

# SYNTHESIS & PHOTOPHYSICAL CHARACTERISTICS OF MULTI-SELF-ASSEMBLY [ICT] HETEROCYCLIC QUINONE FUNCTIONAL & RELATED CYANINES

*Ahmed I. M. Koraiem*

*Chemistry Department, Aswan Faculty of Science, Aswan University, Aswan, 81528, Egypt*

## **ABSTRACT**

Some novel multi self-assembly [ICT] functional & their cyanines incorporating benzo[g]indolizino [1,2-c] quinolin-12-ium iodide (**4a-d**, **5a-d**, **6a-f** & **7a-f**) were prepared via one-pot synthesis based on 1-(2-(3-amino-1, 4-dioxo-1,4-di[H] naphthalen-2-yl)-1-(1-ethyl-pyridin[quinolin-4(1)]-1-ium)-2-oxo-ethyl)-2-methyl-pyridin(quinolin)-1-ium iodide (**2a-d** & **3a-d**). The new synthesized multi 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 to investigate their photophysical characteristics.

**Keywords:** heterocyclic quinone functional & related cyanines, Synthesis, Spectral Behaviour

## **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 [1-3] solar cells, etc [4] 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. Multi self-assembly of intramolecular charge-Transfer compounds into functional molecular systems [5a,b] 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 [6,7]. To date, multi self-assembly process for obtaining organic nanomaterials is still highly desirable for the advancement of organic nanoscience (technology).[8a,b]. Thus, the choice of materials based on the predication of structure–property relationships shows important significance in this field.

