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HETEROCYCLIC KETO-OXIMES PRECURSORS IN THE SYNTHESIS OF SOLVATO (MEDIA)-CHROMIC HEAD HETEROCYCLIC SELF-ASSEMBLY [ICT] FUNCTIONAL [DSSCs] & Related Cyanine DYES

A. I. M. KORAIEM, S.M.SAYED, M. M. GOMAA & M. H. YOUSRY[1]
Chemistry Department, Faculty of Science, Aswan University, Aswan, 81528, Egypt,

ABSTRACT

Heterocyclic keto- or methylene keto-oxime precursor's was oriented towards the synthesis of solvato (media)-chromic N-bridge head heterocyclic cyanines & Self-assembly **[ICT]** functional & related zero-1[4],11(13) [4] methine, bis-zero-7,13[4(4)] methine & di-4[2(4)] methine cyanines. The new self-assembly **[ICT]** functional & their cyanines were identified by elemental & spectral analyses. The visible absorption spectra of some selected dyes were investigated in 95% ethanol, pure organic solvents & universal buffer solution for photophysical characteristics. The UV –Vis. spectral studies showed that the dyes are absorbed in the region of λ_{max} (485-570) nm. Their electron cloud delocalization in HOMO/LUMO levels were studied by **DFT** using Gaussian 09 software. **DFT** results reveal that the dyes showed effective charge separation in its molecular orbitals levels, which reflected in its **ICT** behaviour. Time-dependent density functional theory (TD-DFT) were applied to theoretically explored the first excitation energy (E0-0) of these dyes which in high Compatibility with experimental results with an accuracy of (0.1-0.3 eV). This approach has been successfully applied to describe the great effect of p-conjugation length and substituents of chromophore on the variations of maximum absorption and excitation energy of the dyes

Keywords: Functional & Related Cyanine Dyes, Synthesis, Spectral Solvato (Media) - chromism Behaviors, delocalization in HOMO/LUMO levels

INTRODUCTION

Owing to its importance from both fundamental and applied perspectives, the field of charge transfer has attracted continued interest from scientists over more than 80 years. We then turn from charge migration to intramolecular charge transfer **[ICT]** We then turn from charge migration to intramolecular charge transfer heterocyclic **[ICT]** moieties. Moieties in the heterocyclic **[ICT]** moieties have received considerable attention in the field of synthetic organic chemistry because of their special structural properties **[1a, b].** Intramolecular (Internal) Charge -Transfer N-Bridge Self-Assembly heterocyclic functional as organic dye molecules in particular, are lacking and represent deficiencies in total picture and attracted increasing attention owing to their unique electronic and/or photonic properties **[2,3]** solar cells, etc. **[4].** The most traditional and promising approach is how to reach the goal and trend in order to systematize such dyes in Functional Molecular Systems according

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to their quite different physico-chemical features and possible photosensitizes-chemical structure relationship **[5,6].** We have various self-assembled organic including opportunities for applications in designed molecular sensors based on changes in the efficiency of **[ICT]** process upon complexation. To date, the obtaining of self-assembly process as organic nanomaterial is still highly desirable for the advancement of organic nano science (technology), **[7].**

RESULTS AND DISCUSSION

Reaction of 4-acetyl-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one, **Scheme (1A)**, comp. No. **(1)** & quinolin-8-ol and 2-methyl-pyridine in, equimolar amount, in HCL and/or iodine afforded 1-(2-(hydroxyimino)-2-(3-methyl-5-oxo-1-phenyl-4, 5-di [H]-1H-pyrazol-4-yl) ethyl)-2-methyl pyridin-1-ium-iodide, **Scheme (1A)**, comp. No. **(2a-c)** & 8-hydroxy-1-((1-(3-methyl-5-oxo-1-phenyl-4, 5-di [H]-1H-pyrazol-4-yl) ethylidene) amino) quinolin-1-ium, **Scheme (1A)**, comp. No. **(4).** The later **(4)** Undergo Intramolecular heterocyclization ring closure in, equimolar amount, under piperidine to afford 2-(3-methyl-5-oxo-1-phenyl-4, 5-di[H]-1H-pyrazol-4-yl)-1H-pyrido [3, 2, 1-ij] cinnolin-10-ium chloride, **Scheme (1A)**, comp. No. **(5).** The reaction of 2-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-1H-pyrido[3,2,1-ij]cinnolin-10-ium chloride, dye **(5)** with 1-ethylpyridin-1-ium iodide salts in, equimolar amount, under piperidine catalysis afforded 3-(1-ethylpyridin-4(1H)-ylidene)-2-(3-methyl-5-oxo-1-phenyl-1,5-di[H]-4H-pyrazol-4-ylidene)-2,3-di[H]-1H-pyrido[3,2,1-ij] cinnolin -10-ium chloride, **Scheme (1A)**, comp. No. **(6a-c).** Cyclo condensation reaction of 1-(2-(hydroxyimino)-2-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)ethyl)-2-methyl pyridin-1-ium iodide, **Scheme (1A)**, comp. No. **(2a-c)** in piperidine catalysis afforded 3-(3-methyl-5-oxo-1-phenyl-1,5-di[H]-4H-pyrazol-4-ylidene)-1,2,3,4-tetra[H]-pyrido[1,2-a]pyrazin-5-ium-iodide, **Scheme (1A)**, comp. No. **(7a-c).** Reaction of dyes **(7a-c)** with pyridin-4-ium ethiodide and/or 2-methyl-pyridin-2-ium-ethiodide, in equimolar amount, under piperidine catalysis afforded 4-(1-(1-ethylpyridin-4(1H)-ylidene)-3,4-di[H]-11l4-pyrazino[1,2-a]quinolin-2(1H)-ylidene)-5-methyl-2-phenyl-2,4-di[H]-3H-pyrazol-3-one, **Scheme (1A)**, comp. No. **(8a-c),** 3,11-dimethyl-1-phenyl-1H-pyrazolo [4',3': 5, 6] pyrano [4,3-e]pyrido[1,2-a]pyrazine-10,12-diium chloride iodide **Scheme (1A)**, comp. No. **(9a-c)** & 3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]pyrido [1',2':4,5] pyrazino[2,3-c] quinolizin-10,11-diium iodide **Scheme (1A)**, comp. No. **(10a-c), Scheme (1A)**. Reaction of 3-methyl-1-phenyl-pyrazol-5-one & ethyl acetoacetate under acetic acid catalysis afforded 4-aceto acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, **Scheme (1B)**, comp. No. **(11) [8].** The interaction of **(11)** with glyoxal, in equimolar amount, under Acetic acid catalysis afforded 3-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazole-4-carbonyl)-4-oxopent-2-enal, **Scheme (1B)**, comp. No. **(12)**. Cyclo- condensation of dye **(12)** was conducted under piperidine catalysis to afford 5-acetyl-3-methyl-1-phenyl-1H-indazole-4,7-dione, **Scheme (1B)**, comp. No. **(13)**. Selective quaternization of pyridine, quinolone and isoquinolin by **(13)**, in equimolar amount, using I_2/EtOH achieved 1-(2-(3-methyl-4,7-dioxo-1-phenyl-4,7-di[H]-1H-indazol-5-yl)-2-oxoethyl) pyridin-1-ium iodide dye **(14a)**, 1(2-(3-methyl-4,7-dioxo-1-phenyl-4,7-di[H]-1H-indazol-5-yl)-2 oxoethyl) quinolin-1-ium iodide **(14b)**, and/or 5-(2-(2l4-isoquinolin-2-yl)acetyl)-3-methyl-1-phenyl-1H-indazole-4,7-dione, iodide salt **(14c)** respectively. Continue **Scheme (1B)**. Piperidine catalysis in ethanol for **Scheme (1B)**, comp. No. **(14a-c)** afforded 9-methyl-7,8,12-trioxo-11-phenyl-7,8,11,12-tetra[H]-6H-pyrazolo[4,3-g]pyrido[2,1-a]isoquinolin-5-ium-iodide, **Scheme (1B)**, comp. No. **(16a)**, 9-methyl-7,8,12-trioxo-11-phenyl-7,8,11,12-tetra[H]-6Hpyrazolo [4',3':6,7] isoquinolino[2,1-a]quinolin-5-ium iodide **(16b)** and/or 3-methyl-4,5,14-

trioxo-1-phenyl-4,5,6,14-tetra[H]-1H-isoquinolino[3,2-a]pyrazolo[4,3-g]isoquinolin-7- ium iodide **(16c)**. Reaction of **(16a)** with pyridin-4-ium ethiodide, in equimolar amount, under piperidine catalysis afforded 6-(1-ethyl-1l4,4l5-pyridin-4-ylidene)-9-methyl-7,8,12-trioxo-11-phenyl-7,8,11,12-tetra[H]-6H-pyrazolo[4,3-g]pyrido[2,1-a]isoquinolin-5-ium iodide, **Scheme (1B)**, comp. No. **(17)**. The formation of **Scheme (1B)**, comp. No. **(16a-c)** 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 (1B)**. Reaction of **(18)** with Acetyl acetone, in equimolar amount on conc.H_2SO_4 afforded 3, 5, 8-trimethyl-4, 9-dioxo-6-(3-oxobutanoyl)-1-phenyl-7-(pyridin-1-ium-1-yl)-4,9-di [H]-1H-pyrazolo [3, 4-g] isoquinolin-6-ium chloride iodide, **Scheme (1B)**, comp. No. **(21)**. Piperidine catalysis in ethanol for **(21)** afforded 3,6,8-trimethyl-4,16-dioxo-1-phenyl-4,16-di[H]-1H-indolizino[3,2-c]pyrazolo[3,4-g]pyrido[2,1-a]isoquinolin-9-ium chloride, **Scheme (1B)**, comp. No. **(22).** The formation of 5-(1-(hydroxy-imino) ethyl)-3-methyl-1-phenyl-1H-indazole-4, 7-dione **(15)** was chemically confirmed. Meanwhile, the interaction of **Scheme (1B)**, comp. No. **(13),** hydroxylamine in the presence of sodium acetate in equimolar amount. The later **(15)** was converted into 1-(3,5,8-trimethyl-4,9-dioxo-1-phenyl-4,9-di[H]-1H-pyrazolo[3,4-g]isoquinolin-7-yl)pyridin-1-ium iodide, **Scheme (1B)**, comp. No. **(18)** via the reaction with 1-(2-oxopropyl)pyridin-1-ium iodide in piperidine catalysis in ethanol and then Acetic acid medium. Selective quaternization of pyridine, quinolone and isoquinolin by the later **Scheme (1B)**, comp. No. **(15)**, in equimolar amount, using I_2/EtOH achieved 1-((1-(3-methyl-4,7-dioxo-1-phenyl-4,7-di [H]-1H-indazol-5-yl)ethylidene)amino)pyridin-1-ium chloride, **Scheme (1B)**, comp. No. **(19a)**, 1-((1-(3-methyl-4,7-dioxo-1-phenyl-4,7- di[H]--1H-indazol-5-yl) ethylidene) amino) quinolin-1-ium chloride **(19b)** and/or 2-((1-(3-methyl-4,7- dioxo- 1-phenyl-4,7-di[H]-1H-indazol-5-yl) ethylidene) amino)-2l4-isoquinolin-1-ylium chloride **(19c)** respectively. Fusion in piperidine for **(19a-c)** afforded 7,9-dimethyl-8,12-dioxo-11-phenyl-11,12-di [H]-8H-pyrazolo[4,3-g] pyrido [2,1-a]phthalazin-5-ium chloride, **Scheme (1B)**, comp. No. **(20a)**, 7,9-dimethyl-8,12-dioxo-11-phenyl-11,12- di [H]-8H-pyrazolo[4,3-g]quinolino[2,1-a] phthalazin-5-ium chloride, **Scheme (1B)**, comp. No. **(20b)** and/or 3,5-dimethyl-4,14-dioxo-1-phenyl-4,14-di[H]-1H-7l4-isoquinolino[3,2-a]pyrazolo[4,3-g] phthalazin-8-ylium chloride **(20c)**. The formation of **(16a-c)** 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 (1B),**

The formation of 4-(1,5-Dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido [1',2':4,5] pyrazino[1,2-c] pyrimidin-13-yl)-zero-1[4]methine & 4,4'-(1,5-dimethyl-3-phenyl-3H-pyrazolo [4,3-e]pyrido [1',2':4,5] pyrazino [1,2-c]pyrimidin-7,13-diyl-bis-zero-methine **Scheme (2)**, comp. No. **(7a,b & 8a-f)** was started by preparation of 3-methyl-1-phenyl-pyrazolin-4,4-keto-methylene-pyridin (quinolin)-1-ium ethiodide salts **Scheme (2)**, comp. No. **(1b) [9]**, followed by the reaction of an ethanolic solution of **Scheme (2)**, comp. No. **(1b)** with hydroxyl amine in the presence of sodium acetate to afford 1-ethyl-4-(2-(hydroxyi-mino)-2-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine-4-yl-ethyl-quinolin-1-ium iodide, **Scheme (2)**, comp. No. **(6)**.The reaction of an ethanolic solution of **(6)** with I_2 and pyridine (quinoline) and/or 2-methyl-quinoline afforded 1-ethyl-4-(2-(hydroxyimino)-2-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine--4-yl-1-(2-methyl-pyridin (quinolin)-1-ium-1-yl-ethyl-quinolin-1-ium-iodide, **Scheme (2)**, comp. No. **(7a,b).** Acetylating of **(7a,b)** under acetic acid anhydride afforded 3-(5-acetamido-3-methyl-1-phenyl-1H-pyrazol-4-yl)--1,4-di[H]pyrido [1,2-a]pyrazin-5-ium-iodide-zero-

4[4]methine & 2-(5-acetamido-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(1-ethylquinolin-1-ium-4-yl)-1,4-di[H] pyrazino[1,2-a]quinolin-11-ium iodide **Scheme (2)**, comp. No. **(8a, b**).The later **Scheme (2)**, comp. No. **(8a,b**) undergo ring closure involving dehydration reaction in acetic anhydride to afford 4-(1,5-dimethyl-3-phenyl-3H-pyrazolo [3'',4'':4',5'] pyrimido [1',6':4,5] pyrazino[1,2-a]quinolin-15-yl)-1-ethylquinolin-1-ium,4-(1,5-dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido [1', 2':4,5] pyrazino [1,2-c]pyrimidin-13-yl)-zero-1[4] methine cyanine dye, **Scheme (2)**, comp. No. **(9a,b).** Moreover the reaction of an ethanolic solution of **(9a,b)** with pyridin [quinolin]-4(1)-ium-1-ethiodide salts and few (ml)s of piperidine afforded 4,4'-(1,5-dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido [1',2' :4 ,5] pyrazino[1,2-c]pyrimidin-7,13-diyl-bis-zero-7,13[4(4)]-methine, **Scheme (2)**, comp. No. **(10a-e) Scheme (2).**

Privileged precursors Pyridinium iodide derivative of 4-acetyl-1-phenyl-pyrazol-5-one /5-oxime **Scheme (3A)**, comp. No. **(21A, B) [10,11]** were selected for heterocyclization process in EtOH/piperidine to form 3-methyl-4-oxo-1-phenyl-& 4-(hydroxy-imino)-3-methyl-1-phenyl-4,5-di[H]-1H-Pyrazolo[3,4-a] quinolizin-6-ium-iodide, (**22A, B)** which on acetylation using acetic anhydride afforded 5-acetyl-3-methyl-4-oxo-& 5-acetyl-4-(hydroxyimino)-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo [3,4-a] quinolizin-6-ium-iodide, **Scheme (3A)**, comp. No. **(22C, D) [8].** either, the interaction of **(22A)** with glycine or heterocyclization of **Scheme (3A)**, comp. No. **(22D)** in AcOH achieved 11-methyl-3-oxo-9-phenyl-2,3,3a,9-tetra[H]dipyrrolo[3,4-a:2',3'-c]quinolizin-4-ium iodide, **Scheme (3A)**, comp. No. **(23).** The latter compound when interacted with 3-methyl-1-phenyl-2,4-di[H]-3H-pyrazolin-5-one, Hydantoin (imidazol-2,5-dione), 2-methyl-oxazol-5(4H)-one & Barbituric acid (tetra[H] pyrimidin-2,5-dione) in AcOH to afford 6-(3-methyl-1-phenyl-pyrazolin-5-one-4-yl)-3-methyl-1-phenyl-1,6a-di[H]pyrazolo[3,4-a]pyrrolo [2,3-c] quinolizin-7-ium,6-(2,5-dioxo-imidazolidin-4-yl)-3-methyl-1-phenyl-1,6a-di[H] pyrazolo [3,4-a]pyrrolo[2,3-c] quinolizin-7-ium**,** 11-methyl-3-(2-methyl-5-oxo-4,5-di[H]-oxazol-4-yl)-9-phenyl-3a,9-di[H]-dipyrrolo[3,4-a:2',3'-c]quinolizin-4-ium-iodide & 6-(2,5-dioxohexa [H]pyrimidin-4-yl)-3-methyl-1-phenyl-1,6a-di[H]pyrazolo [3,4-a]pyrrolo [2,3-c]quinolizin-7-ium-iodie, **Scheme (3A)**, comp. No. (**24A-D)** respectively**.** Basic / acidic catalysis in EtOH/piperidine or AcOH of **(24A-D)** afforded self-assembly **[ICT]** functional dye, namely as, 3,11-Dimethyl-5,9-diphenyl-2a1,9-di[H]-5H-pyrazolo[4,3-b]pyrido[2,1,6-de]dipyrrolo[3,4-g:2', 3',4'-ij]quinolizin-12-ium-iodide**,**11-methyl-4-oxo-9-phenyl-2a1,2b,4,5,5a,9-hexa[H]-3H-imidazo[4,5-b]pyrazolo[3,4-g] pyrido[2,1,6-de]pyrrolo[2,3,4-ij]quinolizin-12-ium**,**4,11-dimethyl-9-phenyl-2a1,9-di[H]oxazolo [4,5-b]pyrido [2, 1,6-de]dipyrrolo[3,4-g:2',3',4'-ij] quinolizin-12-ium-iodide **&** 12-methyl-4-oxo-10-phenyl-2a1,3,4,5,6,10-hexa[H]pyrido[2,1,6-de]pyrimido[4,5-b]dipyrrolo[3,4-g:2',3',4'-ij] quinolizin-13-ium-iodide **Scheme (3A)**, comp. No. **(25A-D)** respectively**.** The interaction of **Scheme (3A)**, comp. No. **(22B)** & 4-acetyl-1-phenyl-pyrazolin-5-one under AcOH followed by piperidine catalysis achieve & confirm the formation of 3,11-dimethyl-5,9-diphenyl-2a1,9-di[H]-5H-pyrazolo[4,3-b] pyrido[2,1,6-de]dipyrrolo[3,4-g: 2',3',4'-ij] quinolizin-12-ium iodide **Scheme (3A)**, comp. No. **(25A).** Piperidine catalysis of the interaction of **(25A-D)** & pyridin (quinolin)-4(1)-ium ethyl iodide salts, in equimolar amount, afforded 3,11-Dimethyl-5,9-diphenyl-5,9-di[H]-1H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de] pyrrolo[2,3 ,4-ij]quinolizin-12-ium-zero-2[4]methine, 3,11-dimethyl-5,9-diphenyl-2a1,9-di[H]-5H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrrolo[2,3,4-ij]quinolizin-12-ium-zero-2[4]methine , 3,11-dimethyl-4-oxo-9-phenyl-2a1,4,5,9-tetra[H]-3H-imidazo[4,5-b]Pyrazolo[3,4-g]pyrido [2,1,6-de] pyrrolo [2,3,4-ij]quinolizin-12-ium-zero-2[4]methine cyanine dyes **Scheme (3A)**, comp. No. **(26A-D)** respectively. 5-(1-(Hydroxy- imino) ethyl)-3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrrolo[3,4-a]quinolizin-6-ium iodide, **Scheme (3B)**,

comp. No. **(27) [8]** was selected as a privileged precursor in acetic acid catalyzed with **Scheme (3A)**, comp. No. **(22C),** in equimolar amount, afforded 5,5'-(2H-pyrrole-3,5-diyl)bis(3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]quinolizin-6-ium) iodide, **Scheme (3B)**, comp. No. **(28).** The interaction of **(28)** either with ethyl ortho-formate or formamide under piperidine catalysis or thermal condition, in equimolar amount, afforded 5-(4-(diethoxymethyl)-2H-pyrrole-3,5-diyl)bis(3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]quinolizin-6-ium) iodide, **Scheme (3B)**, comp. No. **(29A)** or 5-(4-(dichloromethyl)-2H-pyrrole-3,5-diyl)bis(3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]quinolizin-6-ium) iodide **Scheme (3B)**, comp. No. **(29B).** Hetero cyclization of the latter two compounds was conducted under piperidine catalysis to achieve 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2,2b,3,6,9b,13,16,16a-octa[H] pyrazolo[4',3' :8,9] quinolizino[4,5,6-ab]pyrrolo[4,3,2-de]pyrrolo [3',4':1,2]quinolizino [4, 5,6-gh] [2,7] naphthyridin-17,18-diium iodide **Scheme (3B)**, comp. No. **(30).**The excess of piperidine catalysis on **(30)** causes either oxidative elimination **(-H_2)** or dehydroiodination **(-HI)** to afford self-assembly **[ICT]**functional dye, namely as, 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-1,2b ,3,6, 13,16-hexa [H]Pyrazolo [4',3':8,9] quinolizino[4,5,6-ab]pyrrolo[4,3,2-de]pyrrolo [3',4':1,2] Quinolizino [4,5,6-gh] [2,7] naphthyridin-17,18-di-ium-iodide **Scheme (3B)**, comp. No. **(31A)** or 4,15-dimethyl-3,16-dioxo-6,13-di-phenyl-2b,3,6,13,16,16a-hexa[H]-1H-pyrazolo[4',3':8,9] quinolizino[4,5,6-ab] pyrrolo[4,3,2-de]pyrrolo[3',4':1,2]quinolizino[4,5,6-gh][2,7]naphthyridin-18-ium-iodide **Scheme (3B)**, comp. No. **(31B).** Piperidine catalysis of the interaction of **(31A, B) &** pyridin (quinolin)-4(1)-ium ethyl iodide salts, in equimolar amount, afforded the corresponding self-assembly **[ICT]** functional dyes, namely as 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2b,3,6,13,16,16a-hexa[H]-1H-pyrazolo [4',3':8,9] quinolizino [4,5,6-ab] pyrolo[4,3,2-de]pyrolo [3',4':1,2] Quinolizino [4,5,6-gh][2,7] naphthyridin-18-ium-iodide-zero-2[4]methine cyanine dyes **(32a-c), Scheme (3B).**

