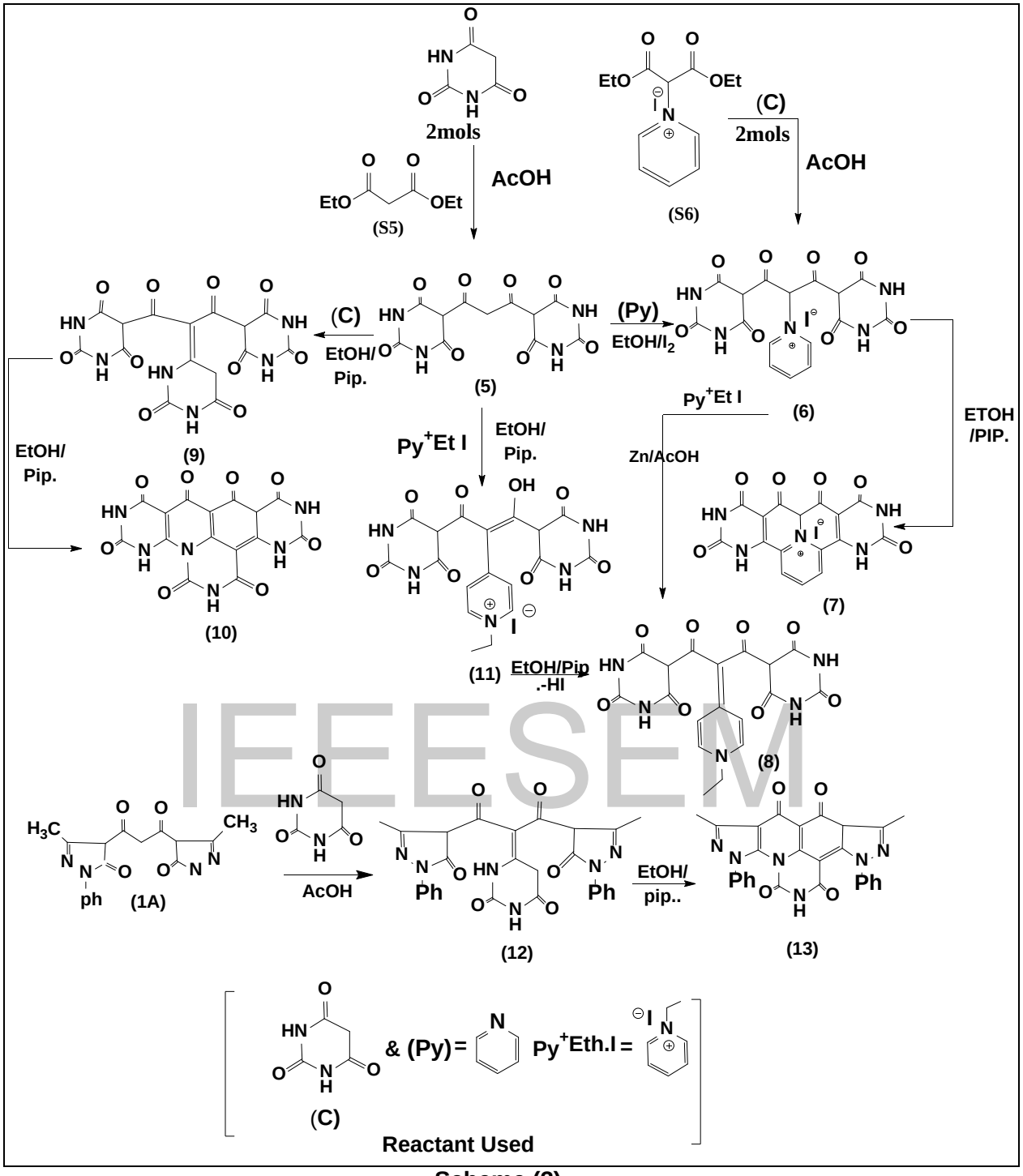


Scheme (2)