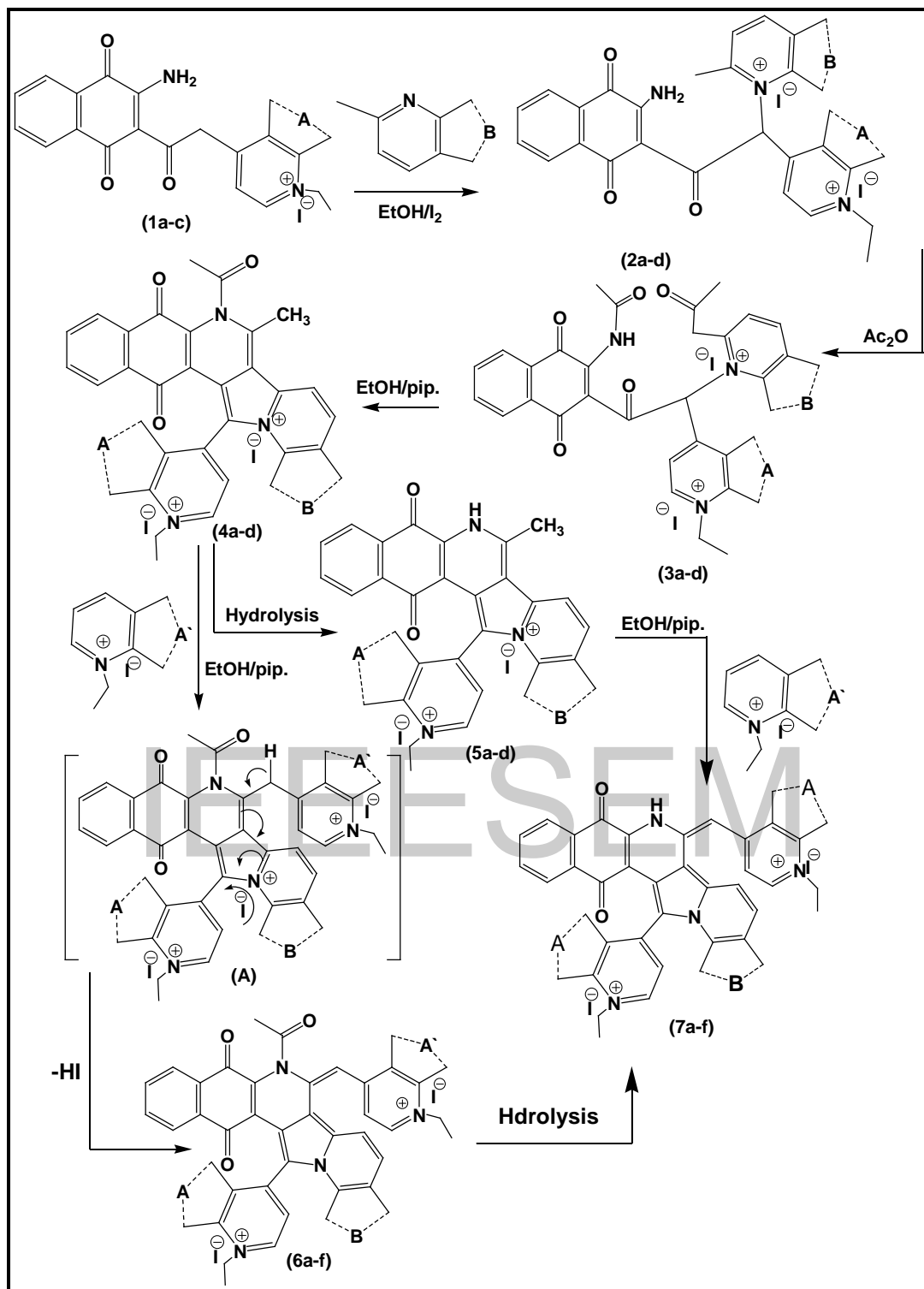
## **2. RESULTS AND DISCUSSION**

### **2.1. SYNTHESIS**

As an extension to our previous work on the synthesis of multi self-assembly N-bridge head heterocyclic [ICT]functional & cyanine dyes [9, 10 & 11a,b], some novel self-assembly heterocyclic quinone [ICT] functional & related cyanine dyes (**4a-d,5a-d, 6a-f & 7a-f**) incorporating benzo[g]indolizino [1,2-c] quinolin-12-ium iodide (**4a-d**), benzo[g]indolizino[1,2-c] quinolin-12-ium-iodide, (**5a-d**), benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine, (**6a-f**) & benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine (**7a-f**) were synthesised via one-pot synthesis based on 1-(2-(3-amino-1, 4-dioxo-1,4-di[H]naphthalen-2-yl)-1-(1-ethyl-pyridin[quinolin-4(1)]-1-ium)-2-oxo-ethyl)-2-methyl-pyridin(quinolin)-1-ium-iodide (**2a-c**) & 1-(2-(1,4-dioxo-3-(prop-1-en-2-ylamino)-1,4-di[H] naphthalen-2-yl)-1-(1-ethyl-pyridin[(quinolin-4(1)]-1-ium-4-yl)-2-oxo-ethyl)-2-(2-oxo-propyl) pyridin (quinolin)-1-ium, (**3a-c**). Thus, the interaction of ethanolic solution of 4-(2-(3-amino-1,4-di-oxo-1,4-di[H]naphthalen-2-yl)-2-oxo-ethyl)-1-ethyl-pyridin [quinolin-4(1)]-1-ium iodide (**1a-c**) with 2-methyl-pyridine (quinoline), in equimolar ratio, under iodine resulted in 1-(2-(3-amino-1, 4-dioxo-1,4-di[H]naphthalen-2-yl)-1-(1-ethyl-pyridin[quinolin-4(1)]-1-ium)-2-oxo-ethyl)-2-methyl-pyridin(quinolin)-1-ium iodide (**2a-d**). Acetylation of (**2a-d**) using acetic anhydride as catalysis afforded 1-(2-(1,4-dioxo-3-(prop-1-en-2-ylamino)-1,4-di[H]naphthalen-2-yl)-1-(1-ethyl-pyridin[(quinolin-4(1)]-1-ium-4-yl)-2-oxo-ethyl)-2-(2-oxo-propyl)pyridin (quinolin)-1-ium (**3a-d**). Intramolecular hetero- cyclization or ring closure of (**3a,b**), in equimolar amount, under piperidine catalysis afforded multi self-assembly heterocyclic [ICT]functional dyes, 6-acetyl-7-methyl-5, 14-di-oxo-6, 14-di[H]-5H-benzo[g]indolizino [1,2-c] quinolin-12-ium iodide-zero-13[4(1)]methine cyanine dyes (**4a-d**) The later multi self-assembly {ICT} functional dyes (**4a-d**) on hydrolysis using NaOH solution afforded multi self-assembly {ICT}