The formation of **(24A)** was suggested to proceed via the converting of **scheme (3A)**, comp. No. **(23A)** from its keto form into corresponding enol form **(23B)**. The interaction between **(23B)** and 3-methyl-1-phenyl-pyrazolin-5-one undergo elimination of water molecule to form an intermediate (A) under acidic acid which converted into enol form (B). the later intermediate (B) undergo ring closer to form the desire 3,11-dimethyl-5,9-diphenyl-5,9-di[H]-1H-dipyrazolo[4,3-b:3',4'-g]pyrido[2,1,6-de]pyrrolo[2,3,4-ij]quinolizin-12-ium iodide, **Equation (1).**

The structure of **Scheme (1A)**, Comp. No. (**2b**, **7b** & **9b)** was characterized and identified by elemental analysis and spectral analyses and Mass spectra data, **Table (6)**. Thus, FT-IR (ν^{KBr} cm^{-1}) of dyes (**2b**, **7a & 9b)** showed in addition to general absorption bands at 1497 cm^{-1} (**ν**, C=N), 1594 cm^{-1} (**ν**, C=C),), 3400 cm^{-1} (**ν**, OH), 2919-2921 cm^{-1} (quaternary ylide iodide), well define absorption band at 1710 cm^{-1} (**ν**, C=O), characteristic absorption band at 3557 cm^{-1} (**ν**, CH-stretching) for **Scheme (1A)**, Comp. No. **2b**, 3457 cm^{-1} (**ν**, spreading CH_2) for **Scheme (1A)**, Comp. No. **7b [12 & 13]**. The structure of **Scheme (1B)**, Comp. No. (**12**, **13, 15, 16a, 16b** & **18**) were characterized and identified by elemental analysis and spectral analyses and Mass spectra data, **Table (6)**, Thus, FT-IR (ν^{KBr} cm^{-1}) of **Scheme (1B)**, Comp. No.**12,13,15, 16a, 16b** & **18** showed in addition to the general absorption bands at 1497 cm^{-1} (**ν**, C=N), 1592 cm^{-1} (**ν**, C=C), 1704 cm^{-1} (**ν**, C=O), well defined absorption band at 3058-3060 cm^{-1} (**ν**, stretching CH), concomitant with the appearance of absorption bands at 1597 (**ν**, CH=CH), 2851-2923 (heterocyclic quaternary residue) for **Scheme (1B)**, Comp. No.**18**, and 2923 cm^{-1} (**ν**, CH3-N+I),510-530 cm^{-1} (M-O) for **Scheme (1B)**, Comp. No.**16a** &

16b, **[12].** The structure of **Scheme (2)**, Comp. No. **6**, **7b**, **9b & 10e** was characterized and identified by elemental analysis, IR, ^{1}H-NMR and Mass spectral data, **Table 3**. Thus, IR ν^{KBr} cm^{-1}) of **Scheme (2)**, Comp. No. **6** showed general frequency absorption bands at 3427 cm^{-1} (**ν**, OH of oxime), 2963 cm^{-1} (**ν**, heterocyclic quaternary salt), 1602 cm^{-1} (**ν**, C=C) conjugated, 1501 cm^{-1} (**ν**, C=N), 750.174 cm^{-1} (Ar.) IR (ν^{KBr} cm^{-1}) of **Scheme (2)**, Comp. No. **7b,** 3423.99 cm^{-1} (**ν**, OH, oxime), 2967 cm^{-1} (**ν,** heterocyclic quaternary salt), 1598 cm^{-1} (**ν**, C=C) conjugated, 1494 cm^{-1} (**ν**, C=N), 756.923 cm^{-1} (**ν**, Ar.). The structure of **Scheme (3A &B)**, Comp. No. **22A-D, 23, 24A, 25A, 28, 29b and 30** was characterized and identified by elemental analysis, IR, ^{1}H-NMR and Mass spectral data, **Table (9)**. Thus, FT-IR (ν^{KBr} cm^{-1}) of **Scheme (3A &B)**, Comp. No. **22A-D, 23, 24A, 25A, 28, 29b & 30** showed in addition to the general absorption bands at 1497 cm-1 (C=N), 1592 cm-1 (**ν**, C=C), 1708 cm-1 (**ν**, C=O), 3400 cm^{-1} (**ν**, OH), the appearance of cyclic pyrazolino (**ν**, C=O, C=NH) at 1708 **[12].** ^{1}H-NMR (DMSO, 400 MHz) spectra of **Scheme (1B)**, Comp. No. (**12, 13, 15, 18 & 16a)** showed in addition to the general single and multiple signals at δ 1.19-1.29 (s, CH_3, of pyrazol), 2.20-2.32 (s, CH_3, of the other pyrazol), 7.16-7.97 (m, 13H, Ar. + Het. +NH) for **Scheme (2)**, Comp. No. **12** &**13,** Well define signals at 3.21-3.32 (s, 2H, N-CH_2), 3.79 (s, 3H, CH_3-CH_2-N^+I), 7.16-7.97 (m, 25H, Ar. + Het. +NH+CH=) for **Scheme (1B)**, Comp. No. (**15**, **18** & **16a)**, **[14, 15].** ^{1}H-NMR (DMSO, 400 MHz) spectra of **Scheme (3A & B),** Comp. No. **22A-D, 23, 24A & 28** showed in addition to the general single and multiple signals at δ 1.19-1.29 (s, CH_3, of pyrazol), 2.20-2.32 (s, CH_3, of the other pyrazol), 7.16-7.97 (m, 13H, Ar. + Het. +NH) for compound **Scheme (3A & B),** Comp. No. **22A** & **22B**, Well define signals at 3.21-3.32 (s, 2H, N-CH_2), 3.79 (s, 3H, CH_3-CH_2-N^+I), 7.16-7.97 (m, 25H, Ar. + Het. +NH+CH=) for **Scheme (3A & B),** Comp. No. **22d, 23,24A & 28, [14,15].** Mass Spectra (ESI-Ft-mass) of **Scheme (1A)**, Comp. No. **2b & 7b.** The structure of **2b** was considered most likely and in agreement with molecular formula ($C_{22}H_{21}IN_4O_2$), resulted in m/z found=502.22313 (Calcd. 500. For [M]+) with an error ΔM=+2.22313ppm for **Scheme (1A)**, Comp. No. **2b**; Molecular formula ($C_{22}H_{19}IN_4O$) resulted in m/z found=484.17785 (Calcd. 482.213 For [M]+) with an error of ΔM=-2.17785 ppm for **Scheme (1A)**, Comp. No. **7b**; Molecular formula ($C_{24}H_{18}ClIN_4O$) resulted in m/z found =489.15980 (Calcd. 490.1201 [M]+) with an error of ΔM=-0.9612 ppm for **Scheme (1A)**, Comp. No. **9a**, **[16]**. Mass Spectra (ESI-Ft-mass) of **Scheme (1B)**, Comp. No. (**12, 13, 14a, 14b, 15, 16a & 16b).**The structure of **Scheme (1B)**, Comp. No. **12** was considered most likely and in agreement with molecular formula ($C_{16}H_{14}N_2O_4$), resulted in m/z found=299.13888 (Calcd. 298.0214 For [M]+) with an error ΔM=-1.11748 ppm; Molecular formula ($C_{21}H_{16}ClN_3O_3$) resulted in m/z found=281.09207 (Calcd. 280.213 For [M]+) with an error of ΔM=-0.87907 ppm for **Scheme (1B)**, Comp. No. **13**; Molecular formula ($C_{16}H_{12}IN_2O_3$) resulted in m/z found=485.2175 (Calcd. 485.213 For [M]+) for **Scheme (1B)**, Comp. No. **14a**; Molecular formula ($C_{25}H_{18}IN_3O_3$) resulted in m/z found=433.18607 (Calcd. 435 For [M]+) with an error ΔM=-1.87698 ppm for **Scheme (1B)**, Comp. No. **14b**; Molecular formula (C22H19IN4O) resulted in m/z found =295.10844 (Calcd. 295 [M]+) with an error of ΔM=+0.10844 ppm for **Scheme (1B)**, Comp. No. **15**; Molecular formula ($C_{21}H_{14}IN_3O_3$) resulted in m/z found =470.25515 (Calcd. 483 [M]+) with an error of ΔM=-12.74485 ppm for compound **Scheme (1B)**, Comp. No. **16a**; Molecular formula ($C_{25}H_{16}IN_3O_3$) resulted in m/z found =517.19875 (Calcd. 533 [M]+) with an error of ΔM=-15.80125 ppm for **Scheme (1B)**, Comp. No. **16b**, **[17]**. Mass spectra of **Scheme (2)**, Comp. No. **9b** agree with a molecular ion (base peaks) at m/z =635 (m/z =158) and 377 for **9b, [16]. Scheme (3A & 3B)**, Comp. No. (**22A,B, D, 23, 24A, 28, 29B & 30).**The structure of **Scheme**

(3A), Comp. No. **22A** was considered most likely and in agreement with molecular formula ($C_{16}H_{12}IN_3O$), resulted in m/z found=391.17606 (Calcd. 389 For [M]+) with an error ΔM=+2.17606 ppm; Molecular formula ($C_{16}H_{13}IN_4O$) resulted in m/z found=403.14084 (Calcd. 404.0012 For [M]-) with an error of ΔM=-0.86036 ppm for **Scheme (3A)**, Comp. No. **22B**; Molecular formula ($C_{19}H_{17}IN_4O_2$), resulted in m/z found=466.18674 (Calcd. 460 For [M]+) with an error ΔM=+6.18674 ppm for **Scheme (3A)**, Comp. No. **22D**; Molecular formula ($C_{21}H_{19}IN_3O$), resulted in m/z found=466.15173 (Calcd. 456 For [M]-) with an error ΔM=+10.15173 ppm for **Scheme (3A)**, Comp. No. **23**; Molecular formula ($C_{29}H_{23}IN_6O$), resulted in m/z found=596.20552 (Calcd. 598 For [M]+) with an error ΔM=-1.79448 ppm for **Scheme (3A)**, Comp. No. **24A**; Molecular formula ($C_{38}H_{29}I_2N_7O_2$), resulted in m/z found=862.24904 (Calcd. 869 For [M]+) with an error ΔM=-6.75096 ppm for **Scheme (3B)**, Comp. No. **28**; Molecular formula ($C_{39}H_{39}Cl_2I_2N_7O$), resulted in m/z found=952.39134 (Calcd. 950 For [M]+) with an error ΔM=+2.39134 ppm for **Scheme (3B)**, Comp. No. **29B**, **[16].**

COLOUR AND SPECTRAL BEHAVIOUR OF SOME SELECTED SELF-ASSEMBLY [ICT] & RELATED CYANINE DYES

The absorption spectra of **Scheme (1A)** comp. No. **6a-c, 8a,b & 10a-c** in 95% ethanol showed absorption bands batho (hypso) chromically shifted depending upon the nature of heterocyclic A, heterocyclic quaternary residue A`, their linkage position and the substituents R in the aza substituted- position (1,2 diaza , 1,4 diaza ) cyanine dyes, **Scheme (1A)** comp. No. **6a-c, 8a,b & 10a-c**. Thus, the visible absorption maxim of **Scheme (1A)** comp. No. **6a** (A= indolizine, A` = pyridine-2-ium methiodide) showed (λ_{max}=418 & 514nm; ε_{max}=743 & 505 $mol^{-1}cm^2$). Substitution of [A`= pyridine-2-ium methiodide] in **Scheme (1A)** comp. No. **6a** by of (A`= quinoline-2-ium methiodide) in **Scheme (1A)** comp. No. **6b** resulted in bathochromic shift of the shorter (longer) wavelength (λ_{max}= 394 nm; ε_{max}=366 $mol^{-1}cm^2$ & λ_{max}=504nm; ε_{max}=246 $mol^{-1}cm^2$) of $\Delta\lambda_{max}$=24 (10) nm, This can be attributed to the more extensive π-delocalization within quinoline-2-ium salt. Changing the linkage position of the pyridinium residue from 2-ium in **Scheme (1A)** comp. No. **6a** to 4-ium in **Scheme (1A)** comp. No. **6c** causes bathochromic shift $\Delta\lambda_{max}$=12nm. This is due to the increasing in the conjugation of the pyridinium in the 4-ium linkage relative to 2-ium analogue, this is due to the more extensive π- delocalization and extra conjugation in the quinoline ring. The visible absorb-maximum of **Scheme (1A)** comp. No. **8a** [A= H-4-ium, B=H-4-ium] showed (λ_{max}=496 & 574 nm; ε_{max}=1800 & 1590 $mol^{-1}cm^2$). Substitution of [A= H-4-ium, B=H-4-ium] in **Scheme (1A)** comp. No. **8a** by [A= H-4-ium, B= C_4H_4-4-ium] in **Scheme (1A)** comp. No. **8b** exhibit (λ_{max}=480 nm; ε_{max}=1970 $mol^{-1}cm^2$) resulted in bathochromic shift of $\Delta\lambda_{max}$=94nm. This is due to the more extensive π- delocalization and extra conjugation in the quinoline ring. The visible absorb-maximum of **Scheme (1A)** comp. No. **10a** [A= H-4-ium, B=H-4-ium] showed (λ_{max}=314 & 510 nm; ε_{max}=1055 & 212 $mol^{-1}cm^2$). Substitution of [A= H-4-ium, B=H-4-ium] in dye **10a** by [A= H-4-ium, B= C_4H_4-4-ium] in dye **10b** exhibit (λ_{max}=390 & 522 nm; ε_{max}=339 & 235 $mol^{-1}cm^2$) resulted in bathochromic shift of $\Delta\lambda_{max}$=12 nm. Substitution of [A= H-4-ium salt, B=H-4-ium salt] in dye **10a** by [A (B) = H-4-ium salt, (C_4H_4-4-ium)] in **Scheme (1A)** comp. No. **10c** exhibit (λ_{max}=394 & 506 nm; ε_{max}=382 & 251 $mol^{-1}cm^2$) resulted in bathochromic shift of $\Delta\lambda_{max}$=80nm, this is due to the more extensive π- delocalization and extra conjugation in the quinoline ring, **Table (1A,B).** In point view of spectral behaviour, it was obvious that **Scheme (1A)** comp. No. **(6a-c)** absorbed fundamental light (Transmitted)

green (purple), yellow-green (violet) for **Scheme (1A)** comp. No. **8a**, blue-green (red) for **Scheme (1A)** comp. No.**8b** & green (purple**)** for **Scheme (1A)** comp. No. **10a-c, Table (1A,B).** The absorption spectra of **Scheme (1B)** comp. No. **16a,b, 19a,b, & 20a-c** in 95% ethanol exhibited absorption bands batho (hypso) chromically shifted depending upon the nature of heterocyclic A, A`. Thus, the absorption spectra of **Scheme (1B)** comp. No. **16a** [A = A` indolizine] showed (λ_{max}=390 & 504nm; ε_{max}=1276 & 660 $mol^{-1}cm^2$). Substitution of [A =A` indolizine] in **Scheme (1B)** comp. No. **16a** by [A =A` benzoindolizine] in **Scheme (1B)** comp. No. **16b** causes hybthochromic shift of $\Delta\lambda_{max}$=10nm accompanied with the appearance of new shoulder of absorption band at (λ_{max}=400nm; ε_{max}=709 $mol^{-1}cm^2$). This due to the more extensive π-delocalisation within the extra phenyl ring in **Scheme (1B)** comp. No. **16b**, **Table 4.** On comparison between the absorption spectra of dye **16a** [A =A` bis pyrazolo (4,5-b) indolizine] and **Scheme (1B)** comp. No. **20a** [A =A` bis pyrazolo (4,5-a) indolizine]. It was obvious that, the visible absorption spectra of **Scheme (1B)** comp. No. **20a** showed hybthochromic shift of $\Delta\lambda_{max}$=102 nm accompanied with the appearance of new absorption band at λ_{max}=390 nm relative to the **Scheme (1B)** comp. No. **16a**. This may be attributed to the position linkage of two nitrogen atoms of the indolizine /indolizinium heterocyclic is closed to methine group leading to easier of the electron transferring from nitrogen atom towards the corresponding positive charge nitrogen atom in **Scheme (1B)** comp. No. **20a, Table (1A,B).** The absorption spectra of **Scheme (1B)** comp. No. **19a** [A = indolizine, A' = pyridine-2-ium methiodide] showed (λ_{max}=356nm; ε_{max}=829 $mol^{-1}cm^2$). Substitution of [A' = pyridine-2-ium methiodide] in **Scheme (1B)** comp. No. **19a** by [A' = quinoline-2-ium methiodide] in **Scheme (1B)** comp. No. **19b** causes the appearance of new absorption bands at the shorter wavelength 306 nm concomitant with the disappearance of the old absorption band, due to the more extensive π-delocalisation within the quinoline moiety in **Scheme (1B)** comp. No. **19b**, **Table (1A, B).** Additionally, substitution of (A = indolizine) in **Scheme (1B)** comp. No. **19a** by (A = benzoindolizine) in **Scheme (1B)** comp. No. **20a** resulted in bathochromic shift of the longer wavelength of $\Delta\ \lambda_{max}$=146 nm concomitant with the appearance of new shoulder of absorption band at 492 nm. This may be attributed to the more extensive π-conjugation within in the extra phenyl ring. On comparison between the electronic absorption spectra of **Scheme (1B)** comp. No. **19b** & **20b**, it was obvious that the appearance of new shoulder of absorption band at $\Delta\lambda_{max}$=92 nm besides the other absorption bands, may be for the easier of electronic transfer occurs from the nitrogen atom heterocyclic N-indolizinium heterobicyclic to the nitrogen atom of heterocyclic residue, **Table (1A, B).** In point view of spectral behaviour, it was obvious that **Scheme (1B)** comp. No. **16(a & c)** absorbed fundamental light (Transmitted) green (purple), violet (yellow-green) for **Scheme (1B)** comp. No. **16b**, blue-green (red) for **Scheme (1B)** comp. No. **20a,** yellow-green (violet**)** for **Scheme (1B)** comp. No. **20b &** violet(yellow-green**)** for **Scheme (1B)** comp. No. **20c , Table (1A, B).** The visible absorb-maximum of **Scheme (2)** comp. No. **9a** [A= H-4-ium] showed (λ_{max}=460nm; ε_{max}=698 $mol^{-1}cm^2$). Substitution of [A= H-4-ium] in **Scheme (2)** comp. No. **9a** by [A = C_4H_4-4-ium] in **Scheme (2)** comp. No. **9b** exhibit (λ_{max}=498nm; ε_{max}=1010 $mol^{-1}cm^2$) resulted in bathochromic shift of $\Delta\lambda_{max}$=38nm. This is due to the more extensive π-delocalization and extra conjugation in C_4H_4-4-ium ring. The visible absorb-maximum of **Scheme (2)** comp. No. **10a** [A= H-4-ium, B=H-4-ium] showed (λ_{max}=390 & 520 nm; ε_{max}=2700 & 2443 $mol^{-1}cm^2$). Substitution of [A= H-4-ium, B=H-4-ium] in **Scheme (2)** comp. No. **10a** by [A= H-4-ium, B= C_4H_4-4-ium] in

