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Novel Zero/monomethine cyanine dyes based on N-Bridgeheadpyrazolo[4', 3’:3,4] pyrido[1,2-c]pyrido[1,2-a] pyrimidine: Synthesis and photophysical properties

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ABSTRACT: Cyanine dyes of Zero/monomethine based on N-Bridgehead pyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidine heterocycle synthesized and characterized using quaternary salt precursor namely 3,5-dimethyl-12-oxo-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride**(24)**.Such Heterocyclic precursors and related dyes were identified by elemental and spectral analysis. The absorption and emission spectra properties of such dyes were investigated in 95% Ethanol to attempt and throw some light on the influence of such new heterocyclic nuclei and to compare or evaluate spectral behaviors. The Acid-Base properties (halochromism) in aqueous solutions universal buffer of some selected cyanine dyes were studied to determine the better pH for these photosensitizers.

KEYWORDS: Synthesis; N-Bridgehead; Cyanine dyes; Halochromism; Spectral behaviour.

I.INTRODUCTION

Special attention is given to the implementation, preparations, and applications of heterocyclic cyanine dyes to show the various aspects in order to satisfy the great demand in industrial, physiology, biochemistry and various biological fields. Cyanine dyes are colorant compounds used in Staining of internal limiting membrane (ILM) [1-3], as fluorescent dyes in DNA detection[4-7], optical sensors [8, 9], organic photoconductors [10],vulcanizing accelerator agents, photographic sensitizers [11], solar cell [12]. This multi-property and numerous applications of cyanine dyes push the scientist to design and improve synthetic procedure of new cyanine dyes based on N-bridgehead heterocycles [13-14]. which characterized by outstanding chemical stability, absorb at long wavelength [15, 16], high solubility and change their optical, thermal or electronic properties to meet the requirements for opto-electronic or biological products. A variety of heterocyclic cyanine dyes incorporating N-bridgehead heterocyclic moieties have been reported [17, 18]. These dyes have many vital general applications this back to the high stability of this type of dyes which attributed to the presence ofC-N linkage in the dye structures [19].

II. SIGNIFICANCE OF THE SYSTEM

In this paper, we designed and synthesized novel highly stable cyanine dyes using N-Bridgehead pyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidine as a main entities for zero/mono methine cyanine dyes synthesis. The spectral, emission and halochromism of the new dyes are described.

III. EXPERIMENTAL RESULTS

A. Physical and Chemical Properties Determinations:

All melting points are uncorrected Elemental analysis was carried out at the Analytical Services Laboratory (Textile Engineering, Chemistry and Science Department-North Carolina State University) and the Micro analytical center (Cairo University). The IR (νKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University) and Thermo Electron FTIR with Nexus 470 bench and Continuum Microscope (NCSU). ^{1}H-NMR spectra were recorded with a Bruker AMX-250 spectrometer (Cairo University). Mass spectra were recorded on a 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 spectrophotometers, Faculty of Science, Aswan. Emission spectra were recorded by Fluorolog spectrophotometer (NC State University).

B. Synthesis

1) **Synthesis of 3-methyl-4-(3-oxo-1-(pyridin-2-ylimino)butyl)-1-phenyl-1H-pyrazol-5(4H)-one (21):**Ethanolic solution mixture of 1-phenyl 3-methyl 4-(1, 3 diketo butane) pyrazol-5-one (1 mmol) and 2-amino pyridine (1 mmol) were refluxed in the presence of few drops of piperidine for 4 h at 140^{0}c. After completion of the reaction, the reaction mixture was allowed to cool, filtered and poured on crushed ice. The solid thus separated was collected by filtration and recrystallized from ethanol, **[Table 1].**

2) **Synthesis of 4-methyl-2-(3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene)-1,2-dihydropyrido[1,2-a]pyrimidin-5-ium chloride (22):** Ethanolic solution of compound **(21)** (1 mmol) and concentrated hydrochloric acid (1mmol) were refluxed for 2 h. After completion of the reaction, the product was dissolved in hot ethanol and filtered to recover the unreacted material. The reaction mixture was allowed to cool and poured on crushed ice. The solid thus separated was collected by filtration and recrystallized from ethanol, **[Table 1].**