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 (2A-D, 4A-D),**Tables (2, 3).**

Similarly, building up some selected N-bridge head heterocyclic self-assembly [ICT] functional & related cyanine dyes based on pyrimido[4,5-f] pyrimido[5',4': 5,6] pyrido[3,2,1-ij]quinozolin-octa-one was conducted & started by the synthesis of 5,5'-malonyl-bis (pyrimidin-2,4,6(1H,3H,5H)-trione) (5) via the interaction of diethyl malonate & bimolar

amounts of barbituric acid in acetic acid. Selective quaternization of pyridine by the later compound (5) 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 (6). The later compound (6) was chemically confirmed via the mutual route of interaction of N-diethyl malonate-pyridin-1-ium iodide (2B) **[14-16]** & bimolar amounts of barbituric 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-tri-oxo–hexa[H]pyrimidin–5–yl–propan–2–yl–pyridin–1–ium-iodide (6) 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 acyclic mero cyanine dye (8) which was chemically confirmed by the direct interaction of 5,5'-malonyl-bis-pyrimidin-2,4,6(1H,3H,5H)-trione) (5) with N-ethyl-pyridin-1-ium-iodide salt, in equimolar amount, under piperidine catalysis & ethanol to give (11) with the same and mixed melting points of (8). The criterion of the formation of (11) is the existence of vapour iodine vapour on warming H_2SO_4 and Deeping of colour when treated with ferric chloride for β-dicarbonyl Enolate. Excess of piperidine catalysis on (11) undergo dehydroiodination to afford 5, 5’ (2-(1-ethylpyridin-4(1H)-ylidene-malonyl-bis-(pyrimidin-2, 4, 6 (1H, 3H, 5H)-trione-acyclic mero cyanine dye (8). Condensation of (5) with barbituric acid, in equimolar amount, in acetic acid afforded 5,5'-(2-(2,6-dioxo-tetra[H]pyrimidin-4(1H)-malonyl-bis-pyrimidin-2,4,6 (1H, 3H,5H-trione cyclic mero cyanine dye (9) which undergoes intramolecular heterocyclization process under piperidine catalysis & ethanol to achieve self-assembly [ICT] pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido [3,2,1-ij] quinozolin-1,3,6,8,9,10,11,13 (2H,5H,7H,10a H, 12H, 14H)-octaone cyclic mero cyanine (10). The interaction of 1,3-bis (3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-β-dicarbonyl (1A) & barbituric acid , in equimolar amount, in acetic acid afforded 1,3-bis(3-methyl–5–oxo–1–phenyl–4,5–di[H]–1H–pyrazolin–4–yl–β-dicarbonyl-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 (3).**



Scheme (3)

IR (υ ^{KBr} cm^{-1}) of (7) showed, in addition to, the general absorption bands at 3344cm^{-1} (γ NH), 1465-1610 cm^{-1}, 2890 cm^{-1}, 2500-3200cm^{-1} broad, (γ C-CH_2CH_3), 1720cm^{-1} (υ C=O), 1600-1545cm^{-1},1575-1540cm^{-1},1510-1410cm^{-1},14711-1330cm^{-1}(γ 3-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} (γ 3-pyrimidine nuclei), 1600cm^{-1} (υ C=C conj. Cyclic), 1570 cm-1 (γ cyclic β-dicarbonyl), 1596cm^{-1}(υ C=C conj. υ C=O), 1730 cm^{-1} (γ acyclic C=O), 1065-1173 cm^{-1} (γ C-

N-C, 1129-092 cm^{-1} (γ exocyclic N-C str , Pyridin, (1610-1600,1590-1580,1520-1470,1460, 1440, 1580, 1572, 1482, 1439 cm^{-1}, 2652-2972 cm^{-1}, (υ intra-mol.-H bonded Keto-Enol tautomer form)', α, β-unsaturated ketones 1685-1666cm^{-}1600cm^{-1} (υ C=C conj. Cyclic),'1465-1610 cm^{-1}(γ), α, β-unsaturated ketones. IR (υ ^{KBr} cm^{-1}) of (10) 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) **[17,18].** The mass spectra of (5) 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, characteristic for barbituric acid, **[21].**

Colour and Spectral Behaviour.