Scheme (2) comp. No. **10b** exhibit (λ_{max}=480nm; ε_{max}=670mol^{-1}cm^{2}) resulted in bathochromic shift of $\Delta\lambda_{max}$=40nm. This is due to the more extensive π-delocalization and extra conjugation in the quinoline ring. Substitution of [A= H-4-ium salt, B=H-4-ium salt] in **Scheme (2)** comp. No. **10a** by [A (B) = H-4-ium salt, (C_4H_4-4-ium)] in **Scheme (2)** comp. No. **10c** exhibit (λ_{max}=500nm; ε_{max}=1780mol^{-1}cm^{2}). Substitution of [A (B) =H-4-ium, (C_4H_4-4-ium)] in **Scheme (2)** comp. No. **10c** by [A(B)= C_4H_4-4-ium, (H-4-ium)] in **Scheme (2)** comp. No. **10d** exhibit (λ_{max}=475nm; ε_{max}=612mol^{-1}cm^{2}) resulted in hypsochromic shift of $\Delta\lambda_{max}$=25nm. This is due to the less extensive π-delocalization and less conjugation in C_4H_4-4-ium ring. Substitution of [A (B)= C_4H_4-4-ium, (H-4-ium)] in **Scheme (2)** comp. No. **10d** by [A(B)= C_4H_4-4-ium, (C_4H_4-4-ium)] in **Scheme (2)** comp. No. **10e** exhibit (λ_{max}=478nm; ε_{max}=1593mol^{-1}cm^{2}) resulted in hypsochromic shift of $\Delta\lambda_{max}$=3nm. This is due to the more extensive π- delocalization and extensive conjugation in C_4H_4-4-ium ring. Substitution of [A (B)= C_4H_4-4-ium, (C_4H_4-4-ium)] in **Scheme (2)** comp. No. **10e** by [A(B)= C_4H_4-4-ium, (C_4H_4-1-ium)] in **Scheme (2)** comp. No. **10f** exhibit (λ_{max}=474nm; ε_{max}=1012mol^{-1}cm^{2}) resulted in hypsochromic shift of $\Delta\lambda_{max}$=4nm. This is due to the less extensive π- delocalization and less conjugation in C_4H_4-1-ium ring. Bis-zero-methine **Scheme (2)** comp. No. **10a-f** are bathochromic shift to **Scheme (2)** comp. No. **9a, b.** This is due to extend of π-delocalization in case of bis zero methine cyanine dyes **Scheme (2)** comp. No. **10a-f.** In point view of spectral behaviour, it was obvious that dyes **(6a, b),** absorbed fundamental light (Transmitted) green-blue (orange) for **Scheme (2)** comp. No. **6a,** blue- green (red) for **Scheme (2)** comp. No. **6b, 8a, b,** absorbed fundamental light (Transmitted) blue (Yellow) for **Scheme (2)** comp. No. **8a &** blue-green (red) for **Scheme (2)** comp. No. **8b. (9a-e),** absorbed fundamental light (Transmitted) green (Purple) for **Scheme (2)** comp. No. **9a,** blue (Yellow) for **Scheme (2)** comp. No. **9b,** blue-green (red) for **Scheme (2)** comp. No. **9c,** blue (yellow) for **Scheme (2)** comp. No. **9d &** blue (yellow) for **Scheme (2)** comp. No. **9e, Table (1A,B).** The absorption spectra of **Scheme (3A)** comp. No. **26A-D** and **Scheme (3B)** comp. No. **32a-c** in 95% ethanol showed absorption bands batho (hypso) chromically shifted depending upon the nature of heterocyclic A, heterocyclic quaternary residue A`, their linkage position and the substituents R in the aza mono substituted-tri-5/(8)[2(4)] methine cyanine dyes **Scheme (3B)** comp. No. **32a-c.** Thus, the visible absorption maxim of dye **Scheme (3A)** comp. No. **26A** showed (λ_{max}=390nm; ε_{max}=755 mol^{-1}cm^{2}). Substitution of [A` = pyridine-2-ium methiodide] in **Scheme (3A)** comp. No. **26a** by of [A` = quinoline-2-ium methiodide] in dye **26b** resulted in bathochromic shift of the longer wavelength of $\Delta\lambda_{max}$=6nm. This can be attributed to the more extensive π-delocalization within quinoline-2-ium salt, **Table (1A,B).** As was observed in the absorption spectra of Scheme **(3A)** comp. No. **26A-D,** and the visible absorption maxim **Scheme (3B)** comp. No. **32a-c** are influenced by the substituents in addition to the nature of heterocyclic A, heterocyclic quaternary residue A` and their linkage position, **Table (1A,B).** Thus, the visible absorption spectra of **Scheme (3B)** comp. No. **32a** [A` = quinoline-2-ium methiodide, R =H] exhibited (λ_{max}=402nm; ε_{max}=322 mol^{-1}cm^{2}). Substitution of [N-bridgehead unit] in **Scheme (3B)** comp. No. **32a** versus **Scheme (3A)** comp. No. **26A** causes hypsochromic shift of the longer wavelength of $\Delta\lambda_{max}$=12nm concomitant with the decreasing number of absorption bands, Table. This may be attributed to decreasing of conjugation through the accepting ability of

electron donating N-bridgehead unit system. In point view of spectral behaviour, it was obvious that **Scheme (3A)** comp. No. **26B** absorbed fundamental light (Transmitted) green (purple), green-blue (orange) for **Scheme (1A)** comp. No. **26D**, violet (yellow-green) for **Scheme (3B)** comp. No.**32a** & blue-green (red**)** for **Scheme (3B)** comp. No. **23c, Table (1A,B).**

Solvatochromic Behaviour of Some Selected Self-assembly [ICT] & related Cyanine Dyes

Cyanine dyes had been useful in studying the colour of organic substances **[17]** and there are several fundamental principles exist that correlate origin of chemical structures colour of the solute as well as natures of solvents **[18-21].** Moreover, these classes of self-assembly heterocyclic functional & related cyanine dyes are useful in various industrial field **[22].** The colour changes of cyanine dyes with solvents (solvatochromism) was previously discussed by **[23, 24 & 25]** and extended **[26]** and his coworkers **[27]** to correlate the effect of structure on molecular orbital energy levels. It is clear that the substituent types and solvent polarity change the electron densities of such dyes. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) shifts in solvents of various polarities. Self-assembly heterocyclic functional & related cyanine dyes are also ascribed a large change in dipole moment upon excitation due to the relative contribution of both dipolar zwitterionic benzenoid and neutral quinoid forms **[29-31]** Therefore, such dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of ground and Franck-Condon excited state, due to the absorption of electromagnetic radiation in UV-VIS region. If the ground state is more stabilized than excited state due to solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck-Condon principle **[32]** the time required for molecules to be exited is much smaller than that required to execute vibration or rotation. Therefore, the first excited state of the molecule in solution, called the Franck-Condon excited state, has the same solvation pattern as in the ground state, called the equilibrium ground state. The first Franck-Condon excited state is much more dipolar than the ground state due to intramolecular charge transfer upon excitation. Stabilization of the Franck-Condon excited state before and after relaxation to the equilibrium excited state and the destabilization of the Frank-Condon ground state relative to the equilibrium ground state by differential solvation leads to the positive solvatochromism. Positive solvato chromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases. From these finding points of view, the visible absorption spectra of some selected of newly synthesized cyanine dyes are discussed. The absorption spectra of the cited cyanine dyes, **Scheme (1A)** comp. No. (**6a-c, 8a-c, 9b** & **10a-c), Scheme (1B),** comp. No. (**16a-c, 19a-c & 20a-c), Scheme (3A),** comp. No.**26A-D** and **Scheme (3B),** comp. No. **(32a-c)** in the wavelength range 250-700 nm, have been studied in different organic solvents (H_2O, DMF, DMSO, EtOH, MeOH, acetone, $CHCl_3$, and C_6H_6) **[33]**, respectively. The colour changes of these dyes with solvents having different polarities are presented in **Tables (2A-D).** In point view of the absorption spectra of dyes, **Scheme (1A),** comp. No. **6a-c** in nonpolar organic solvent, (benzene), it was obvious that they absorbed the fundamental light absorption (violet), as it has got absorption value at (λ_{max}=404nm; ε_{max}=266 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **6a**, (λ_{max}=408nm; ε_{max}=424 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **6b** and (λ_{max}=402nm; ε_{max}=920 $mol^{-1}cm^2$) for **Scheme (1A),** comp.

No. **6c** as was obvious in EtOH absorption value, the absorbed fundamental light absorption (mainting colour) (violet) with bathochromic shift with respect to EtOH, **Tables (2A-D).** In point view of the absorption spectra of dyes, **Scheme (1A),** comp. No. **8a,b** in polar organic solvent, (DMSO), it was obvious that they absorbed the fundamental light absorption yellow-green(green), as they has got absorption value at (λ_{max}=582nm; ε_{max}=280 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8a** and (λ_{max}=510nm; ε_{max}=229 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8b.,** containment with bathochromic shift by $\Delta\lambda_{max}$=182(116)nm with respect to EtOH, in ($CHCl_3$) absorbed fundamental light absorption (yellow), as they has got absorption value at (λ_{max}=408nm; ε_{max}=599 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8a** and (λ_{max}=408nm; ε_{max}=959 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8b.,** containment with bathochromic shift by $\Delta\lambda_{max}$=8(8)nm with respect to EtOH, , in (DMF) absorbed fundamental light absorption yellow-green(green), as they has got absorption value at (λ_{max}=578nm; ε_{max}=216 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8a** and (λ_{max}=512nm; ε_{max}=193 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8b.,** containment with bathochromic shift by $\Delta\lambda_{max}$=8(8)nm with respect to EtOH, **Tables (2A-D).** It is clear from data that λmax of the intramolecular charge transfer absorption bands exhibit a marked bathochromic on transfer from nonpolar to polar solvents (positive solvatochromism), and some exhibits a hypsochromic of absorption bands with increasing solvent polarity (negative solvatochromism). The unexpected blue shift observed in the λmax of such cyanine dye in EtOH & water may be due to strong electrostatic interaction [H-bonding] of solvent that cause hypsochromic shift of λmax. Specific solvation of dyes occurs as a result of electrostatic interaction of the distributed cationic charges with the dipoles of solvated molecules. In point view of the spectral behavior of water they absorbed the fundamental light absorption (blue green), as it has absorption value at (λ_{max}=490nm; ε_{max}=217 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8a** and (λ_{max}=496nm; ε_{max}=216 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8b** containment with hypsochromic shift by $\Delta\lambda_{max}$=84(6) nm with respect to EtOH. The unexpected hypsochromic shift in the absorption spectral maxima in water compared to polar organic solvents and its lower extinction coefficients. This is due to the ease of interactions of water molecules, through intermolecular hydrogen bonding, with the lone pair of electrons on the nitrogen atom of the heterocyclic cyanine dyes, in addition to, intermolecular hydrogen bonding of water molecules on oxygen atom of the two carbonyl groups, through intermolecular hydrogen bonding, which intern preclude the charge transfer from the heterocyclic ring system to the positively charged residue along the conjugated bridge causing antagonistic effect**.** Moreover, the intermolecular hydrogen bonding between CHCl3 molecules and the lone pair of electrons of nitrogen atoms of the heterocyclic ring system is difficult due to the steric hindrance of the three bulk chlorines. Moreover, the solute solvent interactions in cases of CHCl3, generated a residual negative charge on the nitrogen atoms of the heterocyclic ring system which intern facilitated the electronic charge transfer to the positively charged center and this explain the bathochromic shifts in these solvents relative to water**, Tables (2A-D).** In point view of the absorption spectra of dyes, **Scheme (1A),** comp. No. **8a & 8b** in nonpolar organic solvent, In benzene, it was obvious that they absorb the fundamental light absorption (violet) as it has got absorption value (λ_{max}=414nm; ε_{max}=286 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8a** and (λ_{max}=410nm; ε_{max}=393 $mol^{-1}cm^2$) for **Scheme (1A),** comp. No. **8b**, as was obvious in EtOH, they absorbed fundamental light absorption (mainting colour) (violet) concomitant with hypochromic shift with respect to EtOH, **Tables (2A-D).** Dyes, **Scheme (2B),** comp. No. **16a-c &** comp. No. **19a-c & Scheme (2B),** comp. No. **20a-**

c, absorbed violet light in EtOH, $CHCl_3$, and MeOH λ_{max} = 400-450 nm extended and improved to the absorption of green light in DMF and acetone λ_{max} = 500-580 nm. The visible absorption spectra of zero-1[4] methine & bis-zero-methine cyanine dyes, **Scheme (2),** comp. No. **9b** & **10e** in the wavelength range 400-700 nm, have been studied in different organic solvents (H_2O, DMF, EtOH, acetone, CCl_4, $CHCl_3$ & C_6H_6). The colour changes of these dyes with solvents having different polarities. This is constructed with the intention to illustrate the solvatochromic behaviour of these dyes (λ_{max} and ε_{max}) values of the intramolecular charge transfer bands are given in **Tables (2A-D).** These dyes are showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. Also, **Scheme (3A)** comp. No. **26A-D** and **Scheme (3B),** comp. No. **32a-c** absorbed near violet light in EtOH, benzene, $CHCl_3$, CCl_4 and MeOH λ_{max} = 360-420 nm extended and improved to the absorption of green light in DMF and acetone λ_{max} = 520-575 nm. Dye, **Scheme (3A),** comp. No **26B,** absorbed violet light in EtOH, benzene, $CHCl_3$, and MeOH λ_{max} 400-406 nm extended and improved to the absorption of green light in DMF and DMSO λ_{max} = 514-516 nm. Finally, **Scheme (2B),** comp. No. **32a-c** absororbed violet light in EtOH, benzene, $CHCl_3$, and MeOH λ_{max} = 400-410 nm extended and improved to the absorption of green light DMF and DMSO λ_{max} =512 nm, **Tables (2A-D).**

Media chromic and Covalent Hydration of Some Selected Self-assembly [ICT] & related Cyanine Dyes in Aqueous Universal Buffer Solutions

Some selected dyes exhibit highly coloured in the ethanol acidic-medium discharged on basification. This may be due to **"**Covalent hydration in aqueous solution**.** It is not surprising to find that the acidic ethanolic solution of N-bridge head hetero-tri(tetra) cyclic and/or fused benzo heterobicyclic moieties substituted with strong electron withdrawing groups (C=NH, C= O) as in dyes **(12a**, **14b, 20b)** give deeping colour solution and discharge on basification in aqueous solution) showed "4-amino pyridinium and/or amidine types resonance "Covalent hydration " in aqueous solution or in dyes. On the other hand, the existence of benzpyrido-NH group as electron donor supplements the directing effect of (C=NH) imino-nitrogen (C=O) and direct the incoming proton of an aqueous medium into such groups leading to a stabilized covalent hydration through the mesomeric effects of either 4-amino-pyridinium or amidinium types resonance. This phenomenon was studied through dye **14a,** and the resonance stabilization and the bathochromic shift as the pH of the medium increases. In aqueous solution (highly coloured solution) is due to an electron charge transfer in conjugated mesomeric structures from N-bridge head heterocyclic moiety iminium/ hydroxnium cations moieties as an electron charge transfer in conjugated mesomeric structures. The absorption spectra of **Scheme (1A),** comp. No. (**6a-c, 8a-c, 9a-c &10a-c)** in aqueous universal buffer solution of different values of pH (1.92, 2.20, 4.19, 5.96, 6.97, 8.04, 10.25, 12.00) show regular changes with increasing the pH of the medium especially in the n-π* and CT bands **Tables (3A-B).** Also, the spectra of the selected cyanine dyes in aqueous universal buffer solutions of varying pH values showed bathochromic shifts with intensification of the absorption bands at high pH values (alkaline media), otherwise, hypsochromic shifts with quenching the intensity of the absorption bands at low pH values (acidic media) were recorded. Moreover, increasing the 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 spectral behaviour of **Scheme (1A),** comp. No. (**6a-c, 8a-c, 9a-c & 10a-c)** in 95% ethanol and/or in aqueous universal buffer solution showed that these compounds absorbed the blue light λ_{max} = 435-480 nm and the near blue-green light extended to the green light λ_{max} = 490-500 nm. In acid (pH ≥ 2.20) medium these dyes undergo a hypsochromic colour change due to the protonation of the heterocyclic nitrogen atom (oxygen) or the heterocyclic nitrogen atom of heterocyclic quaternary salts (quinolin-2-/ pyridin-4-) ium salts and other non-quaternize N-methyl (quinolin-2-/pyridin-4-) ium. In such cases the intramolecular charge transfer (CT) between the heterocyclic donor nitrogen (oxygen) and the heterocyclic acceptor nitrogen atoms does not occur, and the long wave length CT band disappears. A new short wave length band is observed, which could be assigned to a localized π−π* transition. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated, **Tables (3A,B).** The pK_a values were obtained using the standard procedure **[34]**, the pKa values and spectral characteristics of the protonated forms of dyes are collected in **Tables (3C, D).** Thus, it was suggested that these dyes are sensitive as photosensitizers in both acidic and basic mediums. This may be due to the presence of N-methyl quinolin-2-/ pyridin-4- linkage and the other quinolin-2-/ pyridin-4-ium salts causing the high planarity of the dye molecule. The ethanolic solution of some selected synthesized 12-methyl-4-oxo-10-phenyl-2a1,3,4,5,6,10-hexa[H]Pyrazolo [4,3-b]pyrido[2,1,6-de]pyrimido [5,4-g]pyrrolo [4,3,2-ij]quinolizin-13-ium-zero-2[4]Methine cyanine dyes **Scheme (3A),** comp. No. **26A-D,** and 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2b, 3, 6, 13,16,16a-hexa[H]-1H-Pyrazolo[4',3':8,9]quinolizino[4,5,6-ab]pyrrolo[4,3,2-de] pyrrolo [3',4': 1,2]quinolizino [4,5,6-gh] [2,7] naphthyridin-18-ium iodide-zero-2[4]methine cyanine dyes, **Scheme (3B),** comp. No. (**32a-c)** give a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution in order to ensure optimal pH in the application of these dyes as photosensitizers and determine their pKa values too. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity **[35]**. The absorption spectra of selected cyanine dyes **Scheme (3A),** comp. No.(**26A-D)** & **Scheme (3B),** comp. No. (**32a-c)** in aqueous universal buffer solution of different values of pH (1.92, 2.20, 4.19, 5.96, 6.97, 8.04, 10.25, 12.00) show regular changes with increasing the pH of the medium especially in the n-π* and CT bands **Tables (3C, D).** The spectra of selected cyanine dyes in aqueous universal buffer solutions of varying pH values showed bathochromic shifts with intensification of the absorption bands at high pH values (alkaline media), otherwise, hypsochromic shifts with quenching the intensity of the absorption bands at low pH values (acidic media) were recorded. Moreover, increasing the pH values of 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. Several methods had been adopted for spectrophotometric estimation of the dissociation constants of weak acids, the variation of absorbance at settled wavelength could be utilized. Thus, on plotting the absorbance at settled 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 indicator, 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 the indicator (dye) is in the basic form and the other half in the acidic

form. This point, (pKa value), was determined by the intersection of the S-curve with horizontal line midway between the left and right segments **[36] Tables (3C, D).** The spectral behaviour of **Scheme (3A),** comp. No. (**26A-D)** & **Scheme (3B),** comp. No. (**32a-c)** in 95% ethanol and/or in aqueous universal buffer solution showed that these compounds absorbed the blue light λ_{max} = 360-420 nm and the near violet light extended to the green light λ_{max} = 520-575 nm. Such dyes in aqueous universal buffer solution reveals absorption of the violet light at pH = 2.09 with hypsochromic and bathochromic shifted in the absorption of blue light and blue-green light at pH ≥ 7.0 relative to ethanol. The hypsochromic shift of the violet light at pH = 2.09 is due to the presence of quinolinium methiodide as strong inductively group which increase to some extent the indolizine type resonance causes the protonation of indolizine nitrogen atom in such solution of low pH value and therefore the interaction is inhibited and the protonated form does not absorb energy in the visible region. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to the fact that the protonated compound becomes deprotonated and therefore its mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction within the free base is facilitated, Several methods had been adopted for spectrophotometric estimation of the dissociation constants of weak acids; the variation of absorbance at settled wavelength could be utilized. Thus, on plotting the absorbance at settled 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 indicator, 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 the indicator (dye) is in the basic form and the other half in the acidic form. This point, (pKa value), was determined by the intersection of the S-curve with horizontal line midway between the left and right segments **[36] Tables (3C, D).** The determination of pKa values of **Scheme (3A),** comp. No. **(26A-D) & Scheme (3A),** comp. No. **(32a-c), Tables (3C, D)**. The results showed that the pKa values of these compounds depend upon the nature of such cyanine dye type which contains quinolinium heterocyclic quaternary residue in position -3- reveals pKa. These results were suggested that these dyes are more sensitive as photosensitizers in both acidic and basic mediums. The ethanolic solution of some selected newly synthesized 3-(1-ethylpyridin-4(1H)-ylidene)-2-(3-methyl-5-oxo-1-phenyl-1,5-di[H]-4H-pyrazol-4-ylidene)-2,3-di[H]-1H-pyrido[3,2 ,1-ij]cinnolin-10-ium chloride methine cyanine dyes **(6a-c),** 1-(1-ethyl pyridin-4(1H)-ylidene)-2-(3-methyl-5-oxo-1-phenyl-1,5- di[H]-4H-pyrazol-4-ylidene)-1,2,3,4-tetra [H]-pyrazino [1,2-a]quinolin-11-ium cyanine dyes **(8a-c),** the visible absorption maxim of 3,11-dimethyl-1-phenyl-1H-pyrazolo [4',3':5,6]pyrano[4,3-e]pyrido [1,2-a] pyrazine-10,12-diium chloride iodide cyanine dyes **(9a-c)**, 3-methyl-1-phenyl-4,5-dihydro-1H-pyrazolo[3,4-a]pyrido [1',2':4,5] pyrazino[2,3-c] quinolizine-10,11-diium iodide cyanine dyes **(10a-c), Tables (3C, D).** Thus, such **self-assembly [ICT]** Heterocyclic functional and related Cyanine dyes in **Scheme (1A),** comp. No. (**6a-c, 8a-c, 9a-c & 10a-c)**, **Scheme (3A&B),** comp. No. (**26A-D & 32a-c)** was suggested to be used as DSSCs especially in both aqueous media acidic or basic properties. Some heteroaromatic molecular are known to undergo "covalent hydration" reactions in aqueous solutions **[8, 40 & 41].** Recognition of the existance of covalent hydration in solution has allowed otherwise puzzling chemistry to become under stainable. The presence of strong electron withdrawing in compound **(23, 28, 30, 31A,B)** causes the increasing of the resonance type of such heteroaromatic, consequently supplement and increased the electron density on the heterocyclic annual nitrogen which easily direct the incoming proton of the aqueous media into this site reactivity leading to the stabilized covalent hydration phenomenon. Thus, it was obvious that the acidic ethanol solution of such compounds give a permanent colour (deepening in colour) & discharge on basification. This is due to the suggested covalent

hydration phenomenon or converting from keto form into their enol form causing internal charge transfer **[ICT].** Such phenomenon was occurred in aqueous media, thus concerning **[ICT]** Dyes, **Scheme (3A),** comp. No. **(23)** & **Scheme (3A),** comp. No. **(28, 30 & 31A,B)** that the stability of Enolate **[ICT]^1** Dye 10B is due to an internal charge transfer from hetero atom of pyrrol NH as electron source via10 anticlockwise extended conjugation bonds towards quinolizinium iodide salt more than **[ICT]^2** via 8 clockwise extended conjugation analogous. Meanwhile, the stability of **[ICT]^1** Dye **(30)** is due to an internal charge transfer from pyrrol NH as electron source via 12 anticlockwise extended conjugation bonds towards quinolizinium iodide salt more than **[ICT]^2** via 8 clockwise extended conjugation analogous. In point of view of covalent hydration of self-assembly **[ICT]** Heterocyclic Functional Dyes, it was suggested to be used as Dyes Sensitizer Solar Cell **[DSSCs].**

