

Synthesis & Photophysical Characteristics of Novel Self-Assembly [ICT] Functional & Related Cyanines

Ahmed Ibrahim Koraiem & Mahmoud Hussein Yosry
Chemistry Department, Aswan Faculty of Science, Aswan University, Aswan, 81528, Egypt

ABSTRACT

Some self-assembly [ICT] functional & their cyanines incorporating Pyrazolo [4',3':5,6]pyrido[3,4-a]indolizine & pyrazolo [4'',3'':5',6']pyrido [3',4':3,4] pyrrolo [1,2-a]quinolin-12-ium -10-ium-zero-11(13)[4]methine cyanine dye (**3a-d**), pyrazolo[4',3':5,6]pyrido[3,4-a]indolizine&pyrazolo[4'',3'':5',6']pyrido[3',4':3,4] pyrrolo[1,2-a]quinolin-10(12)-ium-zero-11(13)[4]methine(**4a-d**), pyrazolo [4',3':5,6]pyrido[3,4-a]indolizin-10-ium-iodide-zero-11[4]substituted-di-4[2(4)] methine(**5a-c**),pyrazolo[4,3-e]pyrido[1',2':4,5]pyrazino[1,2-c]pyrimidin-13-yl)-zero-1[4]methine cyanine dye 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(**8a,b& 9a-f**) were prepared via one-pot synthesis based on 1-(1-(1-ethyl-1 λ^4 -pyridin-4-yl)-2-(3-methyl-1-phenyl-5-imine-4,5-di[H]-1H-pyrazol-4-yl)-2-oxo-ethyl-2-methyl-pyridin(quinolin)-1-ium(**2a-d**).The new synthesized self-assembly [ICT] functional & their cyanines were identified by elemental & spectral analyses. The UV-visible absorption spectra of some selected dyes were investigated in 95% ethanol & pure organic solvents and to investigate their photophysical characteristics.

Keywords: Functional Dyes, Synthesis, Spectral, Solvatochromism

1. INTRODUCTION

The literature reviews had attracted much attention for the spectral behaviors and in particular, are lacking and represent deficiencies in total picture of heterocyclic functional dyes. Intramolecular (Internal) Charge-Transfer Heterocyclic organic molecules has attracted increasing attention owing to their unique electronic and/or photonic properties **Kong ,L., et.al. (1969), Ravindran, E. et.al. (2015), Bonifazi, M. D. ET. Al, (2012).** solar cells,

Fenwick, O., ET. al. (2015). The absorption spectra would extend the available range of long wavelength absorbing material depending on nature of heterocyclic residue, their linkage positions, and type of both substituents. The most traditional and promising approach is how to reach the goal and trend in order to systematize such functional dyes according to their quite different physico-chemical features and shed some light upon a possible color-chemical structure relationship in order to permit a criterion for their use as photosensitizers. N-Bridge Self-Assembly of Intramolecular Charge-Transfer Compounds into Functional Molecular Systems, **Yongjun, Li, et.al.,(2016).** Combining heterocyclic [ICT] compounds featuring different degrees of conjugation with phase transfer methodologies we have self-assembled various organic including the ready processability offer great opportunities for applications in designed molecular sensors based on changes in the efficiency of the [ICT] process upon complexation. A moieties in the heterocyclic [ICT] moieties have received considerable attention in the field of synthetic organic chemistry because of their special structural properties **Matsumoto, K., et.al. (1996), Bird, C. W., (1998, 2014).** To date, the self-assembly process for obtaining organic nanomaterials is still highly desirable for the advancement of organic nanoscience and nanotechnology, **Kim ,F. S., et.al. (2011), Mohanty, M.K, ET. al. (1977).**

Thus, the choice of materials based on the predication of structure–property relationships shows important significance in this field

2. EXPERIMENTAL SECTION

All melting points are uncorrected Elemental analysis was carried out at the Micro analytical center (Cairo-University). IR (ν KBr) spectra were determined with Perkin Elmer Infrared 127 β spectrophotometer. ^1H -NMR & Mass spectra were recorded with a Bruker AMX-250 & 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. Synthesis of 3-methyl-1-phenyl-pyrazolin-5-imine-keto-methylene-4[4]pyridin (quinolin)-4(1)-ium ethiodide salts (**1Aa-c**), 1-(1-(1-ethyl-1 λ^4 -pyridin-4-yl)-2-(3-methyl-1-phenyl-5-imine-4,5-di[H]-1H-pyrazol-4-yl)-2-oxo-ethyl-2-methyl-

pyridin (quinolin)-1-ium (**1Ba,b**), 1-(1-(1-ethyl-1 λ^4 -pyridin-4-yl)-2-(3-methyl-1-phenyl-5-imine-4,5-di[H]-1H-pyrazol-4-yl)-2-oxo-ethyl-2-methyl-pyridin (quinolin)-1-ium (**2a-d**) was prepared according to prospective references, **Mohanty, M.K, et. al. (1977), Koraiem, A. I., et.al. (2018).**

2.1. Synthesis of Self Assembly [ICT] functional Pyrazolo[4',3':5,6]pyrido[3,4-a]indolizine & pyrazolo [4'',3''': 5',6']pyrido [3',4':3,4] pyrrolo [1,2-a]quinolin-12-ium-10-ium-zero-11(13)[4]methine cyanine dye (3a-d):

Mixture of (**2a-d**, 0.005 mol) and 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 to give (**3a-d**), Table (1). IR (ν^{KBr} cm^{-1}) of (**3d**), showed the general absorption bands at 1490cm^{-1} (C=N), 1617cm^{-1} (C=C) conjugated, 1711cm^{-1} (COCH₃), **Bellamy, L. J.; (1962).** ¹H-NMR (DMSO, 300 MHz) spectra of (**3b**), showed general single and multiple signals at $\delta, 7.52-7.54$ ppm (m,4H,Ar), $\delta, 7.94-9.01$ ppm (m,6H,quinolin-4-ium), $\delta, 1.57$ ppm (t,3H,CH₃), $\delta, 4.80$ ppm (q, 2H, CH₂), $\delta, 7.57-9.30$ ppm (m,4H, indolizine), $\delta, 4.32$ ppm (S,1H,CH), $\delta, 10.61$ ppm (S,1H,NH), $\delta, 1.65$ ppm (S,3H,CH₃), $\delta, 2.47$ ppm (S,3H,CH₃), $\delta, 1.98$ ppm (S,3H,CH₃ofN-COCH₃), $\delta 1.5-1.8$ (t,3H, CH₃), $\delta 1.87$ (q,2H,CH₂), $2.46-2.47$ (S,3H,CH₃), $\delta 3.49$ (S, 6H, 2CH₃) two acetyl groups, $\delta 7.8-8.8$ (m,15H) three Aromatic systems for (**3d**), **Scheinman, F. (1970), Batterham, T. J.; (1973).** Mass spectra of (**3d**) resulted in a molecular ion peaks at a molecular ion peaks at $m/z = 656$ and base peak at $m/z = 60$, **Porter, Q. N., et.al. (1971).**

2.2. Synthesis of Self Assembly [ICT] functional pyrazolo[4'',3''':5',6']pyrido[3',4':3,4]pyrrolo[1,2-a]quinolin-10(12)-ium-zero-11(13)[4]methine (4a-d).