Self-Assembly [ICT] endocyclic functional dye is highly coloured compounds. Their colour ranging from (pale brown-violet) in colour respectively, easily soluble in polar organic solvents exhibiting coloured solutions (reddish-red). They are soluble in concentrated H_2SO_4 acid liberating iodine vapor on warming. Their ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. They possess interchangeable colours solution. Self-Assembly [ICT] endocyclic functional dyes (8-10) are highly coloured compounds. Their colour ranging from (yellowish-Violet) in colour respectively, easily soluble in nonpolar solvents (partially in organic solvents) exhibiting coloured solutions (reddish-red). Their ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. They possess interchangeable colours solution.

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 & pyrido[2,1,6-de] dipyrimido[5,4-b:4',5'-g]quinolizin-14-ium iodide endocyclic [ICT] functional dyes (1C,7) in 95% EtOH in the range of λ 393-487nm resulted in absorption bands at λ 393nm, ε_{max} 3185 cm^2 mol^{-1} for (1C) λ 462nm, ε_{max} 6825 cm^2 mol^{-1} for (7) respectively. It was obvious that self-assembly [ICT] dyes (7) have got of absorption bands bathochromically shifted of Δ λ (63-94nm) than those of (1C). This is due to the multi-charge transferred from the di-cyclic NH of di pyrimidine di-one 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, 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 (2A-D) in 95% EtOH resulted in absorption bands bathochromically shifted at λ 467nm, ε_{max} 8131cm^2 mol^{-1}, for (2A), λ 456nm, ε_{max} 8154 cm^2mol^{-1} for (2B), λ 469nm, ε_{max} 5839 cm^2 mol^{-1} for (2C), λ 398nm, ε_{max} 3575 cm^2mol^{-1} for (2D) respectively. It was obvious that the dyes (2A-D) have got of absorption bands hypso chromically shifted of Δ λ (5-74nm) than those of (1). 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, **Table (1).** 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 (3A, D) in 95% EtOH resulted in absorption bands at λ477nm, ε_{max} 8521 cm^2 mol^{-1}, for (3A), λ 492nm, ε_{max} 6582 cm^2mol^{-1} for (3B) respectively. It was obvious that the dye (3A, D) have got of absorption bands bathochromically shifted of Δ λ (21-29nm) than those of (2B, 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, Table (1), 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 (4A-D) in 95% EtOH resulted in absorption bands at λ 489 nm, ε_{max} 8574 cm^2 mol^{-1}, for (4A), λ 475nm, ε_{max} 2599 cm^2mol^{-1} for (4B), λ 482nm, ε_{max} 7586 cm^2 mol^{-1} for (4C), λ 463 nm, ε_{max} 6258 cm^2 mol^{-1} for (4D) respectively. It was obvious that the dyes (4A-D) have got absorption bands bathochromically shifted of Δ λ (13-65nm) than those of (2A-D). This is due to the building up 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, Table (1). The absorption spectra of pyrimido[4,5-f]pyrimido [5',4':5,6] pyrido [3,2,1-ij] quinozolin-octaone endocyclic [ICT] functional dye (10) 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 (10), it was obvious that the former dye , λ 492nm, ε_{max} 8564 cm^2 mol^{-1}) has got absorption bands bathochromically shifted of Δ λ (38nm) than those of (10, λ 389nm, 454nm, ε_{max} 8957,9524 cm^2 mol^{-1}). This is due to the sublimating 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 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 endocyclic [ICT] functional mero cyanine dye (1C), It was obvious that the endocyclic [ICT] functional dye (13) have got of absorption bands hypso chromically shifted of Δ λ (99nm) than those of (1C). This is due to the multi-charge transferred in pyrimido[4,5-f]pyrimido[5',4':5,6] pyrido [3,2,1-ij]quinozolin-self-assembly [ICT] functional dye (13) than those of (1C). The absorption spectra of endocyclic [ICT] functional mero cyanine dye of pyrido[2,1,6-de] dipyrimido [5,4-b:4',5'-g]quinolizin-14-ium iodide endocyclic [ICT] functional dye (7) in 95% EtOH in the range of λ 393-487nm resulted in absorption bands at λ 462nm, ε_{max} 6825 cm^2 mol^{-1} for (7). It was obvious that self-assembly [ICT] dyes (7) have got of absorption bands bathochromically shifted of Δ λ (63-94nm) than those of (1C). This is due to the multi-charge transferred from the di-cyclic NH of di pyrimidine di-one 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] cyclic mero cyanine dye types, **Table (1), fig.(1).**