Molecular Modeling Studies Density Functional Theory (DFT) Calculations

Equilibrium molecular geometries of dyes **Scheme (3A&b),** comp. No. **25A,** 2**6E** and **32b** were calculated using density functional theory (DFT) utilizing the energy functional Becke3–Lee–Yang–Parr hybrid (B3LYP) over the parameter SDD basis set. The solvent effect was neglected, implemented in Gaussian 09 **[37]**, and the electron cloud delocalization included HOMO/LUMO levels of dyes, **Scheme (3A&B),** comp. No. **(25A, 26E & 32b)** were studied by DFT using Gaussian 09 software. All DFT jobs were submitted remotely at the normal computer. The quantum calculations (DFT) are considered to be one of the most reliable computational approaches in the field of chemistry. These calculations are applied to calculate the ground state geometries and excitation energies for dyes, **Scheme (3A&b),** comp. No. **(25A, 26E & 32b)**. The Kohn–Sham density functional theory (DFT) calculations were done to evaluate the ground state properties of the organic dye molecules using Becke3–Lee–Yang–Parr hybrid functional (B3LYP) over the parameter SDD basis set. The optimized structures of the dyes were depicted in **Fig. (1A, B)**, and achieved an effective charge separation in HOMO-LUMO energy levels as depicted in **Fig.** (**2)**. As expected, in their Highest occupied molecular orbitals (HOMO) levels, the electron cloud is predominantly localized on both pyrazolo and the fused pyrido-quinolizinium rings (donor part) for all dyes. Conversely, at their lowest unoccupied molecular orbitals (LUMO) levels, the electron cloud is shifted clearly from the electron donor to the electron acceptor (quinolinium) ring in case of dye **(26E)** and to the pyrazolo and carbonyl group of the other side of dye, **Scheme (3A&b),** comp. No. **32b** in different extent due to their varied electron accepting nature as shown in **Fig.** (**1C)**.

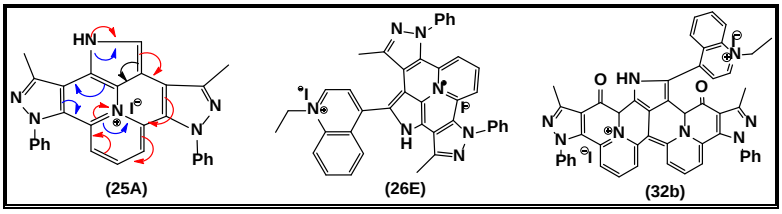
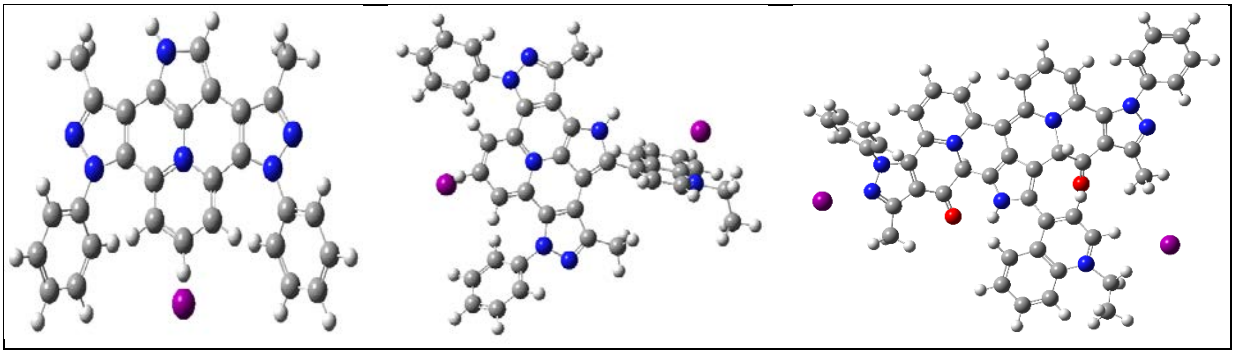


Fig (1A) Chemical Strucures (25A, 26E & 32b) under DFT Calculation



(25A) **(26A)** **(32B)**

Fig (1B) Optimized structures for dyes, **(25A, 26E & 32b)**

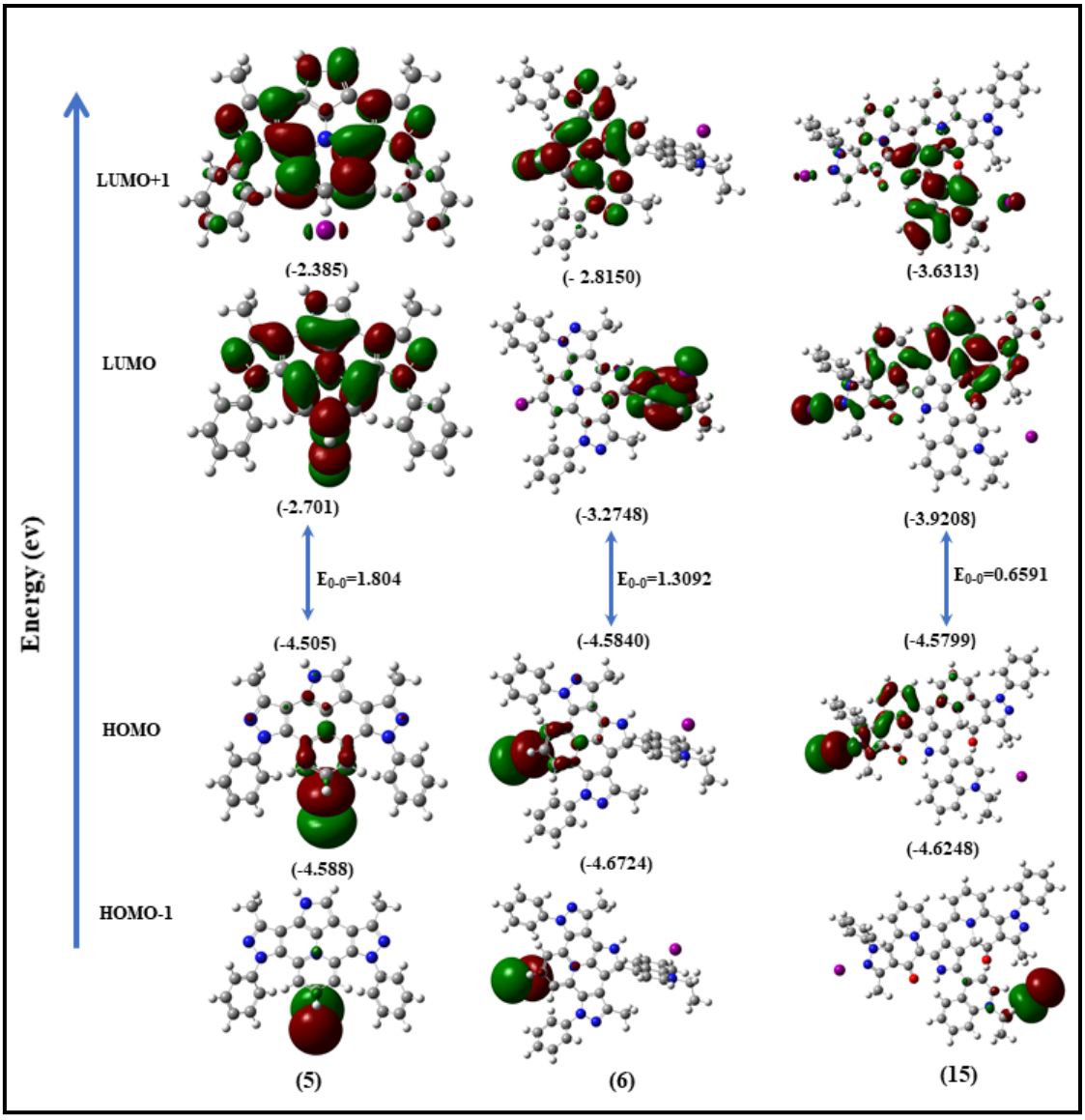


Fig. (1C) simulated molecular orbitals energy levels (HOMO/LUMO) of dyes, **Scheme (3A&b),** comp. No. **25A, 26E & 32b**.

The theoretical energy gab ($E_{0\text{-}0}$) values for dyes, **Scheme (3A&b),** comp. No. **26E & 32b** along with their HOMO/LUMO energy levels have been tabulated in **Table (4).** From the theoretical energy gab ($E_{0\text{-}0}$) values, it was obvious that, dye, **Scheme (3A&b),** comp. No. **16**

26E achieved higher $E_{0\text{-}0}$=1.3092 compared to $E_{0\text{-}0}$=0.6591 for dye **Scheme (3A&b),** comp. **32b**. The energy gap decreased in dye, **Scheme (3A&b),** comp. No. **32b** compared to dye, **Scheme (3A&b),** comp. No. **26E**, this is attributed to dye **32b** achieved an extended π-bridge length over the dye molecule compared to dye **26E** and this explains the great influence of π-bridge length on the excitation energy of the dyes ($E_{0\text{-}0}$) and maximum absorption wavelength values of the dyes **[38].**

Experimental

All melting points are uncorrected Elemental analysis was carried out at the Micro analytical center (Cairo-University). The IR (vKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H–NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on an Hp Ms 6988 spectrometer (Cairo University). The absorption spectra were carried out on a high resolution mass spectrometer – the Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan Orbitrap™ mass spectrometer – using Heated Electrospray Ionization (HESI), the Molecular Education, Technology, and Research Innovation Center (METRIC) at NC State University. Privileged precursors pyridinium iodide derivative of 4-acetyl-1-phenyl-pyrazol-5-one /5-oxime **(1A)** were prepared as was described in prospective references **[10 & 11].** 5-(1-(Hydroxy-imino-ethyl)-3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrrolo[3,4-a]quinolizin-6-ium-iodide **(22C & 27)** was prepared as was described in prospective reference **[8].** All melting points are uncorrected Elemental analysis was carried out at the Micro analytical center (Cairo-University). The IR (v ^{KBr}) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H–NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University). The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-700) on 6405 UV/Visible recording spectrophotometer, Faculty of Science, Aswan. 1-ethyl-4-(2-(hydroxyi-mino)-2-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine-4-yl-ethyl-quinolin-1-ium iodide **Scheme(2),** Comp. No. **6,** 4-acetyl-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one **Scheme (1A)** Comp. No. **1** & 4-acetoacetyl-3-methyl-1-phenyl-2-pyrazolin-5-one **Scheme (1B),** Comp. No. **11** were prepared in way similar to that described in prospective reference **[8, 9, 34].**

Synthesis of 1-(2-(hydroxyimino)-2-(3-methyl-5-oxo-1-phenyl-4,5- di[H]-1H-pyrazol-4-yl)ethyl)-2-methylpyridin-1-ium iodide, Scheme (1A), comp. No. **(2a-c).**

An Ethanolic mixture of **Scheme (1A),** comp. No. (**1**, 0.01mol) and 2- methyl pyridine and/or 2- methyl quinoline (0.01mol) was refluxed for 3 hrs in few drops of piperidine. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol. **Scheme (1A),** comp. No. **(2a-c)**, **Table (6).**

Synthesis of 8-hydroxy-1-((1-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl) ethylidene)amino)quinolin-1-ium chloride, Scheme (1A), comp. No. **(4).**

An ethanolic mixture of **Scheme (1A),** comp. No. (**1**, 0.01mol) and quinolin-8-ol (0.01mol) was refluxed for 3 hrs in few drops of HCl. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol, **Scheme (1A),** comp. No. **(4)**, **Table (6).**

Synthesis of 2-(3-methyl-5-oxo-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-1H-pyrido[3,2,1-ij] cinnolin-10-ium chloride Scheme (1A), comp. No. **(5).**

An ethanolic mixture of **Scheme (1A),** comp. No. (**4**, 0.01mol) in piperidine (1-2 ml) was refluxed for 4-6 hours where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(5), Table (6).**

Synthesis 3-(1-ethylpyridin-4(1H)-ylidene)-2-(3-methyl-5-oxo-1-phenyl-1,5-di[H]-4H-pyrazol-4-ylidene)-2,3-dihydro-1H-pyrido [3, 2, 1-ij]cinnolin-10-ium chloride Scheme (1A), comp. No. **(6a-c).**

An ethanolic mixture of **Scheme (1A),** comp. No. **(5)** & pyridinum-ethiodide salts (0.01 mole) in piperidine (1-2 ml) was refluxed for 6 hrs where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(6a-c), Table (5).**

Synthesis of 3-(3-methyl-5-oxo-1-phenyl-1, 5-di [H]-4H-pyrazol-4-ylidene)-1, 2, 3, 4-tetra[H]pyrido [1, 2-a] pyrazin-5-ium iodide Scheme (1A), comp. No. **(7a-c).**

An ethanolic solution of product **Scheme (1A),** comp. No. **(2a-c),** (0.01 mole) pyridine and (0.01 mole) from Iodine was refluxed for 3 hrs where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(7a-c), Table (6).**

Synthesis of 1-(1-ethylpyridin-4(1H)-ylidene)-2-(3-methyl-5-oxo-1-phenyl-1,5-di[H-4H-pyrazol-4-ylidene)-1,2,3,4-tetrahydropyrazino [1,2-a]quinolin-11-ium Scheme (1A), comp. No. **(8a-c).**

An ethanolic mixture of **Scheme (1A),** comp. No. **(7a-c)** and pyridinum-ethiodide salts (0.01 mole) in piperidine (1-2 ml) was refluxed for 6 hrs where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(8a-c), Table (6).**

Synthesis of 3,11-dimethyl-1-phenyl-1H-pyrazolo [4',3':5,6] pyrano [4,3-e]pyrido[1,2-a] pyrazine-10,12-diium chloride iodide Scheme (1A), comp. No. **(9a-c).**

An ethanolic mixture of **Scheme (1A),** comp. No. **(8a-c)** in acetic anhydride and then in ethanol in the presence of few drops of conc. HCl was refluxed for 3 hrs where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(9a-c), Table (5).**

Synthesis of 3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a] pyrido [1',2' :4,5] pyrazino [2,3-c]quinolizine-10,11-diium iodide Scheme (1A), comp. No. **(10a-c).**

An ethanolic solution of **Scheme (1A),** comp. No. **(7a-c, 0.01 mole),** (0.01 mole) pyridine and (0.01 mole) from Iodine was refluxed for 3 hrs where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed

several times with water, dried and crystallized from ethanol to give **Scheme (1A),** comp. No. **(10a-c), Table (5).**

Synthesis of 3-(3-methyl-5-oxo-1-phenyl-4, 5-di[H]-1H-pyrazole-4-carbonyl)-4-oxopent-2-enal Scheme (1B), comp. No. **(12).**

An Acidic solution of **Scheme (1B),** comp. No. (**11, glyoxal** 0.01mol.) in AcOH was refluxed for 1-2 hrs. The reaction mixture was filtrated hot from unreacted materials. The filtrate concentrated, cooled and precipitated by addition of cold water, filtrated and crystallized from ethanol, **Scheme (1B),** comp. No. (**12), Table (6).**

Synthesis of 5-acetyl-3-methyl-1-phenyl-1H-indazole-4, 7-dione Scheme (1B), comp. No. **(13).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**12**, 0.01mole) in few drops of piperidine was refluxed for 3 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 **Scheme (1B),** comp. No. **(13)**, **Table (6).**

Synthesis of 1-(2-(3-methyl-4,7-dioxo-1-phenyl-4,7-di[H]-1H-indazol-5-yl)-2-oxoethyl) pyridin-1-ium iodide, Scheme (1B), comp. No. **(14a-c).**

An ethanolic solution of **Scheme (1B),** comp. No. **(13)** (0.01mole) and (0.01mole) of pyridine and (0.01 mole) 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 **Scheme (1B),** comp. No. **(14a-c), Table (8).**

Synthesis of 5-(1-(hydroxyimino)ethyl)-3-methyl-1-phenyl-1H-indazole-4,7-dione, Scheme (1B), comp. No. **(15).**

An Ethanolic solution of **Scheme (1B),** comp. No. **(13,** 0.01mole) and hydroxylamine hydrochloride (2 moles) with sodium acetate (3moles) 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 **Scheme (1B),** comp. No. **(15)**, **Table (6).**

Synthesis of 9-methyl-7,8,12-trioxo-11-phenyl-7,8,11,12-tetrahydro-6H-pyrazolo[4,3-g]pyrido[2,1-a]isoquinolin-5-ium iodide, Scheme (1B), comp. No. **(16a-c).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**14a-c**, 0.01mol) in few drops of piperidine was refluxed for 3hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtrated, crystallized from ethanol to give **Scheme (1B),** comp. No. **(16a-c)**, **Table (8).**

Synthesis of 6-(1-ethyl-1l4,4l5-pyridin-4-ylidene)-9-methyl-7,8,12 trioxo-11-phenyl-7,8,11,12-tetrahydro-6Hpyrazolo[4',3':6,7]isoquinolino[2,1-a]quinolin-5-ium iodide, Scheme (1B), comp. No. **(17).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**16,** 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 **Scheme (1B),** comp. No. **(17), Table (6).**

Synthesis of 1-(3, 5, 8-trimethyl-4, 9-dioxo-1-phenyl-4, 9-dihydro-1H-pyrazolo [3, 4-g] isoquinolin-7-yl) pyridin-1-ium iodide, Scheme (1B), comp. No. **(18).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**15,** 0.01 mol.) and 1-(2-oxopropyl) pyridin-1-ium iodide (0.01mol.) in few drops of piperidine was refluxed for 2 hrs and then in acetic acid was refluxed for 2 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 **Scheme (1B),** comp. No. **(18), Table (6).**

Synthesis of 1-((1-(3-methyl-4,7-dioxo-1-phenyl-4,7-di[H]-1H-indazol -5-yl)ethylidene) amino)pyridin-1-ium chloride, Scheme (1B), comp. No. **(19a-c).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**15,** 0.01 mol.) and pyridin-ium-ethiodide salts (0.01mol.) in few drops of conc. HCl 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 **Scheme (1B),** comp. No. **(19a-c), Table (8).**

Synthesis of 7,9-dimethyl-8,12-dioxo-11-phenyl-11,12-di[H]-8H-pyrazolo[4,3-g] pyrido [2,1-a]phthalazin-5-ium chloride Scheme (1B), comp. No. **(20a-c).**

An ethanolic solution of **Scheme (1B),** comp. No. (**19a-c**, 0.01mole) in few drops of piperidine was fusion for 1 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 **Scheme (1B),** comp. No. **(20a-c), Table (8).**

Synthesis of 3,5,8-trimethyl-4,9-dioxo-6-(3-oxobutanoyl)-1-phenyl-7-(pyridin-1-ium-1-yl)-4,9-di[H]-1H-pyrazolo[3,4-g]isoquinolin-6-ium chloride iodide, Scheme (1B), comp. No. **(21).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**18,** 0.01 mol.) & acetyl acetone (0.01mol.) in few drops of conc. HCl 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 **Scheme (1B),** comp. No. **(21), Table (6).**

Synthesis of 3,6,8-trimethyl-4,16-dioxo-1-phenyl-4,16-dihydro-1H-indolizino[3,2-c] pyrazolo[3,4-g]pyrido[2,1-a]isoquinolin-9-ium chloride, Scheme (1B), comp. No. **(22).**

An Ethanolic solution of **Scheme (1B),** comp. No. (**21**, 0.01mol) in few drops of piperidine was refluxed for 3hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtrated, crystallized from ethanol to give **Scheme (1B),** comp. No. **(22)**, **Table (6).**

Synthesis of 1-ethyl-4-(2-(hydroxyl-imino)-2-(3-methyl-1-phenyl-4, 5-di [H]-1H-pyrazol-5-imino--4-yl-ethyl-quinolin-1-ium iodide, Scheme (2), comp. No. **(6).**

A mixture of **Scheme (2),** comp. No. **(1b,** 1 mole), hydroxylamine hydrochloride (2 moles) and sodium acetate (3 moles) was dissolved in ethanol (30 ml) and heated in a water bath for about an hour. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated and cooled. The precipitated products after dilution with water were

separated, filtrated, washed with water several times and crystallized from ethanol, **Table (9)**.