3) **Synthesis of 1-acetyl-4-methyl-2-(3-methyl-5-oxo-1-phenyl-1H-pyrazol -4(5H)-ylidene)-1,2-dihydropyrido[1,2-a]pyrimidin-5-ium chloride (23):** Mixture of (**22**) and acetic anhydride were refluxed for 3 h. After completion of the reaction, the reaction mixture was allowed to cool, filtered and poured on crushed ice. The solid thus separated was collected by filtration and recrystallized from ethanol, **Table [5].**

4) **Synthesis of 3,5-dimethyl-12-oxo-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride (24):** mixture of compound **(22)** and few drops of piperidine were allowed to fused under 1000C then 20ml of anhydrous ethanol were added to the mixture and allowed to reflux for 4 hours then the mixture allowed to cool and quenched by water and extracted by chloroform. The resulted compound recrystallized by petroleum ether, **[Table 1].**

5) **Synthesis of 3,5-dimethyl- zero-13[4(1)] methine- 12-oxo-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride cyanine dyes (24a-c):** A mixture of **(24)** (1mmol) and pyridin[quinolin]-4 (1)-ium-ethiodide salts(1mmol)in the presence of few mls of piperidine catalyst was irradiated in microwave oven for 8 minutes at 114 watt under solvent free condition. After completion of the reaction, the product was dissolved in hot ethanol and filtered to recover the unreacted material. The reaction mixture was allowed to cool and neutralized with small amount of glacial acetic acid then separated the solid crystals by filtration and recrystallized from ethanol, **[Table 1].**

6) **Synthesis of 3,5-dimethyl- mono-12[2(4)] methine -1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride cyanine dyes (25a, b):**A mixture of **(24)** (1mmol), and 2-methyl-pyridin(quinolin)-2(4)-ium-ethiodide salts(1mmol)in the presence of few mls of piperidine catalyst was irradiated in microwave oven for 8 minutes at 114 watt under solvent free condition. After completion of the reaction, the product was dissolved in hot ethanol and filtered to recover the unreacted material. The reaction mixture was allowed to cool and neutralized with small amount of glacial acetic acid then separated the solid crystals by filtration and recrystallized from ethanol, **[Table 1].**

C. Absorption and fluorescence spectroscopy

The electronic visible absorption and fluorescence spectra of the synthesized dyes were examined in 95% ethanol and recorded using 1cm Qz cell by using 10^{-4} M concentration of the dye.

D. Spectral behaviour in aqueous universal buffer solutions

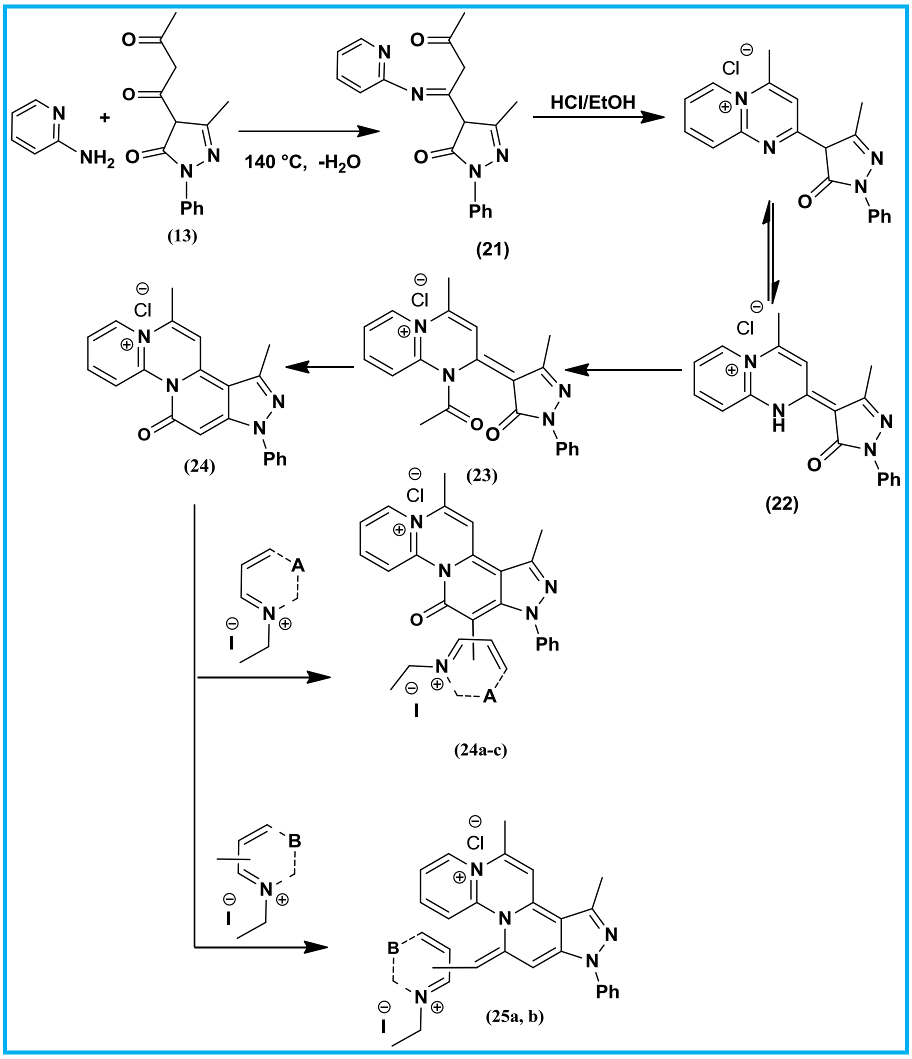
The stock solution of the dye was of the order 10^{-3} M. An accurate volume of the stock solution was added to 5 ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked then the electronic absorption spectra of the dyes in different pH solutions were recorded within a wavelength range (350-700 nm) using 1cm Qz cell.