An ethanolic solution of (**3a-d**) in presence of KOH or K₂CO₃ or 1m M NaHSO₃ and use 0.1N HCl, **Theodorou, V, et.al. (2015)**, was refluxed for 1hour. The reaction mixture was filtrated from unreacted materials, concentrated and cooled; the solid product was collected and crystallized from ethanol to give (**4a-d**), Table (1). ¹H-NMR (DMSO, 300 MHz) spectra of (**4b**), $\delta 7.52-7.54$ ppm(m,4H,Ar-H), $\delta 7.94-9.01$ ppm (m,6H, quinolin-4-ium), $\delta 1.57$ ppm(t,3H,CH₃), $\delta 4.80$ ppm (q,2H,CH₂), $\delta 7.57-8.52$ ppm (m,4H,indolizine)

, δ 1.63 ppm (S,3H,CH₃), δ 2.47 ppm (S,3H,CH₃), δ 10.94 ppm (S,1H,NH)

Scheinman, F. (1970), Batterham, T. J.; (1973)

2.3. Synthesis of pyrazolo [4', 3':5, 6] pyrido [3, 4-a] indolizin-10-ium iodide-zero-11[4] substituted-Di-4[2(4)] methine (5a-c)

An ethanolic solution of (3a-d, 0.01mol) and 2-methyl-pyridin [quinolin]-2(4)-ium-ethiodide salts (0.01mol) in few drops of piperidine were refluxed for 5-7 hrs. 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 to afford cyanine dyes (5a-c), Table (1), IR (ν^{KBr} cm⁻¹) of (5a), showed in addition to the general absorption bands at 1490.7cm⁻¹ (C=N), 1617 cm⁻¹ (C=C) conjugated, 1711 cm⁻¹(COCH₃), well defined absorption band at 3061 cm⁻¹(stretching CH) and 2923 cm⁻¹ (heterocyclic quaternary salt), **Bellamy, L. J.; (1962)**. ¹H-NMR (DMSO, 300 MHz) spectra of (5b), δ 7.52-7.54, ppm(m,4H,Ar-H), δ 7.94-9.01ppm (m,6H, quinolin-4-ium), δ 7.29-8.92ppm (m, 6H, quinolin-2-ium), δ 1.57ppm(t,6H,2CH₃), δ 4.80 ppm(q,4H,2CH₂), δ 7.57-9.30ppm (m,4H,indolizine), δ 1.65,2.28,2.47 ppm (S,9H,3CH₃), δ 5.82 ppm (S,1H,=CH), **Scheinman, F. (1970), Batterham, T. J.; (1973)**

2.4. Synthesis of 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 cyanine dye (7a, b)

Mixture of (6a, b, and 0.01mol) and acetic anhydride (10 ml) were refluxed for 3-5 hrs on a hot plate. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated to one third of its volume, cooled. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol, Table [1]. ¹H-NMR (DMSO, 300 MHz) spectra of (7b), δ 7.52-7.54ppm(m,4H,Ar-H), δ 7.67-8.90ppm (m,6H, quinolin-4-ium), δ 7.29-8.92ppm (m,6H, quinolin-2-ium), δ 1.57ppm(t,3H,CH₃), δ 4.80 ppm(q,2H,CH₂), δ 8.08-8.97ppm (m,4H,pyridin-1-ium) , δ 2.14,2.47 ppm (S,6H,2CH₃), δ 10.61 ppm (S,1H,NH), δ 2.6,2.8 (S,2H,CH,CH₂), **Scheinman, F. (1970), Batterham, T. J.; (1973)**.

2.5. 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 (8a, b)

Mixture of (**6a, b**, 0.005 mol) and acetic anhydride (10 ml), the reaction mixture was reflux for 3 hours. The reaction mixture concentrated to half of its volume, cooled and precipitated with ice water then recrystallised from ethanol, Table [1]. ¹H-NMR (DMSO, 300 MHz) spectra of (**8b**), δ 7.52-8.04ppm(m,4H,Ar-H), δ 7.94-9.01ppm (m,6H, quinolin-4-ium), δ 7.94-9.01ppm (m,6H, quinolin-2-ium), δ 1.57ppm (t,3H,CH₃), δ 4.80 ppm(q,2H,CH₂), δ 7.17-9.10ppm (m,4H, heterocyclic) , δ 2.28,2.47 ppm (S,6H,2CH₃), δ 5.45 ppm (S,1H,=CH), **Scheinman, F. (1970), Batterham, T. J.; (1973)**. Mass spectra of (**8b**) resulted in a molecular ion peaks at m/z =635, and base peaks at m/z =158 and 377, **Porter, Q. N., et.al. (1971)**.

2.6. 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 (9a-f)

An ethanol solution of dye (**8a, 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 [1]. ¹H-NMR (DMSO, 300 MHz) spectra of (**9b**), δ 7.52-8.04ppm(m,4H,Ar-H), δ 7.94-9.01ppm (m,6H, quinolin-4-ium), δ 7.94-9.01ppm (m,12H, 2 quinolin-4-ium), δ 1.57ppm (t,6H,2CH₃), δ 4.80 ppm (q,4H,2CH₂), δ 7.17-9.10ppm (m,4H, heterocyclic) , δ 2.26,2.47 ppm (S,6H,2CH₃), δ 5.45 ppm (S,1H,=CH), **Scheinman, F. (1970), Batterham, T. J.; (1973)**.