functional dyes 13-(1-ethyl-pyridin-1-ium-4-yl)-7-methyl-5,14-dioxo-6,14-di[H]-5H-benzo[g] indolizino [1,2-c]quinolin-12-ium iodide-zero-13[4(1)]methine cyanine dyes **(5a-d)**. The latter two dyes **(4,5a-d)** were characterized by the multi-charge transfer from N-acetyl or NH groups incorporate in benzo[g]indolizino [1,2-c] quinolin-12-ium iodide as electron source towards either heterocyclic quaternary salts **(A)** or Benzo (g) indolizin-ium iodides as electron sink. The reaction of **(4a-d or 5a-d)** with N-ethyl-pyridin (quinolin)-4(1)-ium-ethyl iodide salts, in equimolar ratio, under piperidine catalysis afforded 4-(6-acetyl-5, 14-dioxo-6, 14-di[H]benzo [g] indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine **(6a-f)** and/or 5, 14-dioxo-5,6,7,14-tetra[H]benzo[g] indolizino [1,2-c]quinolin-7(5H) mono-[4(1)]-zero-13[4(1)]methine **(7a-f)** respectively. The reaction was conducted via an oxidative elimination between N-ethyl-pyridin (quinolin)-4(1)-ium-ethyl iodide salts and active hyper-conjugated methyl group in conjugation with benzo[g]indolizino [1,2-c]quinolin-12-ium iodide salts to form the intermediates **(A, B)** followed by elimination of hydrogen iodide to give the desired dyes **(6a-f & 7a-f)**, **Scheme (1)**.

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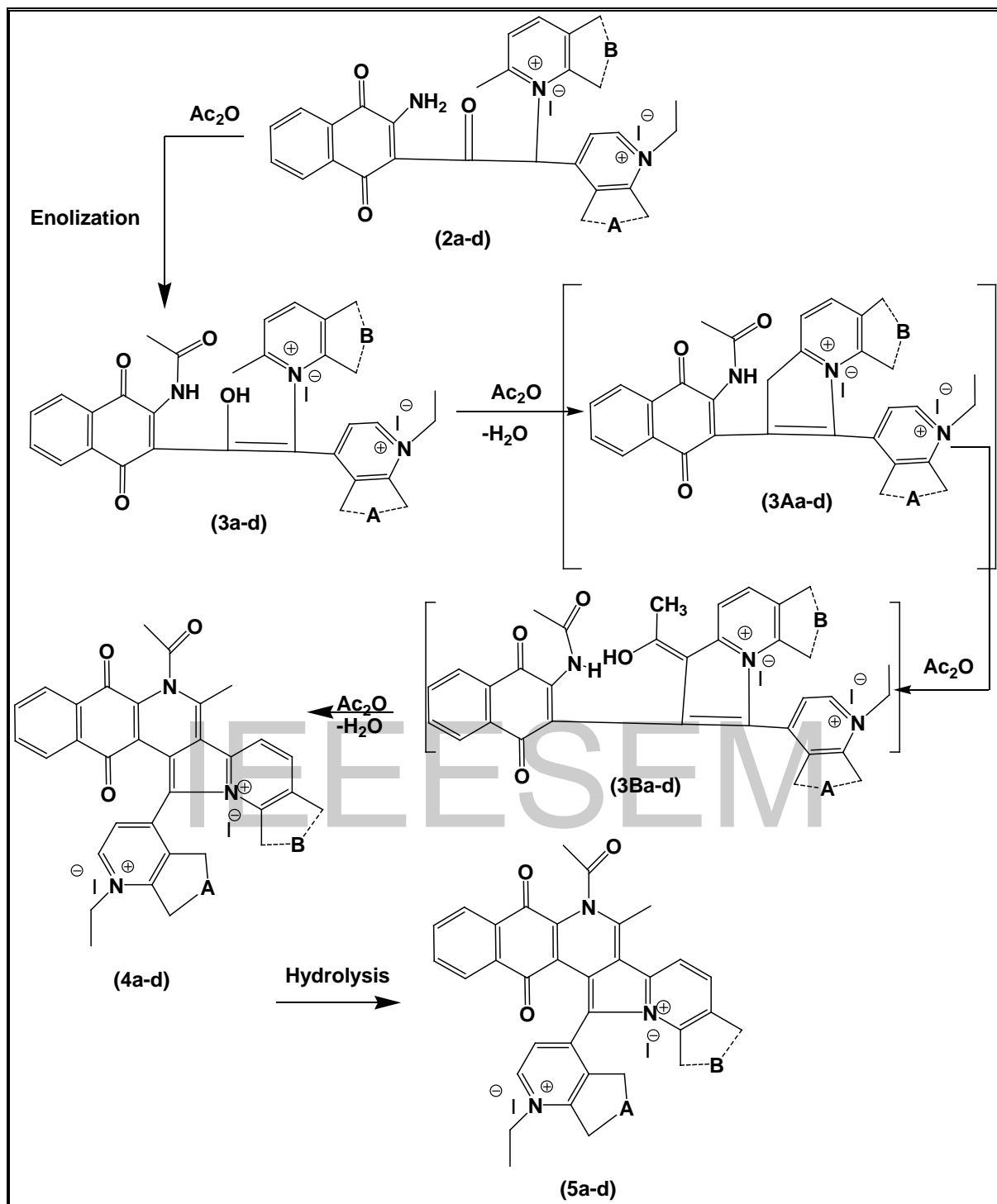
**Scheme (1)**