IV. RESULTS AND DISCUSSIONS

A. Synthesis and structural characterization of dyes

1) Dye synthesis

The precursor compound 1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)butane-1,3-dione **(1)** synthesized by the reaction of ethylacetoacetate and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one followed by condensation reaction with 2-amino pyridine to afford (E)-3-methyl-4-(3-oxo-1-(pyridin-2-ylimino)butyl)-1-phenyl-1H-pyrazol-5(4H)-one **(21).** Compound **(21)** cyclized by hydrochloric acid to form (Z)-4-methyl-2-(3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene)-1,2-dihydropyrido[1,2-a]pyrimidin-5-ium chloride **(22)** then thermal acetylation of **(22)** to afford (Z)-1-acetyl-4-methyl-2-(3-methyl-5-oxo-1-phenyl-1H-pyrazol-4(5H)-ylidene)-1,2-dihydropyrido[1,2-a]pyrimidin-5-ium chloride **(23)** the later compound undergoes thermal cyclization using piperidine catalyst to afford3,5-dimethyl-12-oxo-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride **(24).** Quaternary salt **(24)** reacted with pyridin[quinolin]-4(1)-ium-ethiodide salts to afford 3,5-dimethyl-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride-12-zero[4(1)]methine cyanine dyes**(24a-c)** and reacted with2-methyl-pyridin(quinolin)-2(4)-ium-ethiodide to afford 3,5-dimethyl-1-phenyl-1,12-dihydropyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidin-6-ium chloride-12-mono[4(1)]methine cyanine dyes **(25a, b), Scheme (1).**



Scheme 1. Synthetic routes of dyes **(24a-c)** and **(25a, b)**. Where, **(24a-c)**:A = 1-ethyl pyridin-4-ium salt (a); 1-ethyl-quinolin-4-ium salt (b); 2-ethyl-quinolin-1-ium salt (c) and **(25a, b):** A = 1-ethyl-quinolin-2-ium salt (a); A =1-ethyl-pyridin-4-ium salt (b).