Table (1): Characterization data for (3,4,5)a-d, (7,9)a, b &10a-f

Comp. No.	M.P. °C	Yield %	Colour	Mol. Formula (Mol.wt)	Calcd. % (Found)%			Absorption spectra in EtOH	
					C	H	N	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}, (\text{cm}^2\text{mol}^{-1})$
3a	109	62	brown	$\text{C}_{30}\text{H}_{31}\text{I}_2\text{N}_5\text{O}$ (731.42)	49.26 (49.45)	4.27 (4.60)	9.58 (9.68)	390	1881
3b	132	60	Dark brown	$\text{C}_{33}\text{H}_{29}\text{I}_2\text{N}_5\text{O}$ (765.44)	51.78 (51.53)	3.82 (3.63)	9.15 (9.57)	355	1721
3c	138	68	Brown	: $\text{C}_{34}\text{H}_{33}\text{I}_2\text{N}_5\text{O}$ (781.48)	52.26 (52.93)	4.26 (4.55)	8.96 (8.94)	425	2199
3d	113	63	Pale brown	$\text{C}_{37}\text{H}_{31}\text{I}_2\text{N}_5\text{O}$ (815.50)	54.50 (54.46)	3.83 (3.60)	8.59 (8.68)	415	2105
4a	119	72	brown	$\text{C}_{28}\text{H}_{29}\text{I}_2\text{N}_5$, (689.38)	48.78 (48.95)	4.24 (4.45)	10.16 (10.56)	430	1771
4b	142	70	Dark brown	$\text{C}_{32}\text{H}_{31}\text{I}_2\text{N}_5$, (739.44)	51.98 (52.15)	4.23 (4.45)	9.47 (9.65)	450	2245
4c	148	78	Brown	$\text{C}_{32}\text{H}_{31}\text{I}_2\text{N}_5$, (739.44)	51.98 (52.05)	4.23 (4.50)	9.47 (9.80)	440	2155
4d	123	73	deep brown	$\text{C}_{32}\text{H}_{31}\text{I}_2\text{N}_5$, (739.44)	51.98 (52.10)	4.23 (4.55)	9.47 (9.75)	445	2175
5a	155	82	Intense violet	$\text{C}_{37}\text{H}_{37}\text{I}_3\text{N}_6$ (946.46)	46.95 (46.53)	3.94 (3.55)	8.88 (8.49)	480	1887
5b	180	77	deep violet	$\text{C}_{41}\text{H}_{39}\text{I}_3\text{N}_6$, (996.52)	49.42 (49.69)	3.94 (3.53)	8.43 (8.98)	505	2520
5c	166	75	Violet	$\text{C}_{37}\text{H}_{37}\text{I}_3\text{N}_6$ (946.46)	46.95 (46.54)	3.94 (4.55)	8.88 (8.49)	495	2233
6a	140	75	Dark red	$\text{C}_{31}\text{H}_{30}\text{I}_2\text{N}_6\text{O}$, (756.43),	49.22 (49.54)	4.00 (4.14)	11.11 (11.48)	365, 490	1667 923
6b	145	82	Brown	$\text{C}_{35}\text{H}_{32}\text{I}_2\text{N}_6\text{O}$, (806.49),	52.13 (52.27)	4.00 (4.44)	10.42 (10.31)	365, 495	1789, 1100
8a	127	61	red	$\text{C}_{31}\text{H}_{27}\text{I}_2\text{N}_6$ (610.50)	60.99 (60.75)	4.46 (4.35)	13.77 (13.34)	460	698
8b	170	65	red	$\text{C}_{35}\text{H}_{29}\text{I}_2\text{N}_6$ (660.56)	63.64 (63.45)	4.43 (4.25)	12.72 (12.52)	498	1010
9a	155	74	Red	$\text{C}_{38}\text{H}_{35}\text{I}_2\text{N}_7$ (843.56)	54.11 (54.05)	4.18 (4.34)	11.62 (11.74)	390 520	2700 2443
9b	150	59	red	$\text{C}_{42}\text{H}_{37}\text{I}_2\text{N}_7$ (639.81)	78.85 (78.12)	5.83 (5.90)	15.32 (15.42)	480	670
9c	130	59	Pale Brown	$\text{C}_{42}\text{H}_{37}\text{I}_2\text{N}_7$ (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 ₇ I 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 ₇ I ₂ (689.87)	80.09 (80.45)	5.70 (5.28)	14.21 (14.69)	478	1593

2.15. Solvatochromic:

The organic solvents were used of spectroscopic grade of purified according to the recommended methods, **Reddick, J. A. et.al. (1970; 1969)**. The absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 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.

2.15.1. Preparation of Dyes Solution:

1-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. **2-** 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. **3-** 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

2.15.2- Preparation of Dyes Solutions: Studying the effect of pure organic solvents in the uv and visible range:

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.

2.15.3.Studying spectra behaviour in mixed solvents in the visible range:

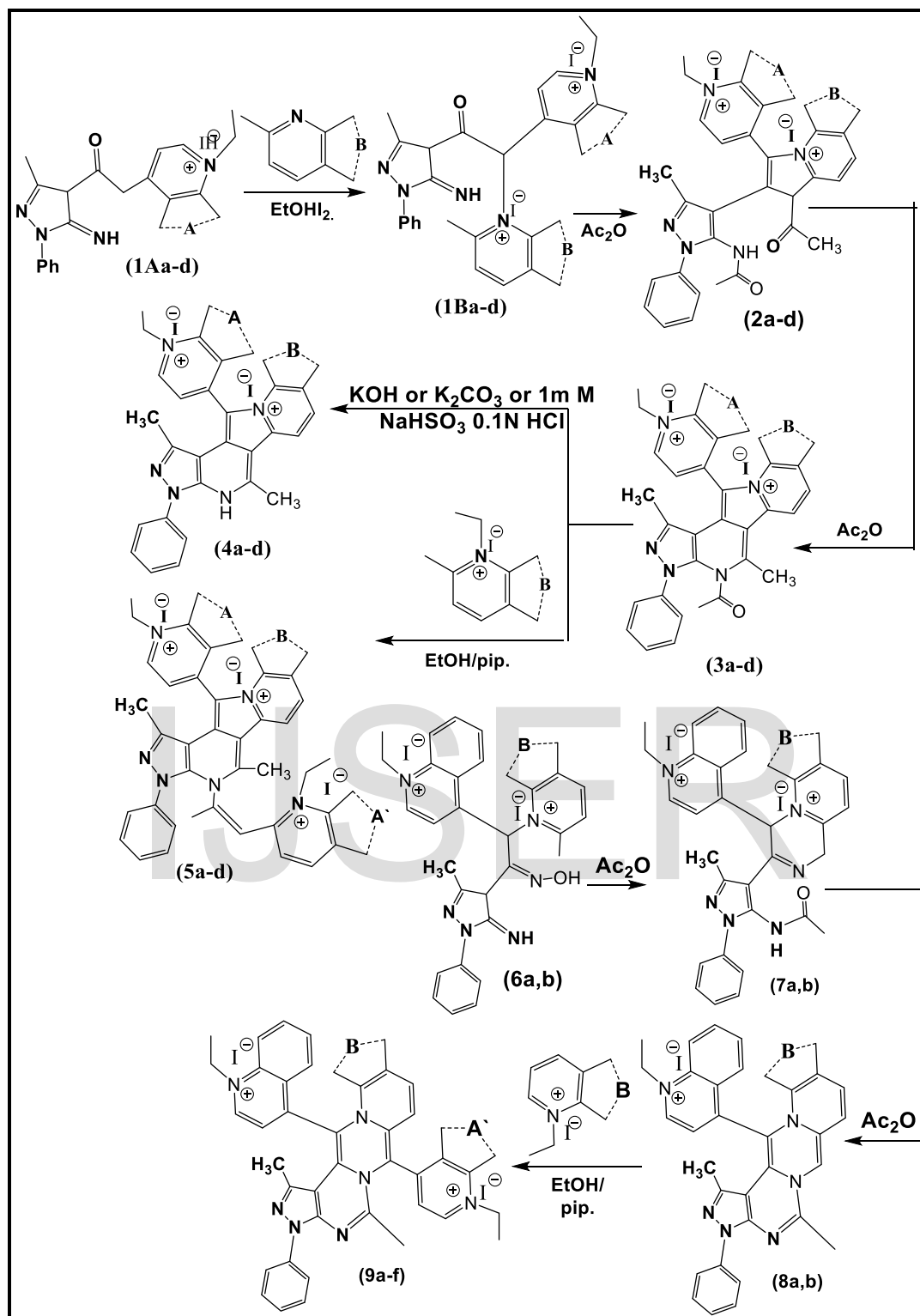
An accurate volume of the stock solution (10^{-3} M in ethanol) of the dye was placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent.