**Scheme (1) Substituents**

(2,3a-c), A(B)=pyridin-4-ium(2-methyl-quinolin-1-ium) (a), A(B)=quinolin-4-ium-, (2-methyl-quinolin-1-ium) (b), A(B)=quinolin-1-ium(2-methyl-quinolin-1-ium) (c), A(B)=quinolin-4-ium,(2-methyl-pyridin-1-ium),(d). (4,5a-d), A(B)=pyridin-4-ium (quinolin-1-ium) (a), A(B)=quinolin-4-ium (quinolin-1-ium) (b), A(B)=quinolin-1-ium

(quinolin-1-ium),(c),A(B)=quinolin-4-ium(pyridin-1-ium),(d)., **(6,7a-f)**, A [A` (B)] pyridin-4-ium[quinolin-4-ium(quinolin-1-ium)](a), A[A` (B)]quinolin-4-ium, [quinolin-4-ium(quinolin-1-ium)](b),A[A` (B)]quinolin-1-ium[quinolin-4-ium, (quinolin-1-ium)] (c), A [A` (B)] quinolin-4-ium[quinolin-4-ium (pyridin-1-ium)] (d), A [A` (B)]quinolin-4-ium,[pyridin-4-ium(quinolin-1-ium)](e),A[A` (B)]quinolin-4-ium[quinolin-1-ium (quinolin-1-ium)] (f). The formation of multi 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] and 13-(1-ethyl-pyridin-1-ium-4-yl)-7-methyl-5,14-dioxo-6,14-di[H]-5H-benzo[g] indolizino [1,2-c]quinolin-12-ium iodide-zero-13[4(1)]methine cyanine dyes cyanine dye **(4a-d, 5a-d)** was suggested to proceed via acetylation process of amino group flowingly of enolization process to afford **(3a-d)**. Further **Ac<sub>2</sub>O** leads to heterocyclization & ring closure for the enolate **(3a-d)** to give the intermediates **(3Aa-d)** flowingly acetylation to give intermediates **(3Ba-d)**. Extra heterocyclization & ring closure of **(3Ba-d)** via elimination of water molecule **(-H<sub>2</sub>O)** process afforded **(4a-d)**, which give directly under effect of water molecules **(5a-d)**, **Equation (1)**.

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Equation (1)

The structure of (2b, 3b, 4b, 5b & 6b, 7b) was confirmed by elemental and spectral analysis, Tables (1-3), [13, 14, and 15]...