2) Structural Characterization

The structures of **13, 21, 22, 23, 16, (24a-c)** and **(25a, b)** was confirmed by elemental analysis as despited in **(Table 1)** and by spectral data analysis IR, ^{1}H-NMR and mass. Thus, FT-IR (ν^{KBr} cm^{-1}) showed general absorption bands at: 2956 (CH for CH_3), 1704 (C=O), 1400-1700 (C=C aromatic), 752 (phenyl substituent) for **(13)**;3027 (CH for CH_3), 1706 (C=O), 1400-1700 (C=C aromatic), 752 (phenyl substituent) for **(24)**;2937 CH of alkyl (hetero cyclic quaternary salt), 1400-1700 (C=C aromatic), 1497 (C=N), 758 (phenyl substituent) for **(24b)** and2940 CH of alkyl (hetero cyclic quaternary salt), 1400-1700 (C=C aromatic), 1495 (C=N), 757 (phenyl substituent) for **(25a).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (m, 1H), 8.20 (m, 1H), 8.01 (m, 1H), 7.96 (m, 1H), 7.88-7.81 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34-7.26 (m, 1H), 6.30 (d, *J* = 1.0 Hz, 1H), 3.60 (s, 1H), 2.30 (s, 3H), 1.71 (d, *J* = 1.1 Hz, 3H) for compound **(22)**and signals atδ 9.30 (m, 1H), 9.06 (m, 1H), 8.44-8.35 (m, 2H), 7.88-7.82 (m, 2H), 7.52-7.44 (m, 2H), 7.30 (m, 1H), 6.30 (d, *J* = 1.0 Hz, 1H), 5.52 (s, 1H), 2.30 (s, 3H), 1.71 (d, *J* = 1.1 Hz, 3H) for compound **(24).** Mass spectra confirmed a molecular formula agree with a molecular ion peaks at m/z=396 and base peak at m/z=77 for **(23);** a molecular ion peaks at m/z=658 and base peak at m/z=77 for **(24)**;a molecular ion peaks at **m/z**=662 and base peak at m/z=57for dye **(24b)** and a molecular ion peaks at m/z=707 and base peak=77 for dye **(25a)**.

Table (1): Characterization data of the synthesized compounds and related dyes

Comp. No.	M.p. °C	Yield %	Colour	Mol. Formula (Mol.wt)	%Calcd. (Found)			Absorption spectra in EtOH	
					C	H	N	$\lambda_{max(nm)}$	$\varepsilon_{max}(M^{-1}cm^{-1})$
21	85	35	Red crystals	$C_{18}H_{16}ClN_4O_2$ 320.34	67.49 (67.48)	5.03 (5.01)	17.49 (17.51)	–	–
22	110	62	Pale brown powder	$C_{19}H_{17}ClN_4O$ 352.8	64.68 (64.65)	4.86 (4.83)	15.88 (17581)	–	–
23	135	65	brownish powder	$C_{21}H_{19}ClN_4O_2$ 394.8	63.88 (63.87)	4.85 (4.87)	14.19 (14.15)	–	–
24	151	52	Brown crystals	$C_{21}H_{17}ClN_4O$ 376.84	66.93 (66.99)	4.55 (4.52)	14.87 (14.81)	–	–
24a	160	70	Reddish crystals	$C_{32}H_{27}ClIN_5O$ 659.94	58.24 (58.33)	4.12 (4.16)	10.61 (10.63)	396	3860
24b	145	79	Red crystals	$C_{32}H_{27}ClIN_5O$ 659.94	58.24 (58.23)	4.12 (4.15)	10.61 (10.60)	501	5104
24c	125	55	Reddish crystals	$C_{32}H_{27}ClIN_5O$ 659.94	58.24 (58.22)	4.12 (4.16)	10.61 (10.66)	468	4967
25a	155	35	Violet powder	$C_{33}H_{29}ClIN_5$ 657.97	60.24 (60.28)	4.44 (4.41)	10.64 (10.65)	513	4463
25b	158	52	Reddish crystals	$C_{29}H_{27}ClIN_5$ 607.91	57.30 (57.33)	4.48 (4.49)	11.52 (11.55)	489	959