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS

Extinction to our work on self-assembly heterocyclic [ICT] functional dyes & related to cyanines, **Koraïem, A. I. M., et. al. (2018)**, The interaction of ethanolic solution of 3-methyl-1-phenyl-pyrazolin-5-imine keto-methylene-4[4]pyridin(quinolin)-4(1)-ium ethiodide salts (**1Aa-c**) [**koraïem et. al. 2018**] with 2-methyl-pyridine(quinoline) under iodine afforded 1-(1-(1-ethyl-1 λ^4 -pyridin-4-yl)-2-(3-methyl-1-phenyl-5-imine-4,5-di[H]-1H-pyrazol-4-yl)-2-oxo-ethyl-2-methyl-pyridin(quinolin)-1-ium(**1Ba,b**). Intramolecular heterocyclization or ring closure of (**1Ba-c**), in equimolar amount, under acetic anhydride catalyses) afforded self-assembly heterocyclic [ICT] functional dyes, Pyrazolo [4',3':5,6]pyrido[3,4-a]indolizin-10-ium-zero-11[4]methine, pyrazolo [4',3': 5,6] pyrido[3,4-a] indolizin-10-ium iodide, pyrazolo [4'',3'':5',6'] pyrido [3',4':3,4] pyrrolo[1,2-a]quinolin-12-ium-zero-13[4]methine (**2c**) & pyrazolo[4'',3'': 5',6'] pyrido [3',4': 3,4] pyrrolo[1,2-a] quinolin-12-ium-zero-13[4]methine cyanine dyes (**2a-b**) which on their treatments with conc. sulphuric acid, liberating iodine vapors on warming. The later self-assembly {ICT} functional dyes (**2a-d**) on hydrolysis using NaOH solution afforded self-assembly {ICT} functional dyes 1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo[4',3':5,6]pyrido[3,4-a]indolizin-10-ium-zero-11[4]methine, 1, 5-dimethyl-3-phenyl-3,4-di[H]pyrazolo [4'',3'': 5',6']pyrido [3',4':3,4] pyrrolo [1,2-a]quinolin-12-ium-zero-13[4]methine, 1,5-dimethyl-3-phenyl-3,4-di[H] pyrazolo [4',3':5,6]pyrido[3,4-a] indolizin-10-ium-zero-11[4] methine (**3a-d**) respectively. The reaction of (**3a-d**) with N-ethyl-pyridin(quinolin)-4(1)-ium-ethyl iodide salts, in equimolar ratio, under piperidine catalysis afforded pyrazolo[4',3': 5,6] pyrido[3,4-a]indolizin-10-ium-iodide-zero-11[4],substituted-di-4[2(4)]methine cyanine dye (**4a,c**) & pyrazolo [4',3': 5,6] pyrido [3,4-a] indolizin-10-ium-zero-11[4]substituted-di-4[2(4)] methine cyanine dye (**4d**),. Synthesis of pyrazolo [4,3-e]pyrido [1',2':4,5] pyrazino[1,2-c]pyrimidin-13-yl)-zero-1[4]methine, pyrazolo[3'',4'':4',5']pyrimido [1',6':4,5]pyrazino[1,2-a]quinolin-15-yl)-zero-1[4] methine cyanine dye (**8a,b**)

& pyrazolo[4,3-e]pyrido [1',2':4,5]pyrazino[1,2-c]pyrimidin-7,13-diyl)bis-zero-methine pyrazolo [3'',4'': 4',5']pyrimido[1',6':4,5]pyrazino [1,2-a]quinolin-7,15-diyl)bis bis-zero-methine (**9a-f**) was started by acetylation of the reported 1-ethyl-4-(2-(hydroxy-imino)-2-(3-methyl-1-phenyl-4,5-di[H]-1H-pyrazol-5-imine-4-yl)-1-(2-methyl-pyridin-1-ium-1-yl-ethyl-quinolin-1-ium (**6a,b**)) to afford 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-ethyl-quinolin-1-ium-4-yl)-1,4-di[H] pyrazino[1,2-a]quinolin-11-ium-zero-4[4]methine cyanine dyes (**7a,b**), **Koraiem, A. I. M., et. al. (2018)**, Intramolecular heterocyclization or ring closure of (**7a, b**) under acetic anhydride, in equimolar ratio, afforded pyrazolo[4,3-e]pyrido [1',2':4,5]pyrazino[1,2-c] pyrimidin-13-yl-zero-1[4]methine & pyrazolo [3'',4'':4',5']pyrimido[1',6': 4,5]pyrazino[1,2-a]quinolin-15-yl)-zero-1[4]methine cyanine dyes (**8a,b**). The reaction of an ethanolic solution of (**8a,b**) with pyridin [quinolin]-4(1)-ium-1-ethiodide salts and few mls of piperidine afforded pyrazolo[4,3-e]pyrido[1',2':4,5]pyrazino[1,2-c]pyrimidin-7,13-diyl-bis-zero-methine & pyrazolo [3'',4'':4',5']pyrimido[1',6':4,5]pyrazino[1,2-a]quinolin-7,15-diyl)bis-zero-methine cyanine dyes (**9a-f**), **Scheme (1)**. The formation of self-assembly [ICT] functional dyes pyrazolo [4'',3'': 5',6'] pyrido [3',4':3,4]pyrrolo[1,2-a]quinolin-12-ium -10-ium-zero-11(13)[4] methine cyanine dye (**3a-d**) was suggested to proceed via acetylation process for both the methyl group attached to heterocyclic pyridin(quinolin)-1-ium-iodide and pyrazolin-5-imine of (**2a-d**) to give the intermediates (**2A,B, a-d**), following ring closure for the enolate intermediate (**2 A,B, a-d**) to afford the di-acetyl i (**3a-d**) via enolization & elimination of water molecule (-H₂O) process.

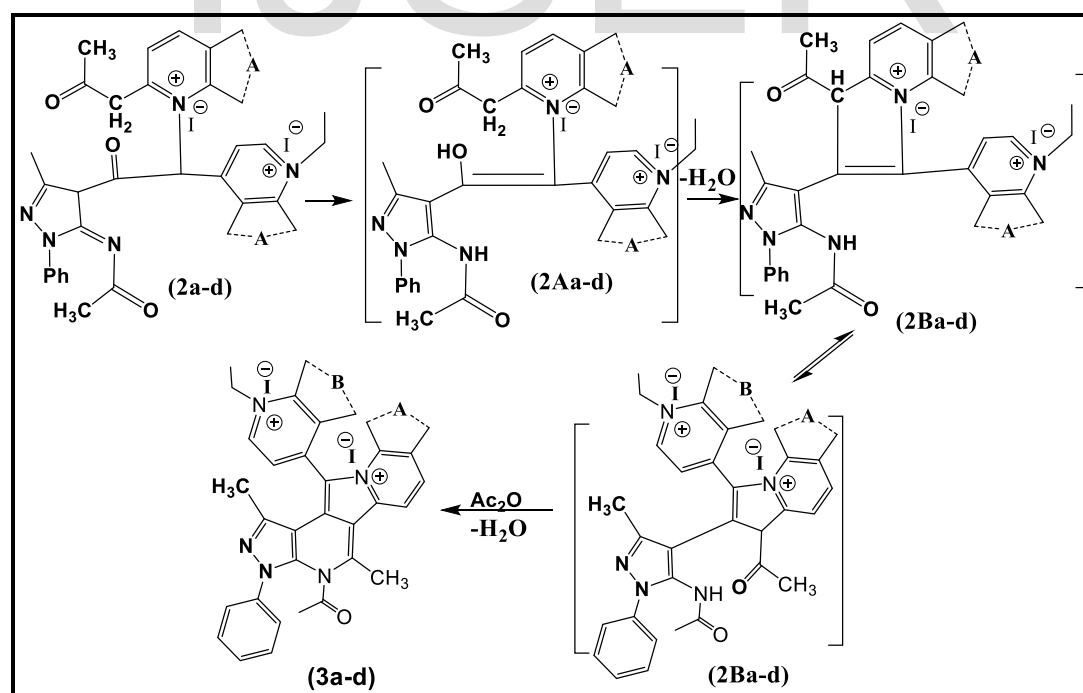


Scheme (1)