Table (1): Absorption Spectra of Some Selected Compounds in 95% EtOH**.**

Comp. No	λ max. nm in EtOH	ε max. Cm^2 mol^{-1}	Absorbed Colour	Transmitted Colour
1C	393	3185	Pale Brown	----------
2A	467	8131	Blue	Yellow
2B	456	8154	Blue	Yellow
2C	469	5839	Blue	Yellow
2D	463	6258	Blue	Yellow
3A	477	6582	Yellow	Blue
3B	492	8574	Reddish Violet	Yellow- green
4A	489	2599	Violet	Yellow- green
4B	475	7586	Yellow	Blue
4C	482	3575	Orange	Green-blue
4D	398	4698	Orange	Green-blue
7	462	6825	Orange	Green-blue
12	456	7631	Blue	Yellow
13	492	8564	Pale Brown	----------

Table (2): Characterization data for (1A, 1B, 6).

Comp No.	Nature of Products				% Calcd. (Found)		
	M.p. °C	Yield %	Color	Mol. Formula (Mol. Wt.)	C	H	N
1A	140	74	Reddish brown	$C_{23}H_{20}N_4O_4$ 416.15	66.34 66.37	4.84 4.88	13.45 13.46
1B	178	71	Brown	$C_{28}H_{24}IN_5O_4$ 621.	54.12 54.17	3.89 3.92	11.27 11.25
6	178	77	orange	$C_{16}H_{12}IN_5O_8$ (529)	36.31 36.34	2.29 2.31	13.23 13.20

Solvatochromic Behaviour of Some Selected Heterocyclic Functional & Related Cyanine Dyes:

The absorption spectra of (8 & 10) have been studied in organic solvents of different polarities (EtOH, Dioxan, and C_6H_6 & DMF) and (λ_{max} and ε_{max}) values of the intramolecular and intermolecular charge transfer bands, **Table (2), 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, **Table (2)** 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. It was worth mentioning that the intermolecular hydrogen bonding between $CHCl_3$ molecules and the lone pair of electrons of nitrogen atoms or oxygen atom of the heterocyclic ring system is difficult due to the steric hindrance of the three bulk chorines. Moreover, the solute- solvent interactions in cases of C_6H_6 generated are sidual 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. **[22]**, in a supplementary, electronic transitions can be localized on the “antenna” or “acceptor” fragments, as they are of the [ICT] type **[23 & 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 polarizable 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 **[23 & 25].** In alcohols, some derivatives form hydrogen bonds with the solvent molecules & demonstrate a dependence on the electrophilic properties of the medium. To prevent the influence of H-bonding and π-complex formation on the spectral parameters of the derivatives, a group of aprotic solvents of different polarity, polarizability, nucleophilicity, and electrophilicity was initially chosen. Then, if the spectral parameters were found to be dependent on solvent basicity or electrophilicity, investigations for a larger group of solvents, including alcohols, were attempted. When such a dependence of spectral on solvent polarity or polarizability was detected, the investigations were performed for both polar and nonpolar solvents. The following spectral characteristics in the different media were measured: maxima of the long-wavelength absorption bands. The dependence of the spectral characteristics on the solvent properties was studied by regression analysis using two groups of solvent parameters: (constant (polarity), polarizability, nucleophilicity, and electrophilicity. The clearest results were obtained for band positions in the absorption spectra. It is worth noting that although changes in the absorption spectra seem to be dependent on solvent polarity. We also detected a tendency towards absorption band shifting with changing solvent polarizability, hence, the increase in the polarity and the nucleophilicity of the medium resulted in a hypsochromic shift of the long wavelength absorption band. Such spectral behaviour can be explained by the redistribution of the incorporate positive charge and C fragments in the ground state and by further interfragmental charge transfer following Excitation. 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 delocalization 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 equalization 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 depolarization following excitation are less intensive. As a result, the dependencies between are weaker:. The data listed in **Table (2)** 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 (7, 10) have been studied in organic solvents of different polarities (EtOH, Dioxan, C_6H_6 & DMF) and (λ_{max} and ε_{max}) values of the intramolecular and intermolecular charge transfer bands and given in **Table (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 (2)** 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. It was worth mentioning that the intermolecular hydrogen bonding between $CHCl_3$ molecules and the lone pair of electrons of nitrogen atoms or oxygen atom of the heterocyclic ring system is difficult due to the steric hindrance of the three bulk chorines. Moreover, the solute- solvent interactions in cases of C_6H_6 generated are negative charge on the nitrogen atoms of heterocyclic ring system which intern facilitated the electronic charge transfer to positively charged centre and this explain the bathochromic shifts in these solvents relative to ethanol.

Table (1): Characterized colour of some selected self-assembly [ICT] endocyclic functional dyes.

SOLVENT USED	SELF ASSEMBLY [ICT] ENDOCYCLIC FUNCTIONAL DYES NUMBERS					METHINE HETEROCYCLIC CYANINE DYES NUMBERS	
	1C	2A-D & 3 A,B	4 A-D & 7	10 & 11	13	12	8
EtOH	Deep pink	Orange	Violet	Pale brown	Deep orange	Orange	Violet
DMF	Deep pink	Yellow	red	Deep yellow	Orange	Deep yellow	Deep red
C_6H_6	Violet	Yellow	Orange	Deep orange	Yellow	Pale brown	Orange
Dioxan	Violet	Yellow	Yellow	Yellow	Yellow	Pale brown	Red
EtOH in H_2SO_4	Pale red	Red	red	Yellow	Red	Orange	Deep orange
EtOH in NaOH	Deep red	Yellow	Yellow	Yellow	Yellow	Yellow	Orange

Table (2): Values of λ_{max} (nm) (ε_{max}) ($mol^{-1}\,cm^{-1}$) of (8 & 10) 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})
8	Pink	518 (7922)	yellow	435 (8173)	Orange	496 (7266)	Pink	494 (4517)
10	red	509 (7266)	Orange	398 (2670)	orange	477 (6142)	red	509 (7266)

Experimental

All melting points are uncorrected Elemental analysis was carried out at the Micro analytical center (Cairo-University). 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 Nicolet evolution 100 spectrophotometer, water company, Aswan..4-Acetyl-3-methyl-1-phenyl-pyrazolin-5-one (S1) & 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid (S2),1-(2-(3-Methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-2-oxo-ethyl-pyridin-1-ium-iodide (S4) & 3-methyl-1-phenyl-pyrazolin-5-one with diethyl malonate (S6) were prepared in way to that described in perspective reference **[7-19, 20].**

Synthesis of 1,3-bis(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl-β-dicarbonyl-(1A):