## 2.2. COLOUR & SPECTRAL BEHAVIOUR

Benzo[g]indolizino [1,2-c] quinolin-12-ium iodide-zero-13[4(1)]methine (4a-d), benzo[g]indolizino[1,2-c]quinolin-12-ium-iodide-zero-13[4(1)]methine (5a-d), benzo [g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine (6a-f) & benzo [g]

indolizino [1,2-c]quinolin- 7(5H) mono-[4(1)]-zero-13[4(1)]methine (**7a -f**) are highly coloured compounds ranging from brownish-red / red, dark brown / deep violet (blue). They are partially soluble in non-polar solvents and easily soluble in polar solvents exhibiting highly coloured solutions with slight or intense green fluorescence depending upon the incorporating anhydro base of N-bridge head heterobicyclic moieties or heterocyclic quaternary residue. Compounds (**4,5a-d, 6a-f & 7a -f**) are highly soluble in concentrated sulphuric acid liberating iodine vapour on warming. Their ethanolic solution turned yellow or became colourless on acidification, while their permanent colour was restored on basification. The absorption spectra of benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine (**4a-d**) in 95% ethanol showed absorption bands batho- chromically (hypsochromically) shifted depending upon the nature of heterocyclic quaternary residue **A(B)**, their linkage position. Thus, the absorption spectra of dye [**4a**, A (B) = pyridin-4-ium (quinolin-1-ium)] showed  $\lambda_{\max}$  455,370 nm ( $\epsilon_{\max}$ , 2000,4000 mol<sup>-1</sup>cm<sup>2</sup>). Substituting of **A(B)** = pyridin-4-ium(quinolin-1-ium) in dye (**4a**) by **A (B)**= quinolin-4-ium(quinolin-1-ium) in dye (**4b**) resulted in bathochromically shifted by (5-10 nm) than (**4a**) [**4b**,  $\lambda_{\max}$  465, 375 nm,  $\epsilon_{\max}$ , 8800,8400 mol<sup>-1</sup>cm<sup>2</sup>]. This is due to the more extensive  $\pi$ -delocalization within benzene ring attached to pyridine ring in dye (**4b**). Substituting of **A (B)** = quinolin-4-ium (quinolin-1-ium) in dye (**4b**) by **A (B)** = quinolin-1-ium (quinolin-1-ium) in dye (**4c**) causes hypso-chromically shifted of 5nm than (**4b**) [**4c**,  $\lambda_{\max}$  460,373 nm  $\epsilon_{\max}$ , 4000,7400 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to an easier charge transfer within extended  $\pi$ -delocalization of 4-ium salt rather than 1-ium **Table (2)**. Substituting **A (B)** =quinolin-4-ium (quinolin-1-ium) in dye (**4b**) by A (B) =quinolin-4-ium (pyridin-1-ium) in dye (**4d**) move the absorption bands towards batho- chromic shift by10 nm than (**4b**). [**4d**,  $\lambda_{\max}$  475 nm  $\epsilon_{\max}$ , 13200 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to that inserting of ring causes the more extensive  $\pi$ -delocalization and extra conjugation, so the absorption takes place at longer wavelength, **Table (2)**. The absorption spectra of benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine (**5a-d**) in 95% ethanol showed absorption bands batho- chromically (hypsochromically) shifted depending upon the nature of heterocyclic quaternary residue **A(B)**, their linkage position. Thus, the absorption spectra of dye [**5a**, A (B) =pyridin-4-ium (quinolin-1-ium)] showed  $\lambda_{\max}$  510,445,415 nm ( $\epsilon_{\max}$ , 6000, 8000, 9600 mol<sup>-1</sup> cm<sup>2</sup>). Substituting of **A (B)** = pyridin-4-ium (quinolin-1-ium) in dye (**5a**) by **A (B)** =quinolin-4-ium(quinolin-

1-ium) in dye **(5b)** resulted in bathochromically shifted by (80nm) than **(5a)** [**5b**,  $\lambda_{\max}$  660, 570, 470, 435 nm,  $\epsilon_{\max}$ , 2400,5400,7800,8800 mol<sup>-1</sup>cm<sup>2</sup>]. This is due to the more extensive  $\pi$ -delocalization within benzene ring attached to pyridine ring in dye **(5b)**. Substituting of **A (B)** =quinolin-4-ium (quinolin-1-ium) in dye **(5b)** by **A (B)** = quinolin-1-ium (quinolin-1-ium) in dye **(5c)** causes hypso- chromically shifted of 45nm than **(5b)** [**5c**,  $\lambda_{\max}$  512,450 nm  $\epsilon_{\max}$ , 6800,14000 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to an easier charge transfer within extended  $\pi$ -delocalization of 4-ium salt rather than 1-ium