Scheme (1) Substituent's:

(2a-d): A (B)=1-ethyl pyridin-4-ium salt, (2-methyl pyridin-1-ium) (a); (3a-d): A (B)=1-ethyl pyridin-4-ium (indolizine) (a); A(B) =1-ethyl-quinolin-4-ium salt, (indolizine) (b); A(B)=1-ethyl-quinolin-4-ium salt(Benzoindolizine) (c); A(B)=1-

ethyl pyridin-4-ium salt(Benzoindolizine) (d). A(B) =1-ethyl pyridin-4-ium (quinolin-1-ium) (b); A(B)=1-ethyl-quinolin-4-ium salt(quinolin-1-ium) (c); A(B)=1-ethyl-quinolin-4-ium (pyridin-1-ium) (d), **(3a-d)**: A(B) =1-ethyl pyridin-4-ium (indolizine) (a); A(B) =1-ethyl-quinolin-4-ium (indolizine) (b); A(B)=1-ethyl-quinolin-4-ium(Benzoindolizine),(c);A(B)=1-ethyl-pyridin-4-ium(Benzoindolizine) (d). A(B)=1-ethyl pyridin-4-ium (quinolin-1-ium) (b); A(B)=1-ethyl-quinolin-4-ium(2-methyl-quinolin-1-ium) (c); A(B)=1-ethyl-quinolin-4-ium salt(pyridin-1-ium),(d)..**(4a-d)**:A(B)=1-ethyl-pyridin-4-ium(indolizine),(a);A(B) =1-ethyl-quinolin-4-ium(indolizine),(b);A(B)=1-ethyl-quinolin-4-ium(Benzoindolizine),(c);A(B)=1-ethyl-pyridin-4-ium(Benzoindolizine),(d).A(B)=1-ethyl-pyridin(quinolin)-4(1)-ium),(b);A(B)=1-ethyl-quinolin(quinolin-4(1)-ium(c); A(B) =1-ethyl-quinolin (pyridin-4(1)-ium (d). **(5a-c)**: A =1-ethyl pyridin-2-ium (a); 1-ethyl-quinolin-2-ium(b);1-ethyl-pyridin-4-ium,(c).B=indolizine.**(9a,b)**:A= pyridin-1-ium-iodide **(a)**, A=quinolin-1-ium, **(9a-f)**: A(B)=pyridin-4-ium(1-ethyl pyridin-4-ium) (a); A(B)=pyridin-4-ium (1-ethyl-quinolin-4-ium) (b); A(B)=pyridin-4-ium(2-ethyl-quinolin-1-ium),(c);A(B)=quinolin-4-ium(1-ethyl-pyridin-4-ium) (d); A(B)=quinolin-4-ium (1-ethyl-quinolin-4-ium) (e); A(B)=quinolin-4-ium (1-ethyl-quinolin-1-ium) (f).



Equation (1)

3.2. COLOUR AND SPECTRAL BEHAVIOUR

Pyrazolo [4'',3'': 5',6']pyrido [3',4':3,4] pyrrolo[1,2-a]quinolin-12-ium-10-ium-zero-11(13)[4]methine, pyrazolo[4',3':5,6]pyrido[3,4-a]indolizin-10-ium-iodide-zero-11[4],substituted-di-4[2(4)]methine,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, 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H] pyrazolo [4',3':5,6] pyrido[3,4-a]3H-pyrazolo[1,5-a]pyridin-8-ium-mono-5[2(4)-methine,1,5-dimethyl-3-phenyl-3,7-di[H]imidazo[1',5':1,2]pyrazolo[4',3':5,6] pyrido[3,4-a] 3H-pyrazolo[1,5-a]pyridin-zero-7[4(1)]methine cyanine dyes 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo[4',3':5,6] pyrido [3,4-a]3H-pyrazolo[1,5-a]pyridin-8-ium-substituted-methyl-di-4[4(1)]-methine & **(3a-d, 5a-c, 8a, b & 9a-f)** are highly coloured compounds. Their colour ranging from (reddish-red) in colour respectively, easily (partially) soluble in polar (non) organic solvents exhibiting coloured solutions (reddish-red) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. They are soluble in concentrated H₂SO₄ acid liberating iodine vapour on warming. Their ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. They possess interchargable colours solution (reddish-red), Tables **(1, 2)**. The visible absorb-maximum of dye **(3a)** [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] showed (λ_{\max} = 390 nm; ϵ_{\max} = 1881 mol⁻¹cm²). Substituting of [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **(3a)** by [A = 1-ethyl pyridin-4-ium salt, B= 1-ethyl pyridin-4-ium salt] in dye **(3b)** exhibit (λ_{\max} = 355 nm; ϵ_{\max} = 1721 mol⁻¹cm²) resulted in hypso- chromic shift of $\Delta\lambda_{\max}$ =35 nm. This is due to the decreasing π - delocalization and less conjugation in pyridine ring. Substituting of [A = 1-ethyl pyridin-4-ium salt, B= 1-ethyl pyridin-4-ium salt] in dye **(3b)** by [A= pyridin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye **(3c)** exhibit (λ_{\max} = 425 nm; ϵ_{\max} = 2199mol⁻¹cm²) resulted in bathochromic shift of $\Delta\lambda_{\max}$ =35 nm. This is due to the more extensive π - delocalization and extensive conjugation in the quinoline ring. Substituting of [A= pyridin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye **(3c)** by [A=1-ethyl-quinolin-4-ium salt, B=1-ethyl pyridin-4-ium salt] in dye **(3d)** exhibit (λ_{\max} = 415 nm; ϵ_{\max} = 2105 mol⁻¹cm²) resulted in hypso- chromic shift of $\Delta\lambda_{\max}$ =25 nm. This is due