B) Photophysical properties

1) Normalized absorption spectral behavior in EtOH

Dyes **(24a-c)** and **(25a, b)** are highly colored compounds. Their color in ethanolic solution are ranging from reddish to intense violet, easily (partially) soluble in polar (non) organic solvents exhibiting colored solutions (red/violet) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. The absorption spectra of **(24a-c)** and **(25a, b)** in 95% ethanol are depicted in **(Fig. 1)**. It was obvious that the absorption bands batho underwent (hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue A and their linkage position. Thus, the visible absorb-maximum of dye **24a** [A = pyridin-4-ium ethiodide] showed absorption band at (**24a;** λ_{max}=396 nm; ε_{max}=3860 $M^{-1}cm^{-1}$). Substitution of [A = pyridin-4-ium ethiodide] in dye **24a** by [A = quinolin-4-ium ethiodide] in dye **24b** showed absorption band at (**24b,** λ_{max}= 501 nm; ε_{max}=5104 $M^{-1}cm^{-1}$) which bathochromically shifted $\Delta\lambda_{max}$ = 105 nm. This is due to the more extensive π-delocalization and extra conjugation in the quinoline ring. Additionally, changing the linkage position of [A = quinolin-4-ium ethiodide] in 24**b** to the 1-ium analogue salt in **24c** exhibited (**24c**, λ_{max}=468 nm; ε_{max} = 4967 $M^{-1}cm^{-1}$) resulted in hypsochromic shift by $\Delta\lambda_{max}$ = 32 nm. This can be related to decreasing the length of conjugated π-delocalization in quinolin-1-ium dye **24c** than that for quinolin-4-ium analogous in dye **24b**. In addition, the visible absorb-maximum of dye **25a** showed absorption band at (**25a,** λ_{max}= 513 nm, ε_{max}= 4463 $M^{-1}cm^{-1}$) which bathochromically shifted $\Delta\lambda_{max}$ = 24 nm when changing the linkage position of [A = quinolin-4-ium ethiodide] in **25a** to the 1-ium analogue salt in 25bexhibited (λ_{max} =489 nm; ε_{max} =959 $M^{-1}cm^{2}$). This is due to the more extensive π-delocalization and extra conjugation in the quinoline ring.

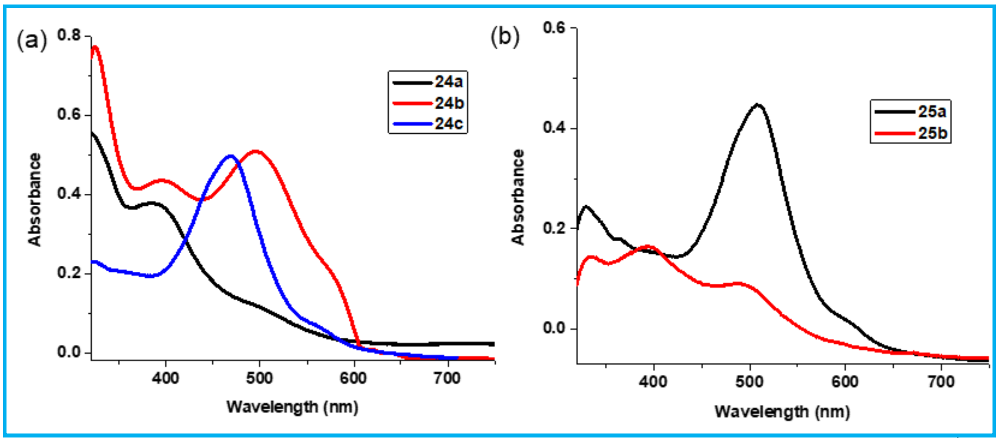


Fig. **1**. (a). UV-visible spectra of **24a-c** (b). UV-visible spectra of **25a, b** in ethanol (1x10^{-4} M).

2) Emission fluorescence spectra and excitation energy

The emission fluorescence spectra allowed transitions with a lifetime in the nanosecond range from higher to lower excited singlet states of molecules while fluorophores are also denoted as chromophores, historically speaking the part or moiety of a molecule responsible for its color. In addition, the denotation chromophore implies that the molecule absorbs light while fluorophore means that the molecule, likewise, emits light. The emission fluorescence spectra showed that the amount and wavelength of the emitted energy depend on both the fluorophore and the chemical environment of the fluorophore. The emission of the relaxed excited state relative to the ground state sometimes called the HOMO-LUMO gap was measured from the intersection of the normalized absorption and emission spectra of dyes **(24a-c)** and **(25a, b)**.The emission spectra for the dyes were recorded in 95 % ethanol and the results are depicted in,**(Fig. 2.)**and summarized in(Table **2**). We noticed that, dyes **24b** and **25a**achieved higher emission maxima compared to dyes **(24a, c)** and **(25b)** respectively. This change in the emission maxima and the excitation energy depend basically on the type of substituents and the nature of heterocyclic quaternary salt (A, B) which have a great effect on the number of π-conjugations in fluorophore.