ROUTE (A): 3-Methyl-4-acetyl-1-phenyl pyrazol-5- one (S5, 0.01 moles) & 3-methyl -4-carboxylic -1-phenyl- pyrazol -5- one (0.01mole) 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 (1A), **Table (3)**

ROUTE (B): N-acetyl- pyridin-3-methyl-1-phenyl- pyrazol -5- one (2A, 0.01mole) and 3-methyl -4-carboxylic -1-phenyl- pyrazol-5- one (0.01 mile) 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 (1A), **Table (3)**

ROUTE (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 (1A), **Table (3)**

Synthesis of 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 (1B)

A. An Ethanolic solution of (1A, 0.01mol.), pyridine (0.01mole) and Iodine (0.01 mol.) were refluxed for 4hrs, 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 **(1B), Table (3)**

Synthesis of di pyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]quino-lizin-12-ium-iodide-mero, diimidazo[4,5-b:4',5'-g]pyrido[2,1,6-de]quinolizin-12-ium-iodide, dioxazolo[5,4-b:4',5'-g]pyrido [2,1, 6-de]quinolizin-12-ium-iodide (1C)

An Ethanolic solution of (1B) 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 **(1C), Table (3)**

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

An Ethanolic solution of (1C) & 3-methyl-1-phenyl-pyrazolin-5-one, (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 (2A-D), **Table (3).**

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 oxonium mero cyanine dyes (3A, B).

An Ethanolic solution of (2 B, 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 (3A, B), Table (3).

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-diiumendo cyclic multi-charge transferred mero cyanine dyes (4A-D).

An Ethanolic solution of (2A-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 (4A-D), **[5a,b,6a],Table (3).**

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

A mixture of Barbituric acid (0.02mol) & diethyl malonate (0.01mole) 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 **(5)**,**Table (3).**

Synthesis of 1,3-dioxo-1,3-bis(2,4,6-trioxo hexa[H] pyrimidin-5-yl)propan-2-yl)pyridin-1-ium iodide (6)

A. An Ethanolic solution of barbituric acid (0.02mole) and diethyl malonate (0.01mole) 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 (6), **B.** An Ethanolic solution of barbituric acid (0.02mole) and diethyl malonate (0.01mole) 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 (6), **Table (3).**

Synthesis of 1-hydroxy-3-oxo-1,3-bis(2,4,6-trioxohexa[H] pyrimidin-5-yl-prop-1-en-2-yl)styryl cyanine (7)

(A): An Ethanolic solution of (6, 0.01 mol.) and pyridin-ium-ethiodide salts (0.01mol.) in few drops of piperidine was refluxed for 4hrs, 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 (7). **(B):** An Ethanolic solution of (6, 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 (7), **Table (4)**

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 (8)

An Ethanolic solution of (6, 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 (8), **Table (4)**

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 (9 & 10)

A-An Ethanolic solution of (5, 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 (9). **B-**An Ethanolic solution of (9, 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 (10), **Table (4)**

Synthesis of 1-hydroxy-3-oxo-1,3-bis(2,4,6-trioxohexa[H] pyrimidin-5-yl-prop-1-en-2-yl)styryl cyanine (11)

(A): An Ethanolic solution of (5, 0.01 mol.) and pyridin-ium-ethiodide salts (0.01mol.) in few drops of piperidine was refluxed for 4hrs, 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 (11), **Table (4).**

(B): An Ethanolic solution of (7, 0.01mole) 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 (11), **Table (4)**

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 (1A, 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 (12), **Table (4).**

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 (4)**

Table (3): Characterization data for (1C, 2A-D, 3A, B & 4A-D)