to both less extensive π - delocalization and conjugation in pyridine ring. On comparison of the absorption spectra 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-N-bridge head indolizin (benzo-indolizin)-zero-1[4(1)] methine (**3a**) and reported 3-methyl-1-phenyl-pyrazolin-5-imin-4(2)-indolizine (benzo indolizine)-zero-3(4)-methine cyanine dye. It was obvious that the former dye (**3a**, λ_{\max} (nm) =390, ϵ_{\max} 1881) showed a hypsochromic shift of 80 nm than the reported dye (**28**, λ_{\max} (nm) 470, ϵ_{\max} 11435) in prospective reference, **EI-Damarany, H.A. (2008)**. This is due to the presence of an acetyl group in a pyrazolin-5-imine group in dye causes an antagonistic effect for CT absorption band for such former new dye. On comparison the absorption spectra of self-assembly [ICT] functional dyes (**3a-d & 4a-d**), it was obvious that the later dyes (24a-d) resulted in absorption bands bathochromically shifted of λ_{\max} =30-40 nm than those of (**3a-d**). This is due to the presence of acetyl group present in (23a-d) causing withdrawing character decreasing of charge transfer from Pyrazolo [4',3':5,6]pyrido[3,4-a]indolizine nitrogen atom as electron source towards both positively charged indolizinium or quinolinium moieties as electron sink. On the other hand, the absorption spectra of (**5a-c**) resulted in absorption bands more batho- chromically shifts of λ_{\max} =50nm than those of (**3a-d & 4a-d**). This is due to the multi-charge transfer from pyrazolo [4', 3':5, 6] pyrido [3, 4-a] indolizine nitrogen atom as electron source towards both positively charged indolizinium and two quinolinium moieties as electron sink. The absorption spectra of pyrazolo[4',3':5,6]pyrido[3,4-a] indolizin-10-ium iodide-zero-11[4], substituted-di-4[2(4)]methine (**5a-c**) in 95% ethanol showed absorption bands undergo batho (hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue **A** and their linkage position. Thus, the visible absorb-maximum of dye (**5a**) [**A** = pyridin-2-ium ethiodide] showed λ_{\max} =480 nm. Substitution of [**A**= pyridin-2-ium ethiodide] in dye (**5a**) by [**A**= quinolin-2-ium ethiodide] in dye (**5b**) resulted in bathochromic shift of $\Delta\lambda_{\max}$ = 25 nm concomitant with an increasing number of absorption bands in dye (**5b**). This is due to the more extensive & extra conjugated π -delocalization in quinoline ring. Changing the linkage position of pyridin-2-ium salt in dye (**5a**) to pyridin-4-ium analogue salt in dye (**5c**) causes bathochromic shift of $\Delta\lambda_{\max}$ = 15 nm. This is due to the extended of π -

delocalization within pyridin-4-ium ethiodide in dye (**5c**). The visible absorb-maximum of (**8a**) [A= pyridin-4-ium salt] showed (λ_{\max} = 460 nm; ϵ_{\max} 698 mol⁻¹cm²). Substitution of [A= pyridin-4-ium salt] in dye (**8a**) by [A = quinolin-4-ium salt] in (**8b**) exhibit (λ_{\max} = 498 nm; ϵ_{\max} = 1010 mol⁻¹cm²) resulted in bathochromic shift of $\Delta\lambda_{\max}$ =38 nm. This is due to the more extensive π -delocalization and extra conjugation in the quinoline ring. The visible absorb-maximum of dye (**9a**) [A= pyridin-4-ium salt, B=1-ethyl pyridin-4-ium salt] showed (λ_{\max} = 390 & 520 nm; ϵ_{\max} = 2700 & 2443 mol⁻¹cm²). Substitution of [A= pyridin-4-ium salt, B=1-ethyl pyridin-4-ium salt] in dye (**9a**) by [A= pyridin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye (**9b**) exhibit (λ_{\max} = 480 nm; ϵ_{\max} = 670 mol⁻¹cm²) resulted in bathochromic shift of $\Delta\lambda_{\max}$ =40 nm. This is due to the more extensive π - delocalization and extra conjugation in the quinoline ring. Substitution of [A= pyridin-4-ium salt, B=1-ethyl pyridin-4-ium salt] in dye (**9a**) by [A= pyridin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye (**9c**) exhibit (λ_{\max} = 500 nm; ϵ_{\max} = 1780 mol⁻¹cm²). Substitution of [A= pyridin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye (**9c**) by [A = quinolin-4-ium salt, B=1-ethyl pyridin-4-ium salt] in dye (**9d**) exhibit (λ_{\max} = 475 nm; ϵ_{\max} = 612 mol⁻¹cm²) resulted in hypsochromic shift of $\Delta\lambda_{\max}$ =25 nm. This is due to the less extensive π - delocalization and less conjugation in the quinoline ring. Substitution of [A = quinolin-4-ium salt, B=1-ethyl pyridin-4-ium salt] in dye (**9d**) by [A = quinolin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye (**9e**) exhibit (λ_{\max} = 478 nm; ϵ_{\max} = 1593 mol⁻¹cm²) resulted in hypsochromic shift of $\Delta\lambda_{\max}$ =3 nm. This is due to the more extensive π -delocalization and extensive conjugation in the quinoline ring. Substitution of [A = quinolin-4-ium salt, B= 1-ethyl-quinolin-4-ium salt] in dye (**9e**) by [A = quinolin-4-ium salt, B=-ethyl-quinolin-1-ium salt] in dye (**9f**) exhibit (λ_{\max} =474 nm; ϵ_{\max} = 1012 mol⁻¹cm²) resulted in hypsochromic shift of $\Delta\lambda_{\max}$ =4 nm. This is due to the less extensive π - delocalization and less conjugation in the quinolin-1-ium ring. 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 (**9a-f**) are bathochromic shift to 3-Methyl-1-phenyl-pyrazolin-5-imine-4-pyrazino(1,2-a)Pyridin(quinoline)-zero-2[4(1)] methine cyanine dyes (**8a, b**), this back to extend of π -delocalization in case of bis zero methine cyanine dyes (**9a-f**).

3.3. SOLVATOCHROMIC BEHAVIOUR

Cyanine dyes had been useful in studying the colour of organic substances **Ficken, G. E., (1971)**, and there are several fundamental principles exist that correlate origin of colour to chemical structures of the solute as well as natures of the solvents, **Abu El-Hamd, R. M., (1997)**, **Ishchenko, A. A., et.al. (1989)**, **Nishimoto, K.; (1993)**. **GAO, J. et.al (1997)**. Moreover, these classes of heterocyclic compounds are useful in various industrial fields, **Koraiem, A. I. M., (1984)**. The colour changes of cyanine dyes with solvents (solvatochromism) were previously discussed by **Da silva, L., et.al. (1995)** **Gibson, H. W. et.al. (1976)**, **Frank, J., (1926)**, **Weast, R. C.et.al. (1980-1981)**. and extended, **Da Silva, L., et.al. (1995)**, **Gibson, H. W. et.al. (1976)**, and his coworkers, **Koraiem, A. I. M., ET. al. (1990, 1991)** to correlate the effect of structure on molecular orbital energy levels. It is clear that the type of substituents and the solvent polarity change the electron densities of cyanine dyes. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) shifts in solvents of various polarities. 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, **Nishimoto, K.; (1993)**., **Da silva, L et. al. (1995) & Morley, J. O.; (1994)**. Therefore, these dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of the ground and Franck-Condon excited state, due to the absorption of electromagnetic radiation in the UV-vis region. If the ground state is more stabilized than the excited state due to solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck-Condon principle, **Frank, J., (1926)**, the time required for molecules to be excited 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 corresponding 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 solvato chromism. 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 is discussed. Such dye is 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo [4'',3''':5',6'] pyrido [3',4': 3,4] pyrrolo[1,2-a] quinolin-12-ium-zero-13[4] methine cyanine dye (**3d**). The absorption spectra of (**3b**) in the wavelength range 350-700 nm have been studied in different organic solvents (H₂O, DMF, EtOH, MeOH, acetone, CCl₄, CHCl₃, and C₆H₆), **Kotzolv, N. S., et.al (1972)** respectively. The colour changes of such dyes with solvents having different polarities are presented in Table (**1**). 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 Table (**1**). These dyes are showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of such self-assembly [ICT] dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. The absorption spectra of the dyes in ethanol are characterized by the presence of one essential band which reflects the presence of intermolecular charge transfer, **Eissa, F. M., (2001)**. This intermolecular charge transfer had arisen from transferring the electron lone pair of the nitrogen atoms of the heterocyclic ring system towards the positively charged residue along the conjugated chain between both. The relevant data in Table (**1**) disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, CHCl₃, and CCl₄. These shifts can be attributed to the following factors: The bathochromic shift occurred in DMF relative to ethanol is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former, Table (**3**). The