**Table (3)**. Substituting **A (B)** =quinolin-4-ium (quinolin-1-ium) in dye **(5b)** by **A (B)** =quinolin-4-ium (pyridin-1-ium) in dye **(5d)** move the absorption bands towards bathochromic shift by10nm than **(5b)**. [**5d**,  $\lambda_{\max}$  690, 595, 560,400nm  $\epsilon_{\max}$ , 3200,12800,11400,9600 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to that inserting of ring causes the more extensive  $\pi$ -delocalization and extra conjugation, so the absorption takes place at longer wavelength, **Table (2)**. The absorption spectra of benzo [g] indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine **(6a-f)** in 95% ethanol showed absorption bands bathochromically (hypsochromically) shifted depending upon the nature of heterocyclic quaternary residue **A[A` (B)]**, their linkage position. Thus, the absorption spectra of dye **[6a, A [A` (B)]** pyridin-4-ium [quinolin-4-ium (quinolin-1-ium)] showed  $\lambda_{\max}$  610, 380 nm ( $\epsilon_{\max}$ , 1800,9800 mol<sup>-1</sup> cm<sup>2</sup>). Substituting of **A[A` (B)]**pyridin-4-ium[quinolin-4-ium (quinolin-1-ium)] in dye **(6a)** by **A[A` (B)]**quinolin-4-ium[quinolin-4-ium (quinolin-1-ium)] in dye **(6b)** resulted in bathochromically shifted by (80nm) than **(6a)** [**6b**,  $\lambda_{\max}$  690,575,460,  $\epsilon_{\max}$ , 2900,6000,4200 mol<sup>-1</sup>cm<sup>2</sup>]. This is due to the more extensive  $\pi$ -delocalization within benzene ring attached to pyridine ring in dye **(6b)**. Substituting of **A [A` (B)]** quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)] in dye **(6b)** by **A[A` (B)]** quinolin-1-ium[quinolin-4-ium, (quinolin-1-ium)] in dye **(6c)** causes hypsochromically shifted of 45nm than **(6b)** [**6c**,  $\lambda_{\max}$  635sh,465,390 nm  $\epsilon_{\max}$ , 2500,2000, 7000 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to an easier charge transfer within extended  $\pi$ -delocalization of 4-ium salt rather than 1-ium

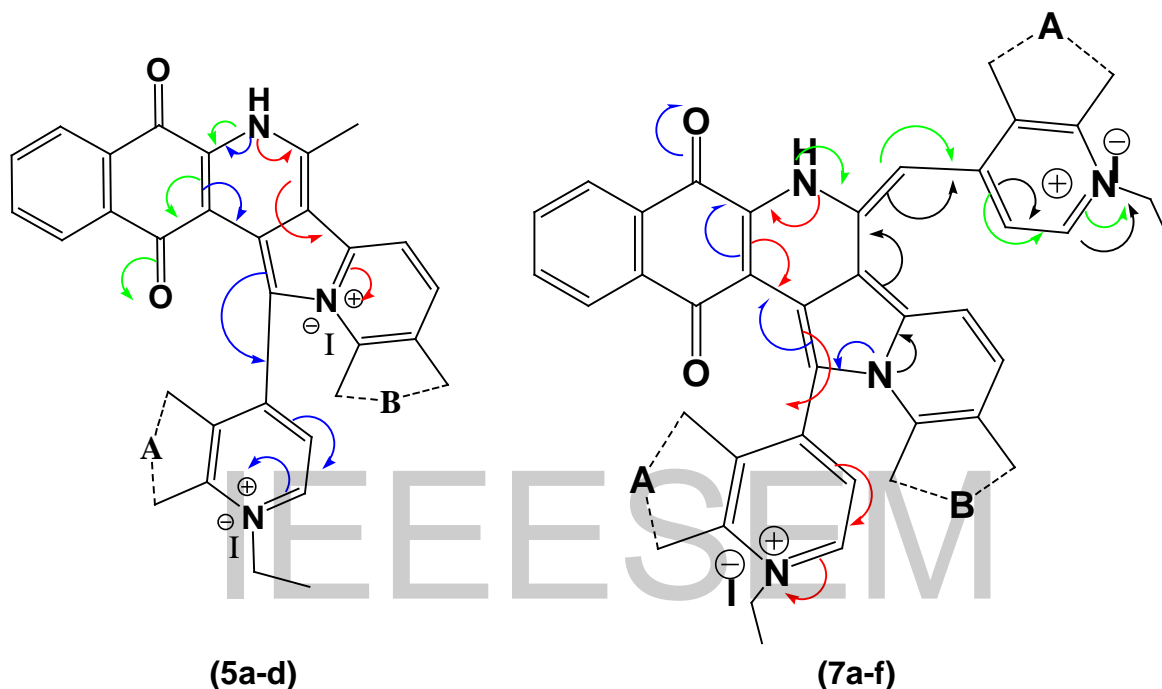
**Table (3)**. Substituting **A [A` (B)]** quinolin-4-ium [quinolin-4-ium (quinolin-1-ium)] in dye **(6b)** by **A [A` (B)]**quinolin-4-ium[quinolin-4-ium(pyridin-1-ium)] in dye **(6d)** move the absorption bands towards bathochromic shift by10nm than **(6b)**. [**6d**,  $\lambda_{\max}$  700, 600, 470 nm  $\epsilon_{\max}$ , 2600,4600,10800 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to that inserting of ring causes the more extensive  $\pi$ -delocalization and extra conjugation, so the absorption takes place at longer wavelength, **Table (3)**. The absorption spectra of **(6e,f)** in 95%