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	λmax (nm)	ε_{max} (cm^2mol^-)
1C	195	66	Red	$C_{28}H_{20}IN_5O_2$ 585	57.45 57.47	3.44 3.41	11.96 11.95	393	3185
2A	185	67	Red	$C_{38}H_{28}IN_7O_2$ (741)	61.55 61.58	3.81 3.85	13.22 13.28	467	8131
2B	205	75	Yellow	$C_{31}H_{22}IN_7O_3$ (667)	55.78 55.77	3.32 3.25	14.69 14.72	456	8154
2C	190	77	Reddish brown	$C_{32}H_{23}IN_6O_3$ (666)	57.67 57.59	3.48 3.49	12.61 12.66	469	5839
2D	215	69	yellow	$C_{32}H_{22}IN_7O_4$ (695)	55.26 55.29	3.19 3.22	14.10 14.14	463	6258
3A	225	81	Violet	$C_{31}H_{20}IN_7O_2$ (649)	57.3 57.39	3.10 3.14	15.10 15.15	477	6582
3B	238	79	orange	$C_{32}H_{22}IN_7O_3$ (679)	56.57 56.59	3.26 3.28	14.43 14.49	492	8574
4A	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
4B	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
4C	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
4D	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

Table (4): Characterization data for (5-13)

Comp. No.	Nature of Product			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^-)
5	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
7	182	79	Orange	$C_{16}H_8IN_5O_6$ (493)	38.97 38.99	1.64 1.67	14.20 14.27	452	6825
8	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
9	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
10	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
11	225	71	Deep orang	$C_{18}H_{16}IN_5O_8$ 557	38.80	2.89	12.57	428	8054
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

Solvatochromic and Acid-Base Properties:

The organic solvents were used of spectroscopic grade of purified **[26].** 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 [26]:

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.

4-Conclusion

Special attention has been focused on chemical structure of selected N-bridge head heterocyclic self-assembly [ICT] functional & related methine (Mero)-cyanine dyes synthesis &. Spectral behaviour in order to permit a criterion for their use as photosensitizes & possible color-chemical structure relationship. The absorption spectra results of the study of synthesized functional & related methine (Mero)-cyanine dyes in ethanol indicated that the absorption bands which were showed depend on the molecular structure of such dyes. Some selected dye formation & their site reactivity's were postulated as in our point view.

This article would consider as guidance in the field of synthetic routes of self-assembly [ICT] functional dyes. The specification, site reactivity's involving formation mechanistic pathway, solvatochromic & media behaviours has been investigated. The absorption spectra of such dyes in some pure solvents having different polarities were examined in the visible region showing solvatochromism to permit a selection of optimal solvent when such dyes are applied as photosensitizers.

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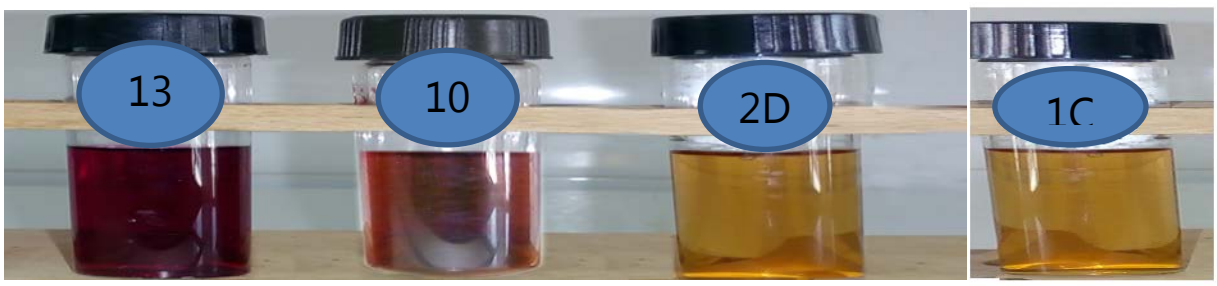
Fig. (1): Photo Colour for (1C, 2D & 10) in EtOH & AcOH)