hypsochromic shifts appeared in ethanol relative to CHCl_3 , and CCl_4 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center, Table (1). It was worth mentioning that the intermolecular hydrogen bonding between CHCl_3 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 CHCl_3 , & CCl_4 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 ethanol. In point view of light absorption, it was obvious that most of the previous selected cyanine dyes, (3b) are absorbed the fundamental light absorption (violet-red) as they have got absorption values in the range 350-660 nm .In accordance with the literature's observations ,**Tolmachev, A. I. et.al (1970), Reddick, J. A. et.al.(1970)**. The selected self- assembly functional & their dimethine cyanine dyes might be suggested to be used as photosensitizers in most polar and non-polar organic solvents in the (violet-red).The visible absorption spectra 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 cyanine dye & 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 cyanine dyes (8b,9e) in the wavelength range 400-700 nm, have been studied in different organic solvents (H_2O , DMF, EtOH, acetone, CCl_4 , CHCl_3 , and C_6H_6) **Weast, R. C. et.al.,(1980-1981)** respectively. 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 Table (1).These dyes are showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This

behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. The absorption spectra of the dyes in ethanol are characterized by the presence of one or two essential bands which reflect the presence of intermolecular charge transfer, **EI-Ezaby M. S.; et.al. (1970)**. This intermolecular charge transfer had arisen from transferring the electron lone pair of the nitrogen atoms of the heterocyclic ring system towards the positively charged residue along the conjugated chain between both. The representing graphs disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, CHCl_3 , and CCl_4 . This shift can be attributed to the following factors: The bathochromic shift occurred in DMF relative to ethanol is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former. The hypsochromic shifts appeared in ethanol relative to CHCl_3 , and CCl_4 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center. It was worth mentioning that the intermolecular hydrogen bonding between CHCl_3 molecules and the lone pair of electrons of nitrogen atoms 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 CHCl_3 , and CCl_4 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 ethanol. The unexpected hypsochromic shifts in the absorption spectral maxima in water relative to ethanol and its lower extinction coefficients were mainly ascribed to the ease of interactions of water molecules, through intermolecular hydrogen bonding, with the lone pair of electrons of the nitrogen atoms of the heterocyclic ring system, through intermolecular hydrogen bonding, which intern preclude the charge transfer from the heterocyclic ring system to the positively charged residue along the conjugated bridge, Table (3).

Table (3): Solvatochromic data obtained for **(3b, 8b & 9e)** in organic solvents

Comp No	C ₆ H ₆		Water		CCl ₄		DMF		EtOH		CHCl ₃		Acetone	
	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}
3b	481	458	481	422.5	474	234.9	478	494	474	1325	492	592.8	471	745.6
8b	470	984.7	474	669.9	449	647.9	501	869	498	918.9	470	977.42	492	771.5
9e	462	642.03	469	534.2	465	9.4	500	568	478	925.5	472	947	478	802

3.4. SPECTRAL BEHAVIOR IN MIXED SOLVENTS:

3.4.1. IN (DMF-Benzene) mixture:

The absorption spectra of 1×10^{-4} M of 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 (**9e**) cyanine dyes in DMF in the presence of different concentrations of C₆H₆. It is shown that in presence of 12.97 M of DMF, the spectrum exhibits a band located at 500 nm. In the presence of 1.16 M of DMF, the band is shifted to 463 nm concomitant with a gradual blue shift. Also, an increase in band intensity at fixed wavelength (500 nm) is observed on increasing of C₆H₆ concentration. The increase in absorbance as well as the gradual blue shift in the maximum absorption wavelength on increasing the C₆H₆, content can be ascribed to the gradual formation of the complex species through intermolecular hydrogen-bond. The graphical representation of absorbance at 500 nm against the mole fraction of DMF reveals that the absorbance increases gradually with increasing mole fraction. To investigate the effect of the dielectric constant of the medium on the band shift ($\Delta\nu$), on plotting versus $\left(\frac{D-1}{D+1}\right)$ (D is dielectric constant of the solvent added), **Dietz, F., et.al. (1975)**.

A straight line is obtained which at 5.19 M DMF give another straight line. Furthermore, a broken line is obtained on plotting the absorbance against the dielectric constant of the medium. Such behaviour indicates that factors other than the change in the dielectric constant of the medium are responsible for the shift of λ_{max} at lower and higher percentage of DMF. These factors mainly include the solute-solvent interaction through intermolecular hydrogen bond which leads to the formation of some molecular complex. On plotting the

excitation energy (E) versus the mole fraction of ethanol, a broken line with three segments, **Chemla D. S., (1987)**, is obtained. The first segment represents the orientation energy of the solvent molecules around the solute. The second segment corresponds to the molecule complex formation, where the third one represents the steady state of energy attained after complete formation of the molecular complex. From the above relations, it is clear that the position of the bands and consequently the excitation energy depends not only on the mole fraction of ethanol, but also on the following: Solvation energy. (b) Orientation of solvent molecules around the solute molecule in the ground states. (c) Dipole moment of the solute in both ground and excited states. (d) Dipole - dipole interaction between solute and solvents. (e) The strength of H-bond between solute and solvent in both ground and excited states. In pure DMF solution, the dye molecule form solvent cage, which is affected on adding C₆H₆. At lower C₆H₆ content, DMF molecules will distribute themselves uniformly on all the solvation sheaths around the molecules. The added molecules may first enter the outer solvation sheaths and then will introduce themselves in the first sheaths as their proportions are increased. This is probably due to the fact that addition of DMF permits the formation of a solvent cage around the solute molecules, through intermolecular hydrogen-bonding which previously discussed. From Table (4), it is possible to evaluate the excitation energy of the solute in pure C₆H₆ is equal to 61.9 K Cal mol⁻¹ whereas the value in pure DMF amounts to 57.2 K Cal mol⁻¹. The difference between the excitation energy in pure DMF and that corresponding to the first inflection point amounts to 3 K Cal mol⁻¹. This value may correspond to the orientation energy of the solvent molecules around the solute molecules **Eugster, C. H.; (1969)**. The value of the stability constant (K_f) of the complex with C₆H₆ was determined from the spectral behaviour in mixed solvents using the relations previously described, **Shawali; A. S., et.al. (1994)**. the value of K_f, ΔG (free energy change of formation) and n (number of C₆H₆ molecules complexed with the solute) indicate that 2:1 complex is formed. The value of K_f is dependent on both solute and solvent used, **Issa, I. M.; et.al. (1971)**, Table (4).