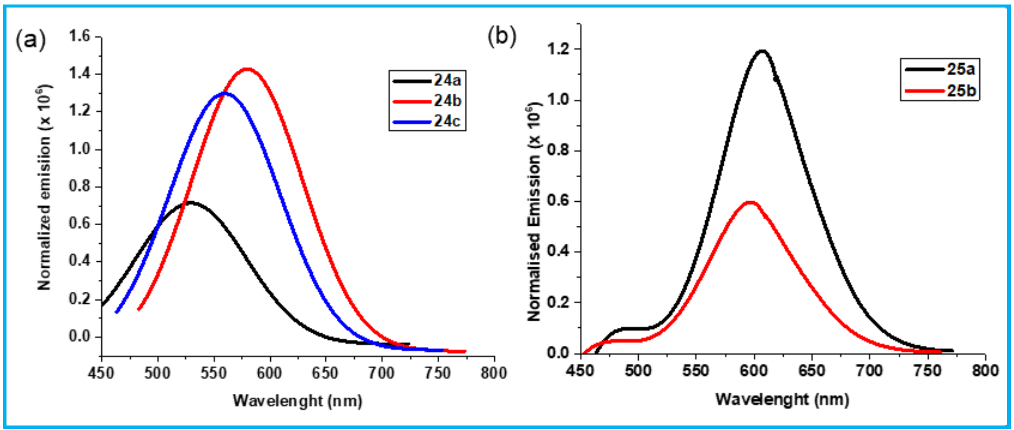


Fig. **2**. (a, b). Fluorescence spectra of **24a-c** and **25a, b** respectively in ethanol (1x10^{-4} M).

Dye	λ_{max}(nm)	ε_{max} ($M^{-1}cm^{-1}$)	E_{max} (nm)	Stock shift (nm)	I (nm)	E_{0-0} (ev)
24a	396	3860	529	133	462	2.68364
24b	501	5104	580	79	540	2.29600
24c	468	4967	560	92	514	2.41214
25a	513	4463	610	97	562	2.20612
25b	489	959	592	103	540	2.29600

Table **(2):** Summary of features for normalized absorption and emission spectra of compounds **4a-f**, **6, 7a-c** and **8a-c** in ($1x10^{-4}$ M) ethanol. Where, N (compound number), λ_{max}(maximum absorption wavelength), ε_{max} (Maximum molar extinction coefficient), E_{max}(maximum emission wavelength), I (intersection of absorption and emission spectra) and E_{0-0} (HOMO-LUMO gap).

3) Halochromic evaluation study and acid dissociation (pk_a)determination (Acid-Base properties)

This is a useful study for the spectral behavior of cyanine dyes in different aqueous universal buffer solution to ensure optimal pH in the application of these dyes as photosensitizers and to evaluate the possibility of uses and/or applications of these dyes as indicators in acid/base titrations in analytical chemistry. The effect of the dyes as photosensitizers increase when they are present in the ionic form (non-protonated form) which has higher polarity and therefore more conjugation [23]. We noticed that, the absorption spectra of dyes **24b** and **25a** in aqueous universal buffer solution in different values of pH **(2.5**, **4.5**, **5.5**, **7**, **8**, **9.3**, **10.6**, **11.9)** showed hypsochromic shift (negative halochromism) in the acidic medium due to the protonation of the heterocyclic nitrogen atom of heterocyclic quaternary salts and other lone pair of electron of non quaternize nitrogen atom of the donor part. In such cases the intramolecular charge transfer (CT) between the lone pair of heterocyclic donor nitrogen and the heterocyclic acceptor nitrogen atoms does not occur and the long wavelength CT band disappears as shown for dyes **24a-c** and **25a, b** in equation **1**. A new short wavelength band is observed which could be assigned to a localized π–π* transition as well as showed bathochromic shift (positive halochromism) with increasing the pH due to that the protonated dyes become deprotonated and intern support the lone pairs of electrons of the heterocyclic ring system and increase its mobility for mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated. The results are depicted in (Table **3)**,Fig. **3 (a, b)**.