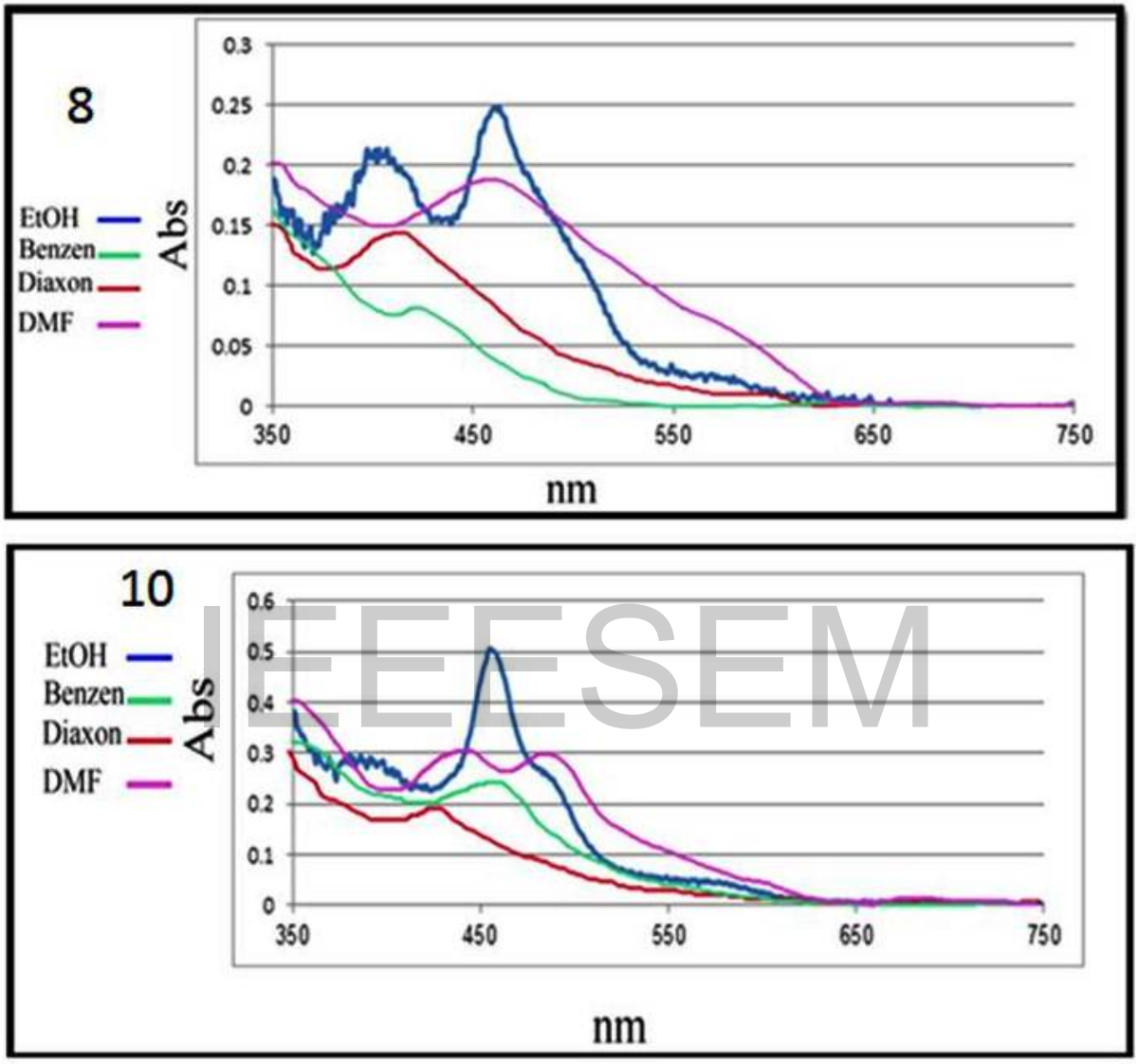


Fig. (2): Solvatochromic behaviour of (8, 10) in organic solvents.