Table (4): Commutative data obtained for dye (9e) in mixed solvents:

Comp No.	Solvent Mix. System	Excitation energy K Cal mol ⁻¹		Orient energy K. Cal mol ⁻¹	H-bond energy K.Cal.mol ⁻¹	Total energy K.Cal.mol ⁻¹	N	Log K _f (-)	K _f (-)	ΔG K.Cal.mol ⁻¹ (+)
		Pure Solvents								
(9e)	(DMF-Benzene)	57.2 (DMF)	61.9 (Benzene)	3	2.3	5.2	2	1.464	29.1	0.3454

REFERENCES

- Abu El-Hamd, R. M., (1997), *Chem. Paper*, 51(2), 117-127,
- Batterham, T. J.; (1973). *¹HNMR spectra of simple heterocycles*” Wiley New York.
- Bellamy, L. J.; (1962), *The infrared spectra of complex molecules*, London; Methuen.
- Bird, C. W., *Tetrahedron*, (1998), 54, 10179.
- Bonifazi, M. D., (2012), *Chem. Soc.Rev.*, 41, 211
- Chemla D. S, (1987), *Nonlinear Optical Properties of Organic Molecules and Crystals* (New York, Academic Press).
- Da silva, L., Machado, C., and Rezande, M. C.; (1995), *J. Chem. Soc. Perki Trans. 2*, 483,
- Derevyanko, N. A., Dyadusha, G. G., Ishchenko, A. A., and Tolmachev, A. I., (1983), *Theoret. Exper. Khim.* 19, 169,
- Dietz, F., Muelle, G. r, Bach, G. and Grossmann, I. V.; (1975). *J. Signal Am.* 3
- Eissa, F. M., (2001), *M.Sc.Thesis, Aswan Faculty of Science, Aswan University*, 122
- El-Damarany, H. A. (2008). *M.Sc., Faculty of Science, Aswan University*
- El-Ezaby M. S.; and Salem, T. M.; Zewail, A. H. and Issa R. M., (1970), *J. Chem. Soc.* 13, 1293
- Eugster, C. H.; (1969), *Progress the Chemistry of organic Natural Products* 27, 261.
- Fenwick, O., Dyck, C. V. K. Murugavel, D., Cornil, F. R. & Haar, S. (2015), *J. Mater. Chem. C*, 3, 3007.
- Ficken, G. E. (1971), *Chemistry of Synthetic Dyes ed. K. Venkataraman Academic Press New York* 4, 212-230
- Frank, J., (1926), *Trans. Faraday Soc.*, 21, 536,

- GAO, J. and Alhambra, C.; **(1997)**. *J. Am. Chem. Soc.*, 119, 2962,
- Gibson, H. W. & Balley, F. C.; **(1976)**, *J. Chem. Soc. Perkin trans. 2(2)*, 196
- Ishchenko, A. A., Svidro, A. A., and Derevyanko, N. A. **(1989)**, *Dyes and Pigments 10*, 85-96.
- Issa, I. M.; Issa R. M.; and Abdel. Aal M. S., **(1971)**, *Egypt J. Chem. 14*, 25
J. Org. Chem. 40, 875
- Kim ,F. S., Ren G. Q. & Jenekhe, S. A., **(2011)**, *Chem. Mater. 23*, 682.
- Kong ,L., Liu, Y., Wang, H., he Tian, X, Chen, Q., Peng T.Yu, Sheng, Li, -
Dewar, M. J. S. & Trinajstic, N., **(1969)**, *J. Chem. Soc. A*, 1754
- Koraiem, A. I. M., Girgis, M. M., Khalil, Z. H. and Abu El-Hamd, R. M.;
(1990), *Croatica Chemica Acta*, 63 (4), 603-616,
- Koraiem, A. I. M., *J. Prakt Chem.* **(1984)**, 4, 695 *ibid:* **(1984)**, 5, 811
- Koraiem, A. I., El-Shafei, A. M. & Abdellah, I. M. **(2018)**, *Organic Chemistry an Indian journal 14*, (2), 1-16
- Koraiem, A. I., El-Shafei, A. M. & Abdellah, I. M., **(2018)**, *international journal of advanced research in Science, Engineering & Technology*, 5, (5), 5711-5721
- Koraiem, A. I., El-Shafei, A. M. & Abdellah, I. M., **(2018)**, *international Journal of Organic Chemistry in press*, 8
- Koraiem, A.I.M., Shindy, H.A., Abu-El-Hamd, R.M. & Ibrahim, M.A. **(2018)**,
.Accepted, **30-7-2018**, *Journal of Applicable Chemistry*
- Koraiem. A. I. M., Girgis, M. M., Khalil, Z. H. & Abu El-Hamd, R. M.; **(1991)**,
Dyes and Pigments, 15, 89-109
- Kotzolv, N. S., Zhikareva, O. O. and Batische, S. A.; **(1972)**. *Kim. Geterotski Sodin*, 12, 1619
- Kuder, J. E., Gibson, H. W. & Wychick, D.; **(1975)**, *J. Org. Chem. 40*, 875
- Matsumoto, K., Katsura, H., Yamauchi, J., Uchida, T., Aoyama, K. & Machiguchi, T., **(1996)**, *Bull. Soc. Chim. Fr*, 133, 891.
- Mohanty, M.K, Sridhar, R, & Padmanavan, SY. **(1977)**; *Indian J.Chem 158:1146*
- Morley, J. O.; **(1994)**, *J. Mol. Struct.*, 304, 191.
- Nishimoto, K.; **(1993)**, *Bull. Chem. Soc. Jpn.* 66, 1876,

- Porter, Q. N., & Baldas, J; **(1971)** *“Mass Spectrometry of Heterocyclic Compounds “ Wiely, New York.*
- Ravindran, E. & Ananthkrishnan, S. J., **(2015)**, *J. Mater. Chem. C, 3, 4359*
- Reddick, J. A. & Banger, W. B.; **(1970)**; *Techniques of Chemistry Organic Solvents (A Weiss Berger, Ed), 3 rd., Ed N. Y. Wiley (1969), 11, Organikum 1 Th. Ed., Berlin: DVW*
- Scheinman, F. **(1970)**, *Nuclear magnetic resonance of complex Molecules, Braunschweig: Vieweg and Sohn GmbH, 1.*
- Shawali; A. S., Fahmi, A. A.; Albar H. A.; Hassaneen, H. M.; Abdelhamid, A, H. **(1994)**, *J. Chem. Res., Synop. J. Chem. Res., Miniprint,*
- Theodorou, V, Paraskevopoulos G., and Skobridis, **(2015)** *K.ARKIVOC (vii) 101-112*
- Tolmachev, A. I. and Koroban, E. E.; **(1970)**, *Ukr. Khim. Zh. 36 (5) 478,*
- Weast, R. C. and Astl, M. **(1980-1981)**.*J. CRC handbook of chemistry and physics, 61 st. Edn. (CRC press, Inc.), 56,*
- Yongjun, Li, Taifeng Liu, Huibiao Liu, Mao-Zhong Tian, & Yuliang, Li Acc. Zhao-ming, Xue & Xian Yang, j., **(2016)**, *J. Mater. Chem. C, 4, 2990*

IJSER