Synthesis of 1-ethyl-4-(2-(hydro-xyimino)-2-(5-imino-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-4-yl)-1-(2-methylpyridin-1-ium-1-yl)ethyl)quinolin-1-ium iodide Scheme (2) comp. No. **(7a, b).**

An ethanol solution of dye, **Scheme (2)** comp. No. **(6)**, (0.01mol) & 2-pyridin [quinolin] (0.01mol) in the presence of (0.01mol) iodine were refluxed for 5-7 hrs on a hot plate. The reaction mixtures were 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, **Table (9)**.

Synthesis of Self Assembly [ICT] functional 4-(1,5-dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido[1',2':4,5]pyrazino[1,2-c]pyrimidin-13-yl)-1-ethylquinolin-1-ium iodide Scheme (2) comp. No. **(9a, b).**

Mixture of (**8a & b,** 0.005 moles) in acetic anhydride (10 ml) 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, **Table (9)**.

Synthesis 4-(1,5-dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido [1',2':4,5] pyrazino [1,2-c]pyrimidin-13-yl)-zero-1[4]methine cyanine dye, Scheme (2) comp. No. **(8a, b)**

Fusion of **Scheme (2)** comp. No. **(7a, b)** with piperidine for about an hour then dissolved the reaction mixture in ethanol and reflux for 3 hours. The reaction mixture concentrated to half of its volume, cooled and precipitated with ice water then recrystallized from ethanol,**Table 4.**

Synthesis of 4,4'-(1,5-dimethyl-3-phenyl-3H-pyrazolo[4,3-e]pyrido [1',2': 4,5] pyrazino [1,2-c] pyrimidine-7,13-diyl)bis-zero-methine Scheme (2) comp. No. **(10a-e).**

An ethanol solution of dye **Scheme (2)** comp. No. **(51a, b)** (0.01mol) and pyridin [quinolin]-2(4)-ium-1-ethiodide salts (0.01mol) in the presence of few drops of piperidine were refluxed for 5-7 hrs on a hot plate. The reaction mixtures were 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, **Table (9)**.

Synthesis of pyridinium iodide derivative of 4-acetyl-1-phenyl-pyrazol-5- oxime, Scheme (3A), comp. No. **(21B)**

An Ethanolic solution of **Scheme (3A),** comp. No. **(21A, 0.01mol.),** hydroxylamine hydrochloride (0.02 moles) & sodium acetate **(3 moles)** was refluxed for 4 hrs the reaction mixture was filtrated hot from unreacted materials. The filtrate concentrated, cooled and precipitated by addition of cold water, filtrated, crystallized from ethanol to give **Scheme (3A),** Comp. No. **(21B), Table (10).**

Synthesis of 3-methyl-4-oxo-1-phenyl-4,5-di[H]-H-pyrazolo[3,4-a]quinolizin-6-ium iodide & 4-(hydroxyimino)-3-methyl-1-phenyl-4,5-di[H]-1H-Pyrazolo [3,4-a] quinolizin-6-ium iodide, Scheme (3A), comp. No. **(22A, B)**

An Ethanolic mixture of **Scheme (3A)** comp. No. (**21A, B**, and 0.01mol.) & piperidine (1-2 ml) was refluxed for 4-6 hours where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (3A),** comp. No. **(22A, B), Table (10).**

Synthesis of 5-acetyl-4-(hydroxyimino)-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a] quinolizin-6-ium-iodide Scheme (3A), comp. No. **(22D)**

An acidic solution of **Scheme (3A),** comp. No. **(22B**, 0.01mol) in Ac_2O was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3A),** comp. No. **(22D), Table (10).**

Synthesis of 11-methyl-3-oxo-9-phenyl-2,3,3a,9-tetra[H] dipyrrolo [3,4-a:2',3'-c] quinolizin-4-ium iodide Scheme (3A), comp. No. **(23)**

Route (A), An acidic solution of **Scheme (3A),** comp. No. **(22D,** 0.01mol**.)** in AcOH was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water, the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3A),** comp. No. **(23), Table (6), Route (B),** An Ethanolic mixture of **Scheme (3A)** Comp. No. **(22A,** 0.01mol**.) &** glycine in piperidine (1-2 ml) was refluxed for 4-6 hours where it gives a deep permanent color at the end of refluxing. It was filtered while hot, concentrated to half of its volume, cooled and precipitated by addition of cold water. The precipitated products was filtered, washed several times with water, dried and crystallized from ethanol to give **Scheme (3A),** comp. No. **(23), Table (10).**

Synthesis of 6-(2,5-dioxo-imidazolidin-4-yl)-3-methyl-1-phenyl-1,6a-di[H] Pyrazolo [3,4-a]pyrrolo[2,3-c] quinolizin-7-ium iodide, 6-(2,5-dioxo-imidazolidin-4-yl)-3-methyl-1-phenyl-1,6a-di[H]pyrazolo[3,4-a]pyrrolo[2,3-c] quinolizin-7-ium, 11-methyl-3-(2-methyl-5-oxo-4,5-di[H]-oxazol-4-yl)-9-phenyl-3a,9-di[H]-dipyrrolo[3,4-a:2',3'-c] quinolizin-4-ium-iodide & 6-(2,5-dioxohexa[H]pyrimidin-4-yl)-3-methyl-1-phenyl-1,6a-di[H] pyrazolo [3,4-a]pyrrolo [2,3-c]quinolizin-7-ium, Scheme (3A), comp. No. **(24A-D)**

An acidic mixture of **Scheme (3A)**, Comp. No. **(23,** 0.01mol.) & 3-methyl-1-phenyl-2,4-di[H]-3H-pyrazolin-5-one, Hydantoin (imidazol-2,5-dione), 2-methyl-oxazol-5(4H)-one & Barbituric acid (tetra[H] pyrimidin-2,5-dione) in AcOH was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water, the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3A),** comp. No. **(24A-D), Table (10).**

Synthesis of 11-methyl-4-oxo-9-phenyl-2a1,2b, 4,5, 5a,9-hexa[H]-3H-imidazo [4,5-b]pyrazolo[3,4-g]pyrido[2,1,6-de] pyrrolo[2,3,4-ij]quinolizin-12-ium, 4,11-dimethyl-9-phenyl- Synthesis of 2a1,9-di[H]oxazolo[4,5-b]pyrido[2,1,6-de]dipyrrolo[3,4-g:2',3',4'-ij] quinolizin-12-ium-iodide&12-methyl-4-oxo-10-phenyl-2a 1,3,4,5,6,10-hexa [H]pyrido [2, 1,6-de]pyrimido[4,5-b]dipyrrolo[3,4-g:2',3',4'-ij]quinolizin-13-ium-iodide, Scheme (3A), comp. No. **(25A-D)**

Route (A), an acidic mixture of **Scheme (3A)** Comp. No. **(24A-D,** 0.01mol.) in AcOH was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water, the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3A)** Comp. No. **(25A-D), Table (6), Route (B)** An acidic mixture of **Scheme (3A)** Comp. No. **(22B,** 0.01mol.) in AcOH & 4-acetyl-1-phenyl-pyrazolin-5-one under AcOH followed by piperidine catalysis was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold

water, the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3A),** comp. No. **(25A), Table (10).**

Synthesis of 3,11-dimethyl-5,9-diphenyl-5,9-di[H]-1H-dipyrazolo[4,3-b:3',4'-g]pyrido [2,1,6-de] pyrrolo[2,3,4-ij]quinolizin-12-ium-zero-2[4] methine, 3,11-dimethyl-5,9-di phenyl-2a1,9-di[H]-5H-dipyrazolo[4,3-b: 3',4'-g]pyrido[2,1,6-de]pyrrolo[2,3,4-ij] quinolizin-12-ium-zero-2[4] methine, 3,11-dimethyl-4-oxo-9-phenyl-2a 1,4,5,9-tetra [H]-3H-imidazo [4,5-b] pyrazolo [3,4-g]pyrido [2,1,6-de]pyrrolo[2,3,4-ij]quinolizin-12-ium-zero-2[4]methine, 4,11-dimethyl-9-phenyl-2a1, 9-di[H]oxazolo[4,5-b] Pyrazolo [3,4-g]pyrido[2,1,6-de]pyrrolo [2,3,4-ij]quinolizin-12-ium-iodide-zero-2[4]methine & 12-methyl-4-oxo-10-phenyl-2a1,3,4,5,6,10-hexa[H] pyrazolo [4,3-b]pyrido[2,1,6-de] pyrimido[5,4-g]pyrrolo[4,3,2-ij]quinolizin-13-ium-zero-2[4]Methine cyanine dyes, Scheme (3A), comp. No. **(26A-D)**

An Ethanolic solution of **Scheme (3A),** comp. No. (**25A-D**, 0.01mol.) & pyridin-4[quinolin-4(1)]-ium-ethiodide (0.01mol.) in few drops of piperidine was refluxed for 1 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 **Scheme (3A),** comp. No. **(26A-D), Table (11).**

Synthesis of 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-1,2b,3,6,13, 16 hexa[H] Pyrazolo [4',3':8,9]quinolizino[4,5,6ab]pyrazolo[4',3':8,9] quinolizino [6,5,4-gh]pyrrolo [2,3,4-de][2,7] naphthyridin-17,18-diium-iodide, Scheme (3B), comp. No. **(28)**

An acidic mixture of **Scheme (3B),** Comp. No. **(22C**, 0.01mol.) & **Scheme (3B),** comp. No. **(27,** 0.01mol.) in AcOH was refluxed for 1 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and precipitated by addition of cold water, the precipitated products, filtrated and crystallized from ethanol to give **Scheme (3B),** comp. No. **(28), Table (10).**

Synthesis of Synthesis of 5-(4-(diethylperoxy)-5-(3-methyl-4-oxo-1-phenyl-4,5-di[H]-1H-pyrrolo [3,4-a]quinolizin-6-ium-5-yl)-2H-pyrrol-3-yl)-4-imino-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]quinolizin-6-ium-iodide & 5-(4-formyl-5-(3-methyl-4-oxo-1-phenyl-4,5-dihydro-1H-pyrrolo[3,4-a]quinolizin-6-ium-5-yl)-2H-pyrrol-3-yl)-4-imino-3-methyl-1-phenyl-4,5-di[H]-1H-pyrazolo[3,4-a]quinolizin-6-ium iodide (29A,B)

An Ethanolic solution of **Scheme (3B),** comp. No. **(28,** 0.01mol.) & ethyl-ortho-formate and/or chloroform (0.01mol.) in few drops of piperidine were refluxed for 1 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 **Scheme (3B),** comp. No. **(29A, B), Table (10).**

Synthesis of 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2,2b,3,6,9b ,13 ,16,16a-octa[H] Pyrazolo [4',3':8,9]quinolizino[4,5,6-ab]pyrrolo[4,3,2-de]pyrrolo [3',4':1,2] quinolizino [4,5,6-gh] [2,7]naphthyridin-17,18-diium iodide, Scheme (3B), comp. No. **(30)**

An Ethanolic solution of **Scheme (3B),** comp. No. **(29A, B,** 0.01mol**.)** & few drops of piperidine was refluxed for 1 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 **Scheme (3B),** comp. No. **(30), Table (10).**

Synthesis of 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-1,2b,3,6,13,16-hexa[H] Pyrazolo [4', 3':8,9]quinolizino[4,5,6-ab]pyrrolo[4,3,2-de] pyrrolo[3',4':1, 2] quinolizino[4,5,6-

gh][2,7]naphthyridin-17,18-diium-iodide & 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2b,3, 6,13, 16,16a-hexa[H]-1H-Pyrazolo [4',3':8,9] quinolizino[4,5,6-ab]pyrrolo [4,3,2-de] pyrrolo[3',4':1,2] quinolizino[4,5,6-gh] [2,7]naphthyridin-18-ium-iodide, Scheme (3B), comp. No. **(31A, B)**

An Ethanolic solution of **Scheme (3B),** comp. No. **(30,** 0.01mol**.)** & few drops of piperidine was refluxed for 1 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 either **Scheme (3B),** comp. No. **(31A or 31B), Table (10).**

Synthesis of self-assembly [ICT] functional dyes 4,15-dimethyl-3,16-dioxo-6,13-diphenyl-2b,3,6,13,16,16a-hexa[H]-1H-pyrazolo [4',3': 8,9]quinolizino [4,5,6-ab] pyrrolo[4,3,2-de] pyrrolo [3',4':1,2] quinolizino[4,5,6-gh][2,7] naphthyridin-18-ium iodide-zero-2[4] methine cyanine dyes, Scheme (3B), comp. No. **(32a-c)**

An Ethanolic solution of **Scheme (3B),** comp. No. **(31A or 31B)** and pyridin-4[quinolin-4(1)]-ium-ethiodide (0.01mol.) in few drops of piperidine was refluxed for 1 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 **Scheme (3B),** comp. No. **(32a-c)**, **Table (11).**

Solvatochromic & Preparation of Dyes Solution:

The organic solvents were used of spectroscopic grade of purified according to the recommended methods **[39]**. The electronic 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 1 cm cell. The stock solution of the dye was of the order 10^{-3} M. Solution of low molarities used in spectral measurements was obtained by accurate dilution. For studying the effect of pure solvents in the UV and visible range: Accurate volumes of the stock solution of the 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. **-** For studying the spectral behaviour in mixed solvents in the visible region: An accurate volume of the stock solution (10^{-3} M in ethanol) of the dyes were placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent. 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. The pH of such solution was checked before spectral measurements. An accurate volume of the stock solution of the dyes was diluted to an appropriate volume in order to obtain the required concentration. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect time**.**

CONCLUSION:

1-Special attention has been focused on the chemical structure of some selected synthesized N-bridge head heterocyclic self-assembly **[ICT**

2-Characteristic attention has been focused on absorption behaviour of such dyes, in order to permit a criterion for their use as photosensitizers & to shed some light upon a possible color chemical structure relationship. The results showed the position of fundamental light absorption and their molar extinction coefficients are influenced by the nature of such heterocyclic residue based on (their linkage position) & nature of the bridge head heterocycles.

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The results of the study of absorption spectra of all the newly synthesized functional & their polymethine cyanine dyes in 95% EtOH indicated that the absorption bands resulted in the bathochromically photosensitization shift for fundamental light absorption color. Some selected dye formation & their sites reactivity were postulated and in our point view, this thesis would be considered as a guidance in the field of synthetic routes of N-bridge head heterocyclic synthesized self-assembly **[ICT]** functional and polymethine cyanine dyes based on, their specification, sites reactivity involving formation mechanistic pathway.

3-The solvato (media)chromic [aqueous universal buffer solution] behavior of some selected N-bridge head heterocyclic synthesized self-assembly **[ICT]** functional polymethine cyanine dyes The fundamental light absorption in color of such dyes in some pure organic solvents (aqueous universal buffer solution) were examined in the visible region resulted in solvatochromism and colour shift of such dyes with solvents having different polarities and/or aqueous universal buffer solution. This permits a selection of optimal solvent and/or aqueous media when these dyes are applied as photosensitizers or dye sensitizer solar cells (DSSCs).

4-The absorption spectra of some selected self-assembly **[ICT]** functional dyes and related cyanine dyes in universal buffer solution absorbed the fundamental green blue light in acid/base media and might be used as photosensitizers in both acidic and basic medium. Thus, it was obvious that the covalent hydrated dyes absorbed the fundamental colour in acid medium and other absorb the fundamental light in basic media.

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References

[1a]-Bird, C. W., Tetrahedron, (1998), 54, 10179. Chem. Res., 47 (4), 1186-1198, **(2014)**.

[1b]-Hans Jakob Worner, € Christopher A. Arrell, Natalie Banerji, Andrea Cannizzo, MajedChergui, Akshaya K. Das, Peter Hamm, Ursula Keller,7 Peter M. Kraus, Elisa Liberatore, Pablo Lopez-Tarifa, Matteo Lucchini, Markus Meuwly, Chris Milne, Jacques-E. Moser Ursula Rothlisberger Grigory Smolentsev, Joel € Teuscher, Jeroen A. van Bokhoven, and Oliver Wenger, STRUCTURAL DYNAMICS 4, 061508**, (2017).**

[2]- Ravindran, E. and Ananthakrishnan, S. J., J. Mater. Chem. C, 3, 4359, (**2015)**.

[3]- Bonifazi, M. D., Chem. Soc. Rev., 41, 211**, (2012)**.

[4]- Fenwick, O., Dyck, C. V. K. Murugavel, D., Cornil, F. R. & Haar, S., J. Mater. Chem. C, 3, 3007, **(2015).**

[5]- Yongjun, Li., Taifeng, Liu, Huibiao, Mao-Zhong, Liu, T. & Yuliang, Li.; Acc. Chem. Res., 47 (4), 1186-1198, **(2014).**

[6] -Yongjun, Li, Taifeng Liu, Huibiao Liu, Mao-Zhong Tian, & Yuliang, Li Acc. Zhao-ming, Xue & Xian Yang, Ij-, J. Mater. Chem. C, 4, 2990, **(2016).**

[7]- Kim, F. S., Ren G. Q. & Jenekhe, S. A., Chem. Mater. 23, 682, **(2011).**

[8]- A.I.M. koraiem, R. M. abu-el-hamd, H. A. Shindy & M. A. Ibrahim, ASW. SCI. TECH. BULL., **(2017).**

[9]-Abd El-Motaleb, A. M., M.Sc.Thesis, Faculty of Science, Aswan University**,** 169-174, **(2011).**

[10]-Mohanty MK, Sridhar R, Padmanavan SY. Indian J.Chem 158:1146 **(1977)**.

25

[11]-B. T. Thakera, Kiran R. Suratia, S. V. Patela & C. K. Modib J. Saudi Chem. Soc., Vol. 10, No. 3; 447-460 **(2006)**.

[12]-L. J. Bellamy; The infrared spectra of complex molecules, London; Methuen, **(1962)**.

[13]-L.Wade, Organic Chemistry 4th.544-604, **(1999).**

[14]-Scheinman, F**.** Nuclear magnetic resonance of complex Molecules, Braunschweig: Vieweg and Sohn GmbH, vol.1. (**1970).**

[15]-Batterham, T. J.; ^{1}HNMR spectra of simple heterocycles" Wiley New York, (**1973).**

[16]-Porter, Q. N., and Baldas, J; "Mass Spectrometry of Heterocyclic Compounds "Wiely, New York, (**1971).**

[17]-Ficken, G. E**.,** Chemistry of Synthetic Dyes ed. K. Venkataraman Academic Press New York 4, 212-230, **(1971)**.

[18]-West, W.; Geddes, A. L. J. Phys. Chem., 68, 4, 837, **(1964)**.

[19]-Ishchenko, A. A., Derevyanko, N. A., Zuarovski, V. M., and Tolmachev, A. I., Theoret. Experiment. Khim. 20,443, **(1984)**.

[20]-A. A. Ishchenko, N. A. Derevyanko, V. M. Zuarovski, & A. I. Tolmachev, Theoret. Experiment. Khim. 20, 443, **(1984)**.

[21]- Ishchenko, A. A., Svidro, A. A., and Derevyanko, N. A., Dyes and Pigments 10**,** 85-96, **(1989).**

[22]-A. I. M. Koraiem & J.F. Prant. Chemie.326 (4), 695, **(1984)**.

[23]-Dietz F, Mueller G, Bach G, I. Von Grossmann, J Signal Am.**1975**; 3.

[24]- Gibson, H. W. and Canad.; J. Chem. Soc., 51, 3065**, (1973, 1976).**

[25]- J.E. Kuder, H.W. Gibson, D. Wychick, Linear free energy relations. III. Electrochemical characterization of salicylaldehyde anils, J Org Chem, 40, 875-879, (**1975)**.

[26]-Koraiem`s article reviews **1990, 1991.**

[27]-A.I.M.Koraiem, R.M.Abu El-Hamd & R.M.Abd El- Aal, .Proc.Indian.Acad.Si. Vol.109 (2):115-134 **(1997).**

[28]-K. Nishimoto, A MO Theoretical Study of Organic Dyes I. Effect of Chemical Softness on the Electronic Spectra, Bull Chem Soc Jpn, 66, 1876-1880, **(1993).**

[29]-J. Gao, C. Alhambra, Solvent Effects on the Bond Length Alternation and Absorption Energy of Conjugated Compounds, J. Am. Chem. Soc., 119, 2962, **(1997).** http://dx.doi:10.1021/JA9700358.