ethanol showed absorption bands at **[6e]**, A [A` (B)] quinolin-4-ium, [pyridin-4-ium (quinolin-1-ium)] (**6e**,  $\lambda_{\max}$  470,335 nm,  $\epsilon_{\max}$ , 3500, 5500 mol<sup>-1</sup> cm<sup>2</sup>), **[6f]**, A[A` (B)] quinolin-4-ium [quinolin-1-ium (quinolin-1-ium)] [**6f**,  $\lambda_{\max}$  500 nm,  $\epsilon_{\max}$ , 13000 mol<sup>-1</sup> cm<sup>2</sup>]. It was obvious that the absorption spectra of (**6f**) showed absorption bands bathochromically shifted by (30nm) than (**6e**) and absorb in the green-blue light region. This is due to the extensive of  $\pi$ -delocalization and an increasing in conjugation within quinolin-1-ium resulted in a charge transfer from ring junction N-bridge atom towards N-heterocyclic quaternary residue. The absorption spectra of benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)] methine (**7a-f**) in 95% ethanol showed absorption bands bathochromically (hypsochromically) shifted depending upon the nature of heterocyclic quaternary residue **A[A` (B)]**, their linkage position. Thus, the absorption spectra of dye **[7a]**, A [A` (B)] pyridin-4-ium [quinolin-4-ium (quinolin-1-ium)] showed  $\lambda_{\max}$  620, 390nm (  $\epsilon_{\max}$ , 1800, 1000 mol<sup>-1</sup> cm<sup>2</sup>). Substituting of **A[A` (B)]** pyridin-4-ium[quinolin-4-ium(quinolin-1-ium)] in dye (**7a**) by **A [A` (B)]** quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)] in dye (**7b**) resulted in bathochromically shifted by (70nm) than (**7a**) [**7b**,  $\lambda_{\max}$  690, 585, 470,  $\epsilon_{\max}$ , (36000), (50000) (50000) mol<sup>-1</sup> cm<sup>2</sup>]. This is due to the more extensive  $\pi$ -delocalization within benzene ring attached to pyridine ring in dye (**7b**). Substituting of A [A` (B)] quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)] in dye (**7b**) by A[A` (B)] quinolin-1-ium[quinolin-4-ium, (quinolin-1-ium)] in dye (**7c**) causes hypsochromically shifted of 45nm than (**7b**) [**7c**,  $\lambda_{\max}$  645sh, 475, 400 nm  $\epsilon_{\max}$ , 7000 ,13500 , 7100 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to an easier charge transfer within extended  $\pi$ -delocalization of 4-ium salt rather than 1-ium **Table (3)**. Substituting A [A` (B)] quinolin-4-ium [quinolin-4-ium(quinolin-1-ium)] in dye (**7b**) by A [A` (B)]quinolin-4-ium, [quinolin-4-ium(pyridin-1-ium)] in dye (**7d**) move the absorption bands towards bathochromic shift by10nm than (**7b**). [**7d**,  $\lambda_{\max}$  700, 620,490 nm  $\epsilon_{\max}$ , (5000, 7500, 10800 mol<sup>-1</sup> cm<sup>2</sup>). This is due to that inserting of ring causes the more extensive  $\pi$ -delocalization and extra conjugation, so the absorption takes place at longer wavelength, **Table (3)**. The absorption spectra of (**7e,f**) in 95% ethanol showed absorption bands at **[7e]**, A [A` (B)] quinolin-4-ium, [pyridin-4-ium (quinolin-1-ium)] ( $\lambda_{\max}$  480, 355 nm,  $\epsilon_{\max}$ , 3500, 5000 mol<sup>-1</sup> cm<sup>2</sup>), **[7f]**, A[A` (B)] quinolin-4-ium [quinolin-1-ium (quinolin-1-ium)]  $\lambda_{\max}$  520 nm,  $\epsilon_{\max}$ , 5500 mol<sup>-1</sup> cm<sup>2</sup>]. It was obvious that the absorption spectra of (**7f**) showed absorption bands bathochromically shifted by (40nm) than (**7e**) and absorb in the green-blue light