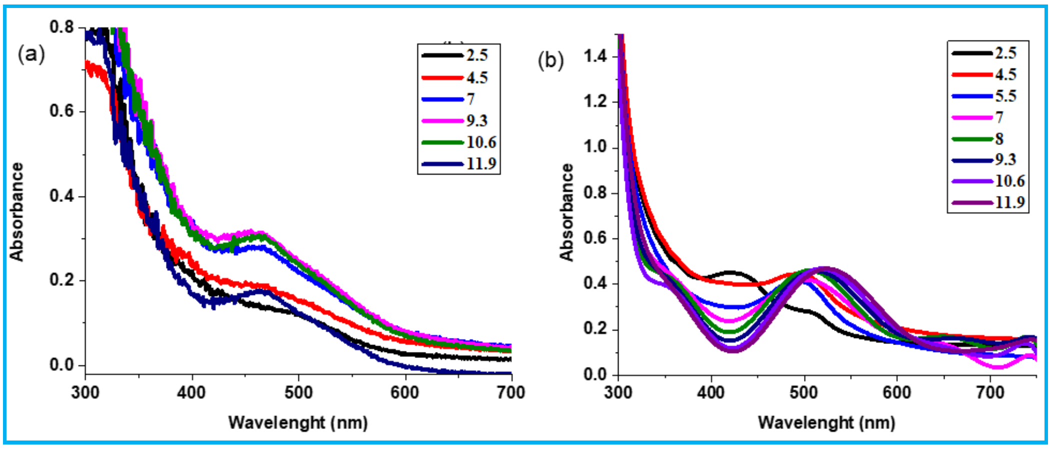
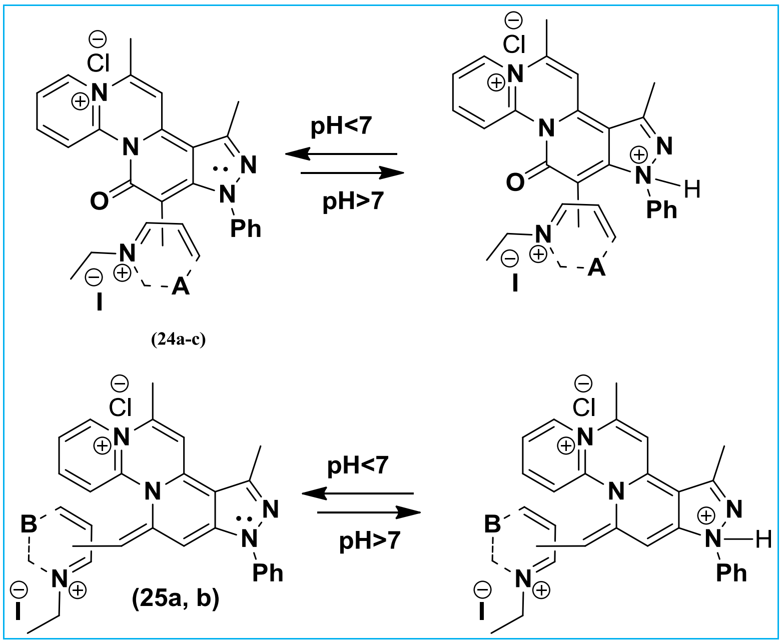


Fig. 3. (a, b): vis. spectra of dyes **(24b** and **25a)** respectively in aqueous universal buffer solutions

Table (3): Values of absorption (nm) and extinction coefficients ($M^{-1}cm^{-1}$) of dyes **24b** and **25a** in aqueous universal buffer solution.

Dye	**Universal buffer**															
	2.5		4.5		5.5		7		8		9.3		10.6		11.9	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
25a	424 503	4527 2827	492	4449	494	41505	500	4261	506	4638	515	4564	519	4715	523	4715
24b	-	-	465	1912	-	-	467	2791	-	-	466	3168	467	3067	469	1759



Eq. **1**. Protonation and deprotonation of dyes **(24a-c)** and **(25a, b)** in acidic and basic mediums respectively

V. CONCLUSION

Cyanine dyes of Zero/monomethine based on N-Bridgehead pyrazolo[4',3':3,4]pyrido[1,2-c]pyrido[1,2-a]pyrimidine heterocycle synthesized with absorption wavelength bands in the region of 400-550 nm. The easier of dye formation is due to that N-bridge head heterocyclic compound used as precursors possess high site reactivity susceptible to be attack by either Electrophile/ Nucleophile in the substitution/ addition reactions. The color of the fluorescence intensity of all dyes depend basically upon the type of dye and solvent used. the UV-Vis absorption spectra of the synthesized cyanine dyes give bathochromic or hypsochromic shifted bands depending on the following factors:a) Increasing and/or decreasing л-delocalization conjugation in the dye moleculeb) Presence of electron pushing and/or electron pulling groupsc) Higher and/or lower planarity of the dye molecule d) The intensity of the color of the synthesized cyanine dyes is due to two suggested mesomeric structures producing a delocalized positive charge over the conjugated system**.**

VI. Acknowledgments

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