[30]-J.O. Morley, Theoretical studies on the electronic structure and spectra of the merocyanines, J Mol Struct THEOCHEM, 304, 191-202, **(1994),** http://dx.doi:10.1016/0166-1280(94)80016-2.

[31]- Da silva, L., Machado, C. And Rezande, M. C.; J. Chem. Soc. Perki Trans. 2, 483, **(1995).**

[32]- Frank, J.; Trans. Faraday Soc., 21, 536, **(1926)**.

[33]-Weast, R. C. and Astl, M. J. CRC handbook of chemistry and physics, 61 st. Edn. (CRC press, Inc.) 56, **(1980-1981).**

[34]- M. Mitewa, N. Mateeva, L. Antonov & T. Deligeorgiev, Dyes and Pigments, 27, 219-225, **(1995).**

[35]-Mahmoud, M. R.; Khalil, Z. H. and Issa, R. M., Acta. Chim.Acad. Sci. Hung, 87(2), 121-5, **(1975).**

26

[36]-Ewing, G., Instrumental Methods for Chemical Analysis Mc. Graw-Hill Book Co Inc. 22 **(1960)**.

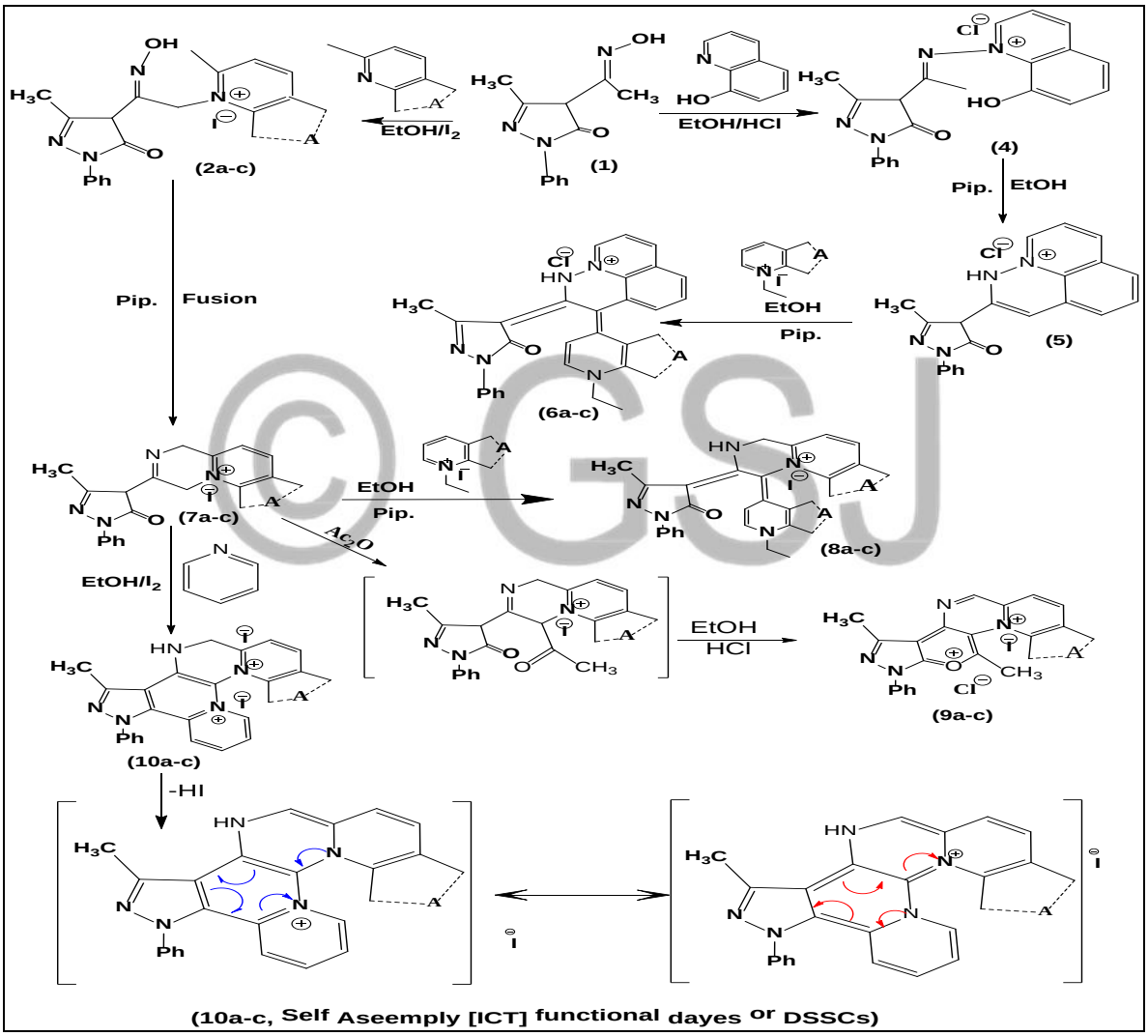
[37]-M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson et al., Gaussian 09, Revision A.02; Gaussian Inc.: Wallingford CT, **(2009)**.

[38]-A. I. Koraiem, A. El-Shafei, I. M. Abdellah, F. F. Abdel-Latif, R. M. Abd El-Al, Journal of Molecular Structure, 1173, 406-416, **(2018)**.

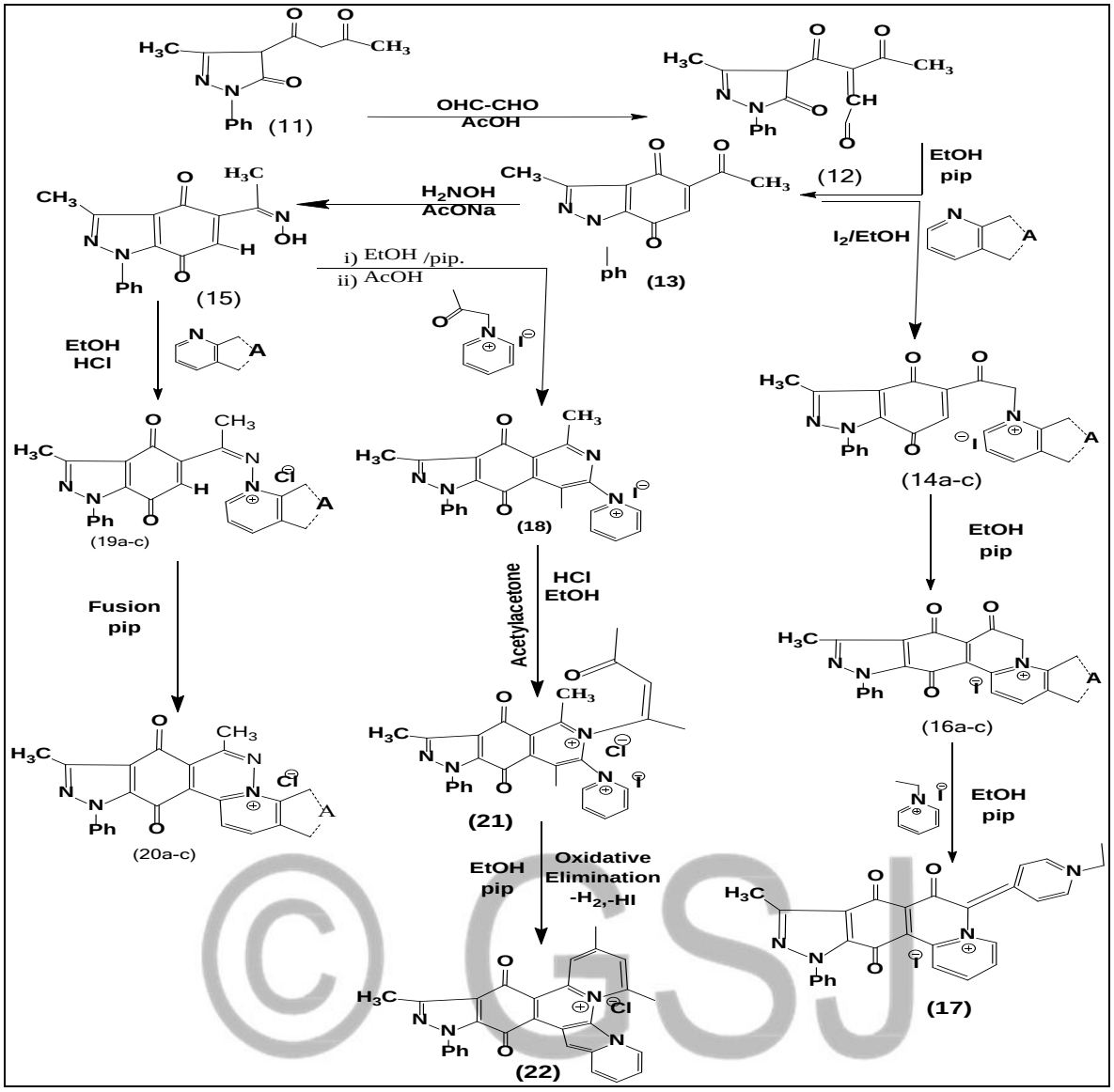
[39]-Reddick, J. A. and Banger, W. B**.;** Techniques of Chemistry Organic Solvents (A Weiss Berger, Ed), 3 rd., Ed N. Y. Wiley Vol. 11, **(1970).**

[40]-S.M. Sayed, Ph.D Thesis, Chemistry Department, Faculty of Science, Aswan University, **(1998).**

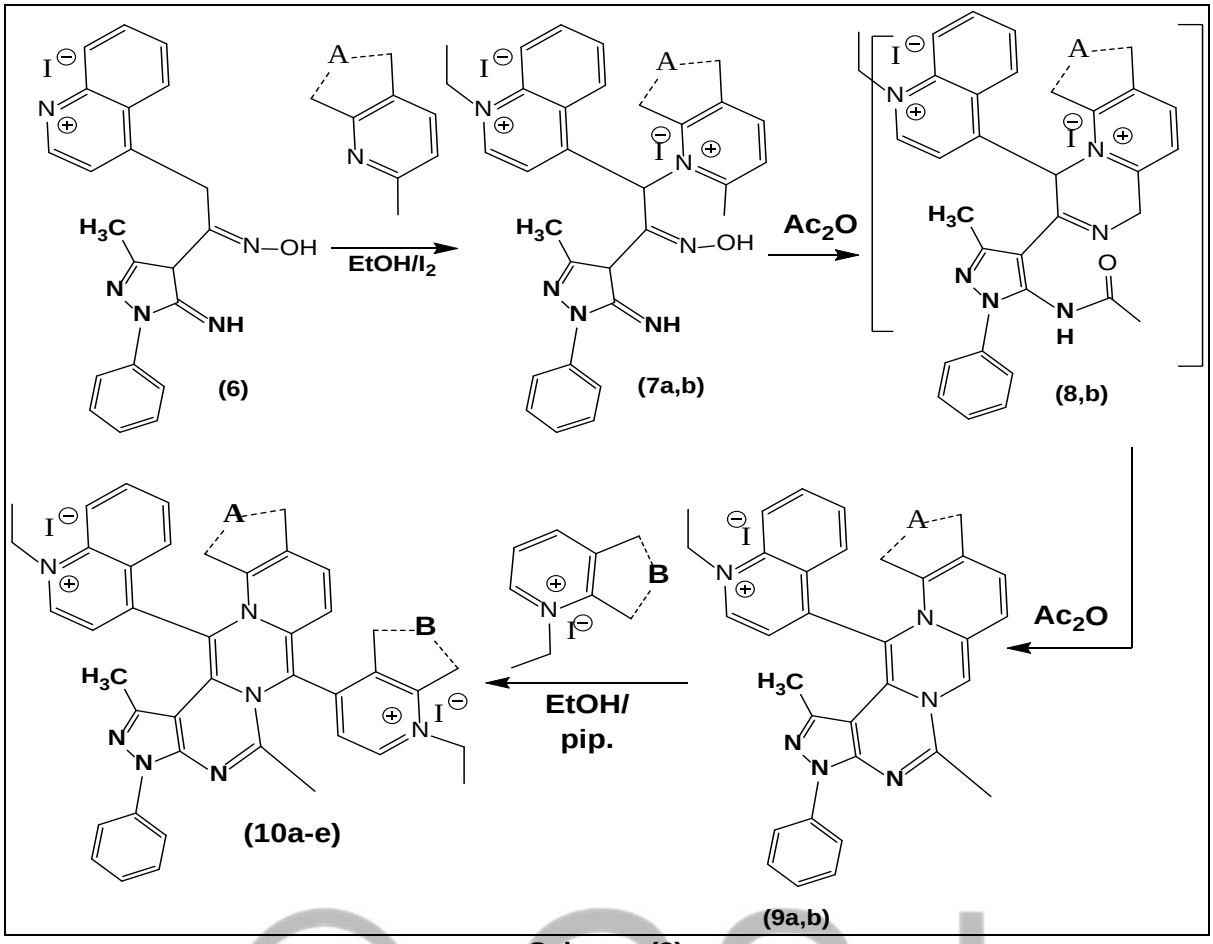
[41]-N.Y. Mahmoud, Ph.D Thesis, Chemistry Department, Facluty of Science, Aswan University, **(2006).**



Scheme (1A)


(11)
OHC-CHO
AcOH
(12)
EtOH
pip
I2/EtOH
H2NOH
AcONa
(13)
(15)
i) EtOH /pip.
ii) AcOH
EtOH
HCl
(14a-c)
(19a-c)
(18)
Acetylacetone
HCl
EtOH
Fusion
pip
(16a-c)
(20a-c)
(21)
EtOH
pip
Oxidative
Elimination
-H2,-HI
(17)
(22)

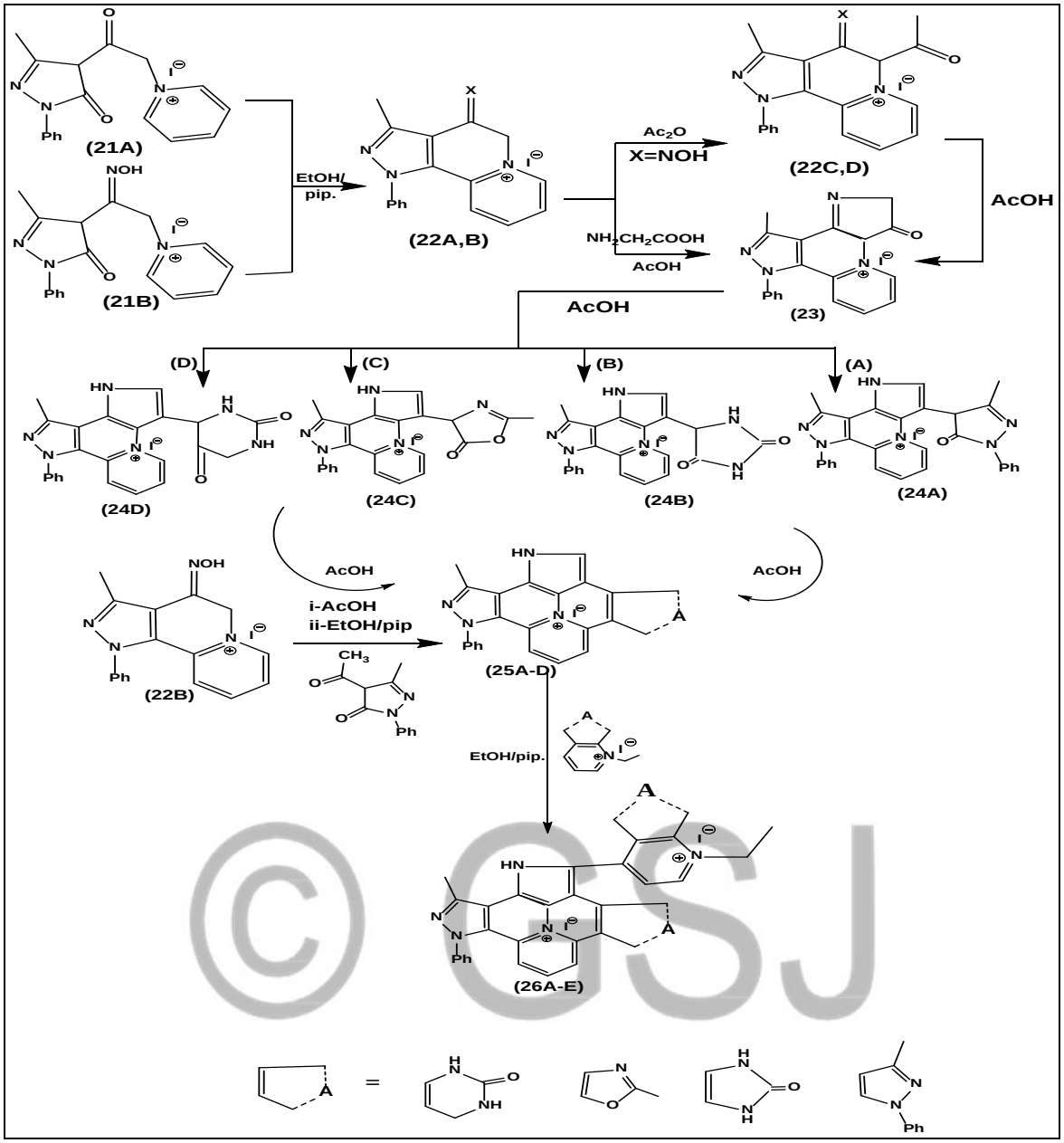
Scheme (1B)



Scheme (2)

Scheme (2) Substituted

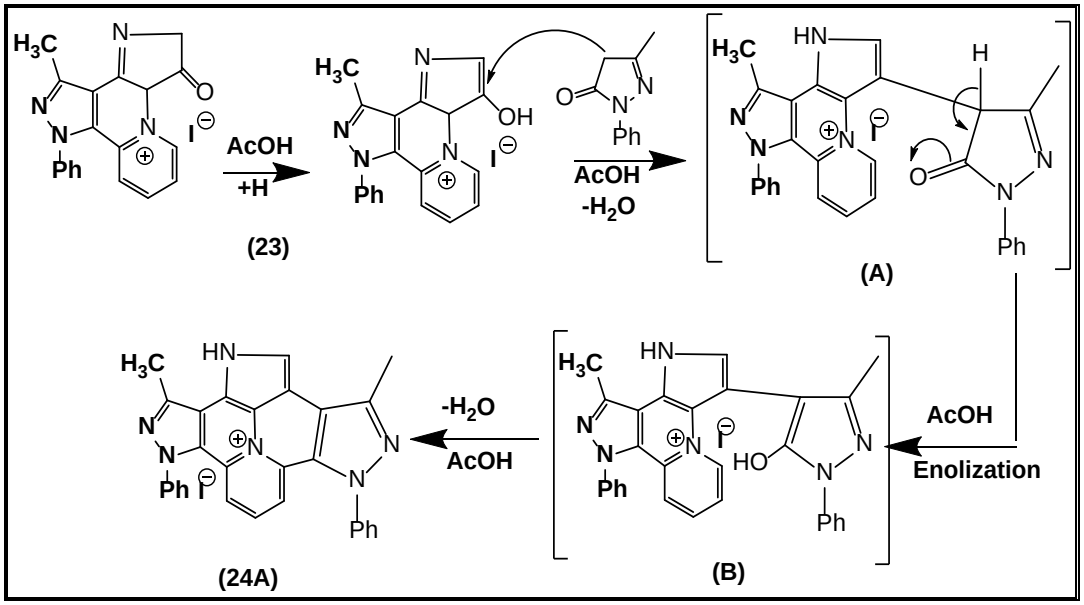
(9a,b):A=H-1-yl **(a),** A=C_4H_4-1-yl, **(10a-e):** A(B)= H-4-yl(H-4-ium) (a); A(B)= H-4-yl salt(C_4H_4-4-ium) (b); A(B)= H-4-yl(C_4H_4-1-ium) (c); A(B)= C_4H_4-4-yl, (H-4-ium) (d); A(B)= C_4H_4-4-yl (C_4H_4-4-ium) (e).



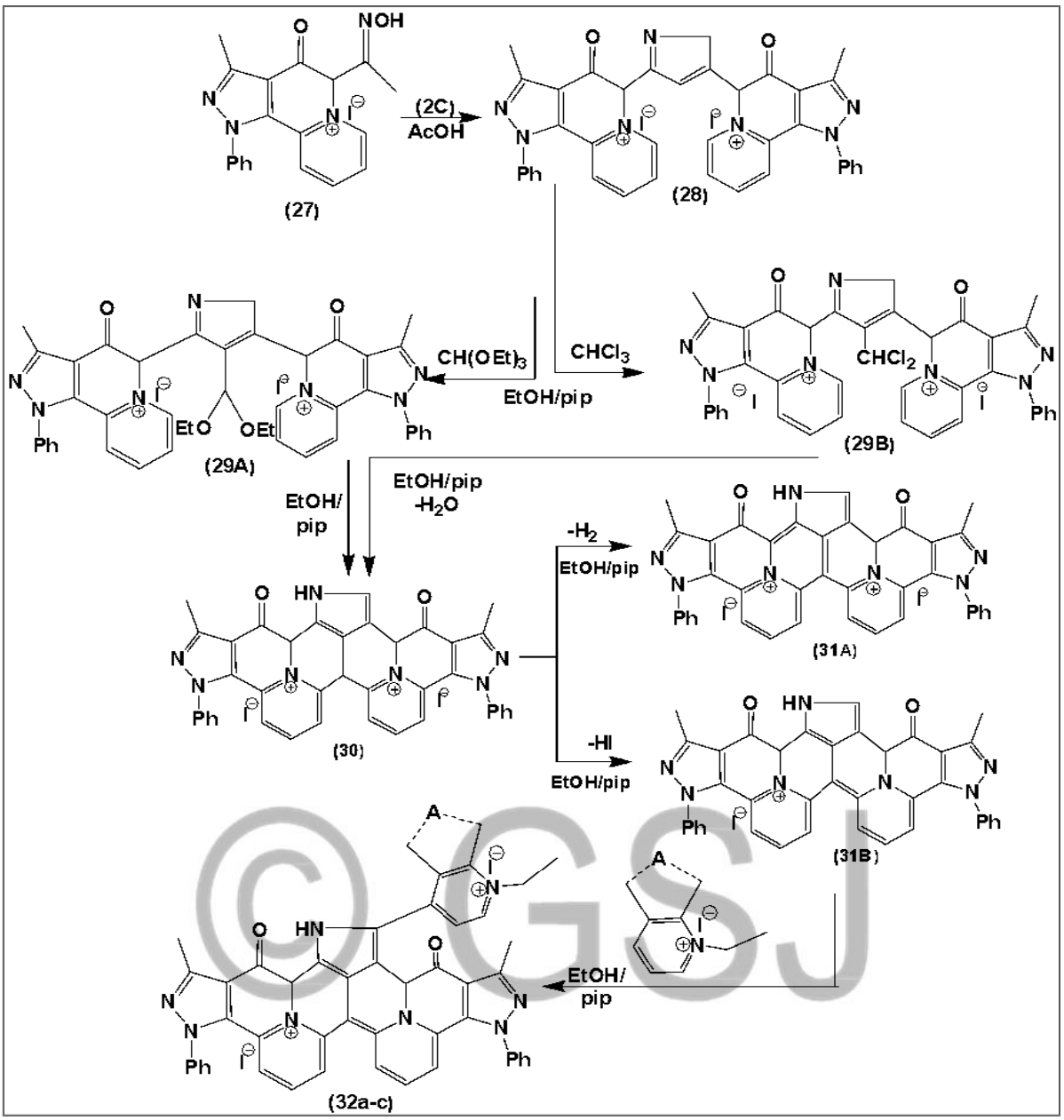
Scheme (3A)

Scheme (3A) Substituents:

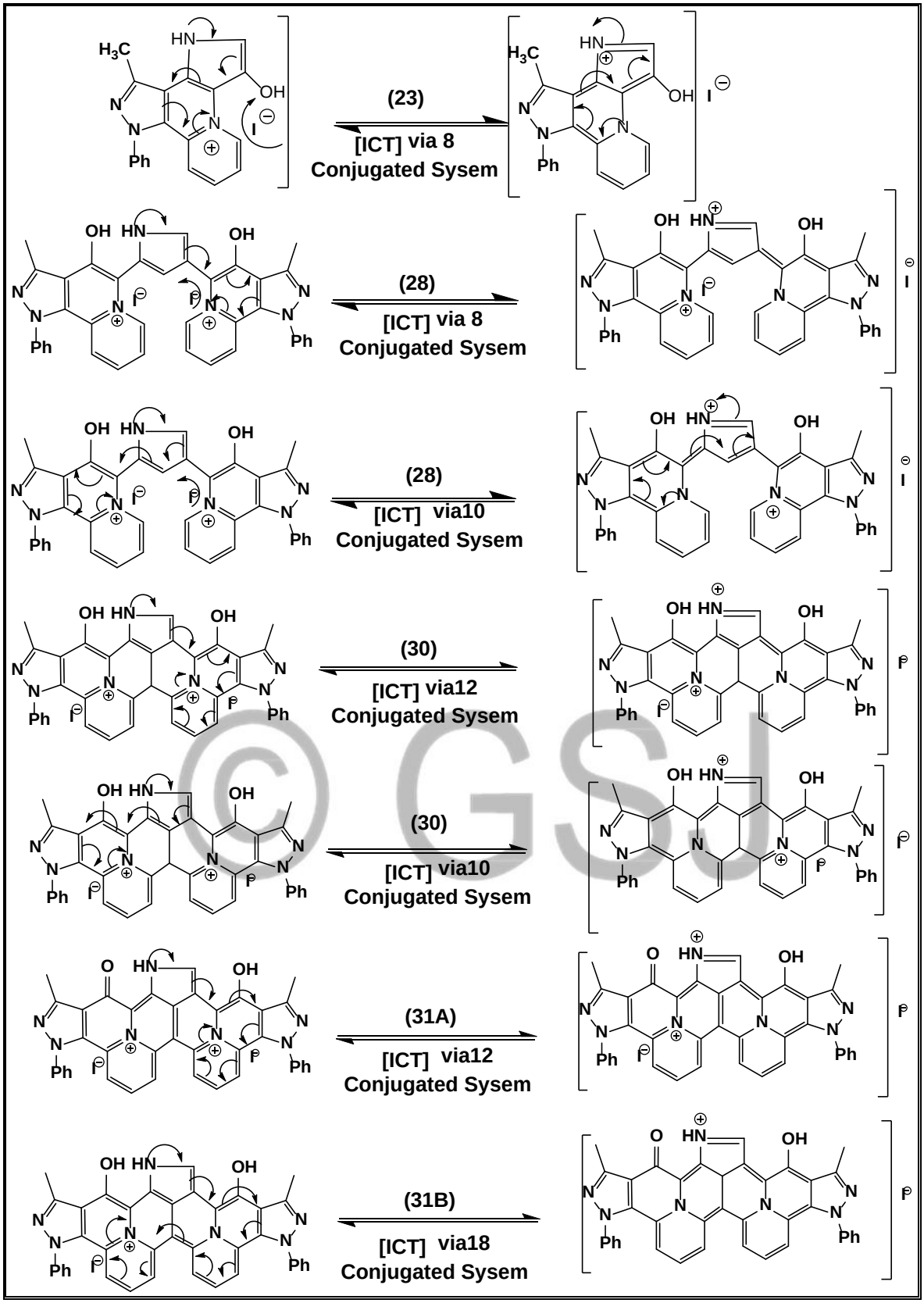
(22A-E) X=O(a),X=NOH(b),X=O(c),X=NOH(d), (A): 3-methyl-1-phenyl-2,4-di[H]-3H-pyrazol-5-one,(B), Hydantoin (imidazol-2,5-dione), 2-methyl-oxazol-5(4H)-one (C) & Barbituric acid (tetra[H] pyrimidin-2,5-dione),(D), (25A-D): A(B),continue 3-methyl-1-phenyl-2,4-di[H]-3H-pyrazole,(a), A(B), continue (imidazol-2-one),(b), A(B),continue 2-methyl-oxazole (c) & A(B),continue tetra[H] pyrimidin-2,5-dione),(d).



Equation (1)



Scheme (3B)



Equation (2): Mesomeric Structures for Stability & Pathways of [ICT], DSSCs, **(23, 28, 30 &31A, B)**

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Table (1A): Summary of Feature for Normalized Absorption Spectra **of Scheme (1A),** comp. No. **(6a-c, 8a-c & 10a-c)** & **Scheme (1B)**, (**16a-c, 17, 19a-c & 20a-c)** in (1x 10^{-4} M) Ethanol.

No.	λ_{max} (ε_{max})	Absorbed color	Transmitted color
6a	514 (0.5051)	Green	Purple
6b	504 (0.2460)	Green	Purple
6c	526 (0.4812)	Green	Purple
8a	574 (0.1592	Yellow-green	Violet
8b	498 (0.1974)	Blue- green	Red
9b	360 (1.107)	Violet	Yellow-Green
10a	510 (0.2120)	Green	Purple
10b	522 (0.2120	Green	Purple
10c	506 (0.251)	Green	Purple
16a	504 (0.661)	Green	Purple
16b	400 (0.7091)	Violet	Yellow- Green
16c	522 (0.491) 412 (0.7091	Green Violet	Purple Yellow- Green
19b	306 (1.586)	Violet	Yellow-Green
20a	492 (0.2350)	Blue- green	Red

Table (1B): Summary of Feature for Normalized Absorption Spectra of **Scheme (2), (8a-b & 9a-e), Scheme (3A),** comp. No. **(26A-D) & Scheme (3B)**, comp. No. **(26a-d & 32a-c) in** (1x 10^{-4} M) Ethanol.

No.	λ_{max} (ε_{max})	Absorbed color	Transmitted color
20b	580 (0.255) 500 (0.289)	Yellow-green Green	Violet Purple
20c	400 (0.798)	Violet	Yellow- green
8a	460 (0.698)	Blue	Yellow
8b	498 (1.010)	Blue- green	Red
9a	520 (2.443)	Green	Purple
9b	480 (670)	Blue	Yellow
9c	500 (1.780)	Blue- green	Red
9d	475 (0.612)	Blue	Yellow
9e	478 (1.593)	Blue	Yellow
26A	390 (0.755)	Violet	Yellow-Green
26B	504 (0.356)	Green	Purple
26D	480 (670)	Green-Blue	Orange
32a	402 (0.322)	Violet	Yellow- green
32c	500 (0.440)	Blue- green	Red

Table (2A): Values of Maximum Absorption (nm) and Extinction Coefficients (mol^{-1} cm^{-1}) of **Scheme (1A),** comp. No. **(6a-c, 8a-c, 9a-c & 10a-c)** in pure organic solvents.

Dye	Polar Organic solvent														Nonpolar Organic solvent	
	Water		DMF		$CHCl_3$		DMSO		Acetone		MeOH		EtOH		C_6H_6	
	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)
6a	498 (0291)	Blue-green (Red)	502 (0.225)	Green (Purple)	400 (0.51)	Violet (Yellow-green)	510 (0.321)	Green (Purple)	396 (0.615)	Violet (Yellow-green)	500 (0.279)	Blue-green (Red)	528 (0.358)	Green (Purple)	404 (0.266)	Violet (Yellow-green)
6b	494 (0.30)	Blue-green (Red)	548 (0.274)	Green (Purple)	506 (0.209	Green (Purple)	514 (0.372)	Green (Purple)	508 (0.310)	Green (Purple)	496 (0.467)	Blue-green (Red)	504 (0.246)	Green (Purple)	516 (0.220)	Green (Purple)
6c	512 (0.47)	Green (Purple)	508 (0.142)	Green (Purple)	540 (0.209)	Green (Purple)	540 (0.425)	Green (Purple)	530 (0.395)	Green (Purple)	524 (0.423)	Green (Purple)	524 (0.486)	Green (Purple)	544 (0.254	Green (Purple)
8a	568 (0.17)	Yellow-green (Violet)	578 (0.216)	Yellow-green (Violet)	408 (0.599)	Violet (Yellow-green)	582 (0.280)	Yellow (Blue)	576 (0.416)	Yellow-green (Violet)	570 (0.287)	Yellow-green (Violet)	574 (0.159)	Yellow-green (Violet)	414 (0.286)	Violet (Yellow-green)
8b	496 (0.21)	Blue-green (Red)	512 (0.193)	Green (Purple)	408 (0.595)	Violet (Yellow-green)	510 (0.229)	Green (Purple)	508 (0.493)	Green (Purple)	500 (0.246)	Blue-green (Red)	500 (0.197	Blue-green (Red)	506 (0.204)	Green (Purple)
8c	400 (0.31)	Violet (Yellow-green)	442 (0.601)	Blue (Yellow)	412 (3.43)	Violet (Yellow-green)	370 (0.986)	Violet (Yellow-green)	-	-	360 (1.035)	Violet (Yellow-green)	366 (0.542)	Violet (Yellow-green)	408 (0.516)	Violet (Yellow-green)
9b	-	-	366 (1.529)	Violet (Yellow-green)	376 (2.709)	Violet (Yellow-green)	362 (0.603)	Violet (Yellow-green)	402 (3.175)	Violet (Yellow-green)	-	-	358 (1.110)	Violet (Yellow-green)	368 (2.101)	Violet (Yellow-green)
10a	318 (1.33)	Violet (Yellow-green)	440 (0.330)	Blue (Yellow)	400 (0.522)	Violet (Yellow-green)	440 (0.255)	Blue (Yellow)	510 (0.372	Green (Purple)	518 (0.242)	Green (Purple)	516 (0.210)	Green (Purple)	-	-
10b	522 (0.19)	Green (Purple)	538 (0.287)	Green (Purple)	408 (0.364)	Violet (Yellow-green)	540 (0.250)	Green (Purple)	522 (0.342)	Green (Purple)	520 (0.202)	Green (Purple)	530 (0.231)	Green (Purple)	-	-
10c	502 (0.31)	Green (Purple)	448 (0.367)	Blue (Yellow)	528 (0.183)	Green (Purple)	434 (0.408)	Blue (Yellow)	506 (0.254)	Green (Purple)	504 (0.244)	Green (Purple)	506 (0.251)	Green (Purple)	-	-

Table (2B): Values of Maximum Absorption (nm) and Extinction Coefficients (mol^{-1} cm^{-1}) of **Scheme (2),** comp. No. **(8b & 9e)** in pure organic solvents.

Dye	Polar Organic solvent										Nonpolar Organic solvent	
	Water		DMF		$CHCl_3$		Acetone		EtOH		C_6H_6	
	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)
8b	474 (0.339)	Blue (Yellow)	501 (0.869)	Green (Purple)	470 (0.977)	Blue (Yellow)	492 (0.771)	Blue-green (Red)	498 (0.918)	Green (Purple)	470 (0.984)	Violet (Yellow-green)
9e	469 (0.534)	Blue (Yellow)	500 (0.568)	Green (Purple)	472 (0.947)	Blue (Yellow)	478 (0.802)	Blue (Yellow)	478 (0.925)	Green (Purple)	462 (0.642)	Green (Purple)

Table (2C): Values of Maximum Absorption (nm) and Extinction Coefficients (mol^{-1} cm^{-1}) of **Scheme (1B),** comp. No. **(16a-c, 19a-c, & 120a-c)** in pure organic solvents.

Dye	Polar Organic solvent														Nonpolar Organic solvent	
	Water		DMF		$CHCl_3$		DMSO		Acetone		MeOH		EtOH		C_6H_6	
	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)
16a	496 (0.264)	Blue-green (Red)	298 (1.945)	Violet (Yellow-green)	400 (1.260)	Violet (Yellow-green)	518 (0.321)	Green (Purple)	392 (0.722)	Violet (Yellow-green)	506 (0.410)	Green (Purple)	510 (1.276)	Green (Purple)	514 (0.380)	Green (Purple)
16b	320 (0.595)	Violet (Yellow-green)	548 (0.274)	Green (Purple)	402 (1.291)	Violet (Yellow-green)	442 (0.420)	Blue (yellow)	402 (0.602)	Violet (Yellow-green)	410 (0.494)	Violet (Yellow-green)	406 (0.684)	Violet (Yellow-green)	404 (0.220)	Violet (Yellow-green)
16c	520 (0.158)	Green (Purple)	508 (0.142)	Green (Purple)	414 (0.874)	Violet (Yellow-green)	530 (0.254)	Green (Purple)	414 (0.529)	Violet (Yellow-green)	502 (0.278)	Green (Purple)	516 (0.502)	Green (Purple)	540 (0.230)	Green (Purple)
19a	-	-	350 (2.020)	Violet (Yellow-green)	360 (1.501)	Violet (Yellow-green)	366 (1.312)		-	-	358 (0.892)	Violet (Yellow-green)	362 (0.810)	Violet (Yellow-green)	358 (0.714)	Violet (Yellow-green)
19b	308 (1.318)	Blue-green (Red)	-	-	-	-	-	-	-	-	304 (0.246)	Violet (Yellow-green)	308 (1.572)	Violet (Yellow-green)	602 (0.160)	Red (Blue-green)
19c	506 (0.289)	Green (Purple)	452 (0.286)	Blue (Yellow)	402 (3.43)	Violet (Yellow-green)	-	-	512 (0.379)	Green (Purple)	246 (2.251)	Violet (Yellow-green)	252 (1.302)	Violet (Yellow-green)	-	-
20a	498 (0.285)	Blue-green (Red)	494 (0.362)	Blue-green (Red)	-	-	496 (0.230)	Blue-green (Red)	496 (0.351)	Blue-green (Red)	500 (0.231)	Blue-green (Red)	494 (0.234)	Blue-green (Red)	406 (0.583)	Violet (Yellow-green)

Dye	Polar Organic solvent														Nonpolar Organic solvent	
	Water		DMF		$CHCl_3$		DMSO		Acetone		MeOH		EtOH		C_6H_6	
	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)
20b	498 (0.264)	Blue-green (Red)	576 (0.317)	Yellow(Green-Violet)	410 (2.301)	Violet (Yellow-green)	580 (0.286)	Yellow (Blue)	576 (0.420)	Yellow(Green-Violet)	578 (0.245)	Yellow (Blue)	578 (0.257)	Yellow-green (Violet)	510 (0.167)	Green (Purple)
20c	312 (0.939)	Violet (Yellow-green)	446 (0.328)	Blue (Yellow)	488 (0.246)	Green-blue (Orange)	450 (0.245)	Blue (Yellow)	402 (0.960)	Violet (Yellow-green)	408 (0.365)	Violet (Yellow-green)	400 (0.353)	Violet (Yellow-green)	408 (0.764)	Violet (Yellow-green)

Table (2D): Values of Maximum Absorption (nm) and Extinction Coefficients (mol^{-1} cm^{-1}) of **Scheme (3A),** comp. No. **(26A-D) & Scheme (3B),** comp. No. **(32a-c)** in pure organic solvents.

Dye	Polar Organic solvent														Nonpolar Organic solvent	
	Water		DMF		$CHCl_3$		DMSO		Acetone		MeOH		EtOH		C_6H_6	
	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)	λ_{max} (ε_{max})	Color Abs. (Trans.)
26A	378 (0.598)	Violet (Yellow-green)	378 (1.402)	Violet (Yellow-green))	398 (0.732)	Violet (Yellow-green)	384 (1.111)	Violet (Yellow-green)	256 (3.175)	Violet (Yellow-green)	378 (0.441)	Violet (Yellow-green)	390 (0.755)	Violet (Yellow-green)	398 (0.576)	Violet (Yellow-green)
26B	498 (0.235)	Blue-green (Red)	514 (0.617)	Green (Purple)	406 (0.947)	Green (Purple)	516 (0.377)	Green (Purple)	314 (1.435)	Violet (Yellow-green)	500 (0.349)	Green (Purple)	502 (0.357)	Green (Purple)	514 (0.211)	Green (Purple)
26C	316 (1.078)	Violet (Yellow-green)	-	-	-	-	-	-	312 (0.933)	Violet (Yellow-green)	502 (0.204)	Green (Purple)	498 (0.235)	Blue-green (Red)	-	-
26D	408 (0.511)	Violet (Yellow-green)	442 (0.330)	Blue (Yellow)	498 (0.235)	Blue-green (Red)	406 (0.372)	Violet (Yellow-green)	498 (0.235)	Blue-green (Red)	496 (0.399)	Blue-green (Red)	402 (0.625)	Violet (Yellow-green)	498 (0.235)	Blue-green (Red)
32a	-	-	440 (0.517)	Blue (Yellow)	440 (0.374)	Blue (Yellow)	440 (0.398)	Blue (Yellow)	-	-	404 (0.319)	Violet (Yellow-green)	398 (0.325)	Green (Purple)	410 (0.517)	Violet (Yellow-green)
32c	498 (0.351)	Blue-green (Red)	440 (1.023)	Blue (Yellow)	408 (1.107)	Blue-green (Red)	512 (0.647)	Green (Purple)	-	-	504 (0.385)	Green (Purple)	500 (0.440)	Green (Purple)	410 (1.401)	Violet (Yellow-green)

Table (3A): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of **Scheme (1A)**, comp. No. **(6a-c, 8a-c, 9a-c & 10a-c), Scheme (2A)**, comp. No. **(16a-c, 19a-c** and **20a-c), Scheme (3A),** comp. No. **(26A-D) & Scheme (3B)**, comp. No. **(32a-c)** in aqueous universal buffer solution.

Comp. No.	Universal buffer															
	1.92		2.20		4.19		5.96		6.97		8.04		10.25		12	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
6a	398	0.390	498	0.123	388 498	0.598 0.351	500	209	498	172	496	0.248	490	0.353	496	0.218
6b	502	0.176	504	0.140	498	0.227	498	0.396	498	0.236	496	0.252	494	0.302	394	0.511
6c	386 526	0.943 0.214	380 530	0.344 0.118	348 526	0.811 0.258	436 530	0.745 0.323	438 528	1.089 0.403	438 530	0.634 0.307	438 528	0.882 0.415	440 532	0.351 0.179
8a	402 494	0.247 0.150	402 498 574	0.245 0.162 0.122	500 576	0.213 0.163	572	0.168	566	0.340	566	0.147	560	0.192	498 554	0.270 0.211
8b	498	0.214	498	1.902	498	0.250	500	0.511	496	0.197	496	0.143	498	0.171	500	0.163
8c	366	1.601	362	0.813	364	1508	436	0.666	434	0.729	432	0.355	430	0.260	440	0.384
9b	360	1.516	360	1.640	358	1804	360	2.157	356	1.380	536	0.143	---	---	---	----
10a	316 396 514	1.189 0.268 0.144	316 402 512	1.924 0.397 0.230	274	2.275	314 430 532	1.644 0.362 0.229	286	2.114	314 438	1.499 0.291	252	1.471	360	0.895
10b	402	0.443	396	0.263	276	2.738	432	0.233	250	1.683	432	0.194	256	2.352	254	1.954
10c	400	0.301	502	0.119	276	1338	-----	----	442	0.229	434	0.427	250	2.536	436	0.388
16a	396	2.022	396	0.959	376 506	1.016 0.538	504	0.513	502	0.442	503	0.389	500	0.365	350 430 506	0.784 0.529 0.368
16b	320 398	2.111 1.238	322 398	1236 0.759	390	0.744	424	1.566	432	0.459	430	0.869	436	0.433	350 436	0.970 0.640
16c	416	1.187	414	0.734	514	0.325	---	---	520	0.220	416 516	0.701 0.501	416 516	0.269 0.187	526	0.285
19a	360	1.020	358	1.190	356	0.909	356	1.308	358	2.443	472	0.255	262	1.801	486	0.235
19b	248 308	3.263 1.884	252 308	2.874 1.674	248 286	3.311 2.937	308	1.803	252	3.374	--	--	256	2.671	256	0.254
19c	404 510	0.278 0.172	400 508	0.218 0.152	510	0.291	434 514	0.290 0.246	--	---	434 510	0.375 0.323	250	1.572	256 432	0.135 247
20a	--	---	250	1.947	--	--	252 488	2.223 0.131	482	0.452	488	0.184	254 488	2.402 0.199	256 496	2.636 0.205
20b	248 402 502	2.422 0.210 0.157	398 500 584	0.253 0194 0.134	402 500 578	0.372 0.281 0.241	248 400 580	1.950 0.187 0.145	402 498 574	0.421 0.345 0.309	502 570	0.195 0.185	256 500	1.717 0.191	254 498	1.610 0.191
20c	314 398	1.202 0.489	230 398	2.131 0.272	276	2.985	312 434	1.085 0.397	256 432	4.000 0.564	250 434	2.317 0.294	250 436	1.535 0.247	250 438	1.952 0.311
26A	390	1.449	390	0.65	-	-	396	3039	-	-	364	1.125	-	-	-	-
26B	404	0.524	242 400	2.87 0.34	252 502	2.879 0.281	256 298 504	2.672 1.369 0.308	246 504	2.783 0.194	502	0.474	498	0.384	352 504	1.000 0.504
26C	-	-	318	1.62	-	-	258 294	3.436 2.498	-	-	262	4.000	246	3.913	346	1.060
26D	252 432 506	3.436 0.375 0.328	248 400 508	1.55 0.21 0.15	256 498	2.543 0.196	252 496	1.945 0.143	248 396 500	3.101 0.249 0.190	252 506	3.436 0.328	272	1.790	272 444	2466 0.395
32a	274 400	1.002 0.346	502	0.245	---	--	262 296	0.827 0.635	434	0.145	434	0.260	438	0.18	343	0.221
32b	398	0.349	--	---	384	0.302	262 296	2.256 1.787	250 434	1.081 0.149	238	0.152	--	---	--	---
32c	270 404	2.261 0.833	400	0.539	508	0.279	--	---	504	0.260	498	0.751	494	257	296	0.411

Table (3B): The variation of absorbance in λ_{max} characteristic for **Scheme (1A),** comp. No. (**6a- c, 8a-c, 9a-c &10a-c) & Scheme (1B),** comp. No. (1**6a- c, 19a-c & 20a-c)** in different buffer solution.

Comp. No.	Absorbance											
λ_{max} pH	**6a** λ_{428}	**6b** λ_{500}	**6c** λ_{530}	**8a** λ_{498}	**8b** λ_{500}	**8c** λ_{440}	**9a** λ_{354}	**9b** λ_{336}	**9c** λ_{604}	**10a** λ_{514}	**10b** λ_{432}	**10c** λ_{442}
1.92	0.272	0.179	0.209	---	0.211	0.506	1.827	1.054	0.075	0.144	0.334	0.21
2.20	0.149	0.143	0.118	0.162	0.19	0.303	0.662	1.143	0.072	0.228	0.203	0.138
4.19	0.429	0.225	0.253	0.214	0.249	0.635	1.595	1.575	0.232	0.236	0.374	0.104
5.96	0.211	0.393	0.323	0.174	0.511	0.679	1.034	1.648	0.13	0.25	0.233	0.387
6.97	0.177	0.234	0.397	0.340	0.195	0.734	0.297	1.169	0.129	0.259	0.125	0.229
8.04	0.251	0.248	0.307	0.150	0.142	0.356	0.715	1.346	0.119	0.211	0.194	0.417
10.25	0.360	0.294	0.410	0.216	0.17	0.26	0.468	0.996	0.12	0.347	0.357	0.262
12	0.288	0.340	0.181	0.270	0.163	0.393	1.156	1.335	0.139	0.306	0.242	0.382
pKa	4.1 10.2	6.0 -	7.0 10.2	7.0 -	6.0 -	7.0 -	4.2 8.0	6.0 8.1	4.2 -	7.0 10.1	4.2 10.2	6.0 8.0

Comp. No.	Absorbance								
λ_{max} pH	**16a** λ_{500}	**16b** λ_{436}	**16c** λ_{520}	**19a** λ_{360}	**19b** λ_{308}	**19c** λ_{510}	**20a** λ_{488}	**20b** λ_{500}	**20c** λ_{432}
1.92	0.712	1.753	0.505	1.02	1.884	0.172	0.176	0.159	0.323
2.20	0.392	1.05	0.338	1.181	1.674	0.152	0.11	0.194	0.19
4.19	0.54	0.858	0.319	0.894	2.467	0.291	0.223	0.281	0.602
5.96	0.52	2.237	0.939	1.265	1.803	0.249	0.131	0.155	0.398
6.97	0.445	0.746	0.22	2.422	1.534	0.134	0.442	0.346	0.564
8.04	0.391	1.339	0.493	0.698	1.973	0.323	0.184	0.195	0.294
10.25	0.365	0.686	0.184	0.275	1.041	0.24	0.199	0.191	0.249
12	0.378	0.969	0.292	0.492	0.859	0.209	0.211	0.191	0.314
pKa	4.0 -	6.0 8.0	6.0 8.0	2.2 7	4.2 8	4.2 8.0	4.2 7.0	4.1 7.0	4.1 7.0

Table (3C): The variation of absorbance in λ_{max} characteristic for **Scheme (3A)**, comp. No. **(26A-D)** in different buffer solution.

Comp. No.	Absorbance			
λ_{max} pH	**26A** λ_{390}	**26B** λ_{500}	**26C** λ_{346}	**26D** λ_{508}
1.92	1.449	0.286	0.931	0.326
2.20	0.65	0.211	0.503	0.152
4.19	0.26	0.282	0.631	0.187
5.96	3.19	0.311	0.754	0.135
6.97	1.943	0.196	0.41	0.179
8.04	1.008	0.475	0.661	0.326
10.25	1.084	0.384	0.599	0.109
12	0.654	0.351	0.907	0.192
pKa	6.0 10.0	6.0 8.0	6.0 8.0	4.0 8.0

Table (3D): The variation of absorbance in λ_{max} characteristic for **Scheme (3B),** comp. No. (**32a-c)** in different buffer solution.

Comp. No.	Absorbance		
λ_{max} pH	**32a** λ_{438}	**32b** λ_{398}	**32c** λ_{508}
1.92	0.266	0.349	0.446
2.20	0.271	0.401	0.313
4.19	0.205	0.282	0.279
5.96	0.198	0.875	0.815
6.97	0.143	0.158	0.256
8.04	0.258	0.203	0.728
10.25	0.189	0.087	0.245
12	0.22	0.174	0.391
pKa	2.3 8.1	2.1 6.0 8.0	6.0 8.0

Table (4): HOMO-LUMO energy levels for the suggested molecules **Scheme (3A&B), comp**. No. **25A, 26E & 32b**

Code	E_{HOMO} (au)	E_{HOMO} (ev)	E_{LUMO} (au)	E_{LUMO} (ev)	E_{0-0}
25A	-0.09927	-4.588	-0.16557	-2.701	1.804
26E	-0.16846	-4.5840	-0.12035	-3.2748	1.3092
32b	-0.1683	-4.5799	-0.1440	-3.9208	0.6591

Table (5): **Characterization Data of Scheme (1A),** comp. No. **(6a-c, 8a-c, 9a-c & 10a-c).**

Comp. No.	Nature of Products				% Calcd.(Found)			95% EtOH Absorption ($1x10^{-3}$g/mol.)	
	M.P. °C	Yield %	Color	Mol. Formula (Mol.wt)	C	H	N	λ_{max} (nm)	ε_{max} ($cm^{-1}mol^{-1}$)
6a	181	84	Red	$C_{28}H_{24}ClN_5O$ (481)	69.78	5.02	14.53	418 514	743 505
6b	196	87	Dark red	$C_{32}H_{26}ClN_5O$ (531)	72.24	4.93	13.16	504 394	246 366
6c	201	79	Reddish pink	$C_{32}H_{26}ClN_5O$ (531)	72.24	4.93	13.16	526 414	481 753
8a	172	67	Reddish Brown	$C_{29}H_{26}IN_5O$ (587)	59.29	4.46	11.92	574 496 396	1590 1800 247
8b	190	77	Pale red	$C_{29}H_{26}ClN_5O$ (587)	59.29	4.46	11.92	498 392	197 234
8c	201	81	Dark brown	$C_{29}H_{26}ClN_5O$ (587)	59.29	4.46	11.92	-	-
9a	159	66	Orange	$C_{20}H_{16}ClIN_4O$ (490)	48.95	3.29	11.42	358	738
9b	134	72	Violet	$C_{24}H_{18}ClIN_4O$ (540)	53.30	3.36	10.36	360	1107
9c	146	86	Pale brown	$C_{24}H_{18}ClI\ N_4O$ (540)	53.30	3.36	10.36	358	460
10a	225	59	Deep Orange	$C_{23}H_{19}I_2N_5$ (619)	44.61	3.09	11.31	510 314	212 1055
10b	215	70	brown	$C_{27}H_{21}I_2N_5$ (669)	48.45	3.16	10.46	522 390	235 339
10c	225	69	Brownish orange	$C_{27}H_{21}I_2N_5$ (669)	48.45	3.16	10.46	506 394	251 382

Table (6): **Characterization Data of Scheme (1A),** comp. No. **(2a, 2b, 4, 5 & 7a-c), & Scheme (1B)** comp. No. **(11, 12, 13, 14a-c, 15, 17).**

Comp. No.	Nature of Products				% Calcd (Found)		
	M.P. °C	Yield %	Colour	Mol. Formula (Mol.wt)	C	H	N
2a	132	67	Brown	$C_{18}H_{19}IN_4O_2$ (450)	48.01	4.25	12.44
2b	128	79	Dark Brown	$C_{22}H_{21}IN_4O_2$ (500)	52.8	4.23	11.2
4	134	82	Yellowish Brown	$C_{21}H_{19}ClN_4O_2$ (394)	63.88	4.85	14.19
5	129	73	Red	$C_{21}H_{17}ClN_4O$ (376)	66.93	4.55	14.87
7a	136	80	Reddish Brown	$C_{18}H_{17}IN_4O$ (432)	50.02	3.96	12.96
7b	132	84	Brownish Red	$C_{22}H_{19}IN_4O$ (482)	54.78	3.97	11.62
7c	131	86	Yellowish Brown	$C_{22}H_{19}IN_4O$ (482)	54.78	3.97	11.62
12	125	81	Reddish Brown	$C_{16}H_{14}N_2O_4$ (298)	64.42	4.73	9.39
13	166	77	Violet	$C_{16}H_{12}N_2O_3$ (280)	60.56	4.32	9.99
14a	139	70	Pale Brown	$C_{21}H_{16}ClN_3O_3$ (485)	51.98	3.32	8.66
14b	141	75	Brownish Orange	$C_{25}H_{18}IN_3O_3$ (535)	56.09	3.39	7.85
14c	240	80	Violet	$C_{25}H_{18}IN_3O_3$ (535)	56.09	3.39	7.85
15	202	88	Brownish Orange	$C_{22}H_{19}IN_4O$ (295)	65.08	4.44	14.23
18	187	83	Reddish Orange	$C_{24}H_{19}IN_4O_2$ (522)	55.19	3.67	10.73

Table (7): Characterization Data of **Scheme (3B),** comp. No **(27, 28, 29A-B, 30, 12 & 31A, B).**

Comp. No.	Nature of Products				% Calcd. (Found)		
	M.p. °C	Yield %	Color	Mol. Formula (Mol. Wt.)	C	H	N
27	139	67	Greenish Brown	$C_{19}H_{17}IN_4O_2$ (460)	49.58	3.72	12.17
28	146	74	Deep Dark Red	$C_{38}H_{29}I_2N_7O_2$ (869)	52.49	3.36	11.28
29A	187	65	Reddish Brown	$C_{43}H_{39}I_2N_7O_4$ (971)	53.15	4.05	10.09
29B	179	71	Deep dark brown	$C_{39}H_{39}Cl_2I_2N_7O_2$ (950)	49.18	3.07	10.29
30	201	81	Brown	$C_{39}H_{27}I_2N_7O_2$ (879)	53.26	3.09	11.15
31A	198	77	Greenish brown	$C_{39}H_{27}I_2N_7O_2$ (877)	53.38	2.87	11.17
31B	189	75	Reddish Yellow	$C_{39}H_{26}IN_7O_2$ (751)	62.33	3.49	13.05

Table (8): Characterization Data of **Scheme (1B),** comp. No. **(16a-c, 19a-c & 20a - c).**

Comp. No.	Nature of Products				% Calcd (formed)			95% EtOH Absorption ($1x10^{-4}$g/mol.)	
	M.P. °C	Yield %	Color	Mol. Formula (Mol.wt)	C	H	N	λ_{max} (nm)	ε_{max} ($cm^{-1}mol^{-1}$)
16a	169	64	Brown	$C_{21}H_{14}N_3O_3$ (483)	52.19 (52.20)	2.92 (2.94)	8.70 (8.72)	504 390	660 1.276
16b	164	77	Dark Brown	$C_{25}H_{16}N_3O_3$ (533)	56.30 (56.32)	3.02 (3.04)	7.88 (7.89)	400	709
16c	159	79	Pale Orange	$C_{25}H_{16}N_3O_3$ (533)	56.30 (56.32)	3.02 (3.03)	7.88 (7.89)	522 412	491 758
19a	176	81	Reddish Orange	$C_{21}H_{17}ClN_4O_2$ (392)	64.21 (64.22)	4.36 (4.37)	14.26 (14.27)	356	829
19b	181	89	Orange	$C_{25}H_{19}ClN_4O_2$ (442)	67.80 (67.81)	4.32 (4.34)	12.65 (12.67)	306	1586
19c	186	79	Yellow	$C_{25}H_{19}ClN_4O_2$ (442)	67.80 (67.79)	4.32 (4.33)	12.65 (12.66)	250	1323
20a	164	67	Red	$C_{25}H_{19}ClN_4O_2$ (391)	64.54 (64.56)	3.87 (3.88)	14.34 (14.36)	492	235
20b	159	82	Reddish Brown	$C_{25}H_{19}ClN_4O_2$ (440)	68.11 (68.13)	3.89 (3.92)	12.71 (12.73)	580 500 398	255 289 359
20c	166	75	Dark Brown	$C_{25}H_{19}ClN_4O_2$ (440)	68.11 (68.13)	3.89 (3.94)	12.71 (12.72)	400 312	353 798

Table (9): Characterization Data of **Scheme (3),** comp. No **(7a, b, 9a, b &10a-f**).

Comp. No.	Nature of Products				% Calcd (found)			Absorption spectra in EtOH ($1x10^{-4}$g/mol.)	
	M.P. °C	Yield %	Color	Mol. Formula (Mol.wt)	C	H	N	λ_{max} (nm)	ε_{max} ($cm^{-1}mol^{-1}$)
8a	127	61	Red	$C_{31}H_{27}IN_6$ (610.50)	60.99 (60.75)	4.46 (4.35)	13.77 (13.34)	460	698
8b	170	65	Red	$C_{35}H_{29}IN_6$ (660.56)	63.64 (63.45)	4.43 (4.25)	12.72 (12.52)	498	1010
9a	155	74	Red	$C_{38}H_{35}I_2N_7$ (843.56)	54.11 (54.05)	4.18 (4.34)	11.62 (11.74)	520	2443
9b	150	59	Red	$C_{42}H_{37}N_7I_2$ (639.81)	78.85 (78.12)	5.83 (5.90)	15.32 (15.42)	480	670
9c	130	59	Pale Brown	$C_{42}H_{37}N_7I_2$ (639.81)	78.85 (78.12)	5.83 (5.90)	15.32 (15.42)	500	1780
9d	185	68	Brown	$C_{42}H_{37}N_7I_2$ (639.81)	78.85 (78.12)	5.83 (5.90)	15.32 (15.42)	475	612
9e	185	75	Red	$C_{46}H_{39}N_7I_2$ (689.87)	80.09 (80.45)	5.70 (5.28)	14.21 (14.69)	478	1593

Table (10): Characterization Data of **Scheme (3A),** comp. No **(22A-D, 23, 24A-D & 25A-D),**

Comp No.	Nature of Products				% Calcd. (Found)		
	M.p. °C	Yield %	Color	Mol. Formula (Mol. Wt.)	C	H	N
22A	155	79	Brownish Orange	$C_{16}H_{12}IN_3O$ (389)	49.38 (49.40)	3.11 (3.13)	10.80 (10.82)
22B	148	69	Brownish Red	$C_{16}H_{13}IN_4O$ (404)	47.54 (47.55)	3.24 (3.25)	13.86 (13.87)
22C	134	78	violet	$C_{19}H_{16}IN_3O_2$ (445)	51.25 (51.26)	3.62 (3.63)	9.44 (9.45)
22D	153	77	Greenish Brown	$C_{19}H_{17}IN_4O_2$ (460)	49.58 (49.59)	3.72 (3.73)	12.17 (12.18)
23	195	83	Muddy Brown	$C_{21}H_{19}IN_3O$ (456)	55.28 (55.30)	4.20 (4.21)	9.21 (9.22)
24A	225	67	Brownish Red	$C_{29}H_{23}IN_6O$ (598)	58.20 (58.22)	3.87 (3.88)	14.04 (14.05)
24B	198	73	Red	$C_{22}H_{17}IN_6O_2$ (524)	50.40 (50.42)	3.27 (3.28)	16.03 (16.04)
24C	234	77	Brown	$C_{22}H_{19}IN_5O_2$ (524)	51.58 (51.59)	3.74 (3.75)	13.67 (13.68)
24D	238	75	Dark Brown	$C_{22}H_{19}IN_5O_2$ (524)	50.11 (50.12)	3.82 (3.83)	15.94 (15.96)
25A	225	82	Deep Dark brown	$C_{29}H_{21}IN_6$ (580)	60.01 (60.03)	3.65 (3.64)	14.48 (14.50)
25B	187	67	Dark red	$C_{22}H_{17}IN_6O$ (506)	52.19 (52.20)	2.99 (3.98)	16.60 (16.61)
25C	221	72	Brown	$C_{23}H_{16}IN_5O$ (504)	54.67 (54.68)	3.19 (3.20)	13.86 (13.87)
25D	225	77	Dark brown	$C_{23}H_{16}IN_5O$ (520)	53.09 (53.11)	3.29 (3.30)	16.15 (16.17)

Table (11): Characterization Data of **Scheme (3A&3B),** comp. No **(26A-D) & (32a-c).**

Comp. No.	Nature 0f Products				% Calcd. (Found)			95% EtOH Absorption ($1x10^{-4}$g/mol.)	
	M.p. °C	Yield %	Color	Mol. Formula (Mol. Wt.)	C	H	N	λ_{max} (nm)	ε_{max} (cm^2mol^{-1})
26A	198	70	Dark brown	$C_{36}H_{29}I_2N_7$ (813)	53.15 (53.16)	3.59 (3.60)	12.05 (12.06)	390	755
26B	201	67	Reddish orange	$C_{29}H_{23}I_2N_7O$ (739)	47.11 (47.12)	3.14 (3.15)	13.26 (13.27)	396 504	373 356
26C	210	77	Pale Brown	$C_{30}H_{24}I_2N_6O$ (738)	48.80 48.81)	3.28 (3.29)	11.38 (11.39)	---	--
26D	200	82	Brown	$C_{30}H_{24}I_2N_6O$ (622)	42.40 (42.41)	3.07 (3.08)	11.24 (11.25)	402	625
32a	165	77	Brownish yellow	$C_{46}H_{34}I_2N_8O_2$ (984)	56.11 (56.12)	3.48 (3.49)	11.38 (11.39)	402	322
32b	171	71	Yellowish brown	$C_{50}H_{36}I_2N_8O_2$ (1034)	58.04 (58.05)	3.51 (3.52)	10.83 (10.84)	248	865
32c	179	73	Dark red	$C_{50}H_{36}I_2N_8O_2$ (1034)	58.04 (58.06)	3.51 (3.52)	10.83 (10.84)	390 500	568 440