region. This is due to the extensive of  $\pi$ -delocalization and an increasing in conjugation within quinolin-1-ium resulted in a charge transfer from ring junction N-bridge atom towards N-heterocyclic quaternary residue. On comparison of the absorption spectra of dyes (**6d**, **7d**), it was obvious that the absorption bands of [**7b**,  $\lambda_{\max}$  700, 620, 490 nm  $\epsilon_{\max}$ , (5000, 7500, 10800 mol<sup>-1</sup> cm<sup>2</sup>)] move to bathochromic shift of 20nm than those of [**6d**,  $\lambda_{\max}$  700, 600, 470 nm  $\epsilon_{\max}$ , 2600, 4600, 10800 mol<sup>-1</sup> cm<sup>2</sup>], **Table (3)**. This is due to that the ring junction nitrogen atom in the former dye affected on the charge transfer by both electron releasing inductive and mesomeric effects better than those of the latter dye in which the ring junction nitrogen atom represents as electron withdrawing character (electron withdrawing inductive effect) due to its neighboring. Additionally, the former dye incorporates an endocyclic quinoid structure causes an increasing in  $\pi$ -delocalization better than the latter dye incorporating an exocyclic quinoid analogous. **Table (3)**. On comparison of the absorption spectra of dyes (**5a-d**, **7a-f**), it was obvious, that the absorption spectra of (**7e,f**) in 95% ethanol showed absorption bands in of great values  $\lambda_{\max}$  and  $\epsilon_{\max}$  than those of (**5a-d**). This is due to of the more multi internal charge transfer pathways of (**7a-f**) than those of (**5a-d**), as was observed in **Equation (2)**, at [**7e**, A [A` (B)] quinolin-4-ium, [pyridin-4-ium (quinolin-1-ium)] ( $\lambda_{\max}$  480, 355 nm,  $\epsilon_{\max}$ , 3500, 5000 mol<sup>-1</sup> cm<sup>2</sup>), [**7f**, A[A` (B)] quinolin-4-ium [quinolin-1-ium (quinolin-1-ium)]  $\lambda_{\max}$  520 nm,  $\epsilon_{\max}$ , 5500 mol<sup>-1</sup> cm<sup>2</sup>]. It was obvious that the absorption spectra of (**7f**) showed absorption bands bathochromically shifted by (40nm) than (**7e**) and absorb in the green-blue light region. This is due to the extensive of  $\pi$ -delocalization and an increasing in conjugation within quinolin-1-ium resulted in a charge transfer from ring junction N-bridge atom towards N-heterocyclic quaternary residue. Meanwhile, the absorption spectra of dye [**5a**, A (B) =pyridin-4-ium (quinolin-1-ium) showed  $\lambda_{\max}$  510, 445, 415 nm ( $\epsilon_{\max}$ , 6000, 8000, 9600 mol<sup>-1</sup> cm<sup>2</sup>). Substituting of **A (B)** = pyridin-4-ium (quinolin-1-ium) in dye (**5a**) by **A (B)** =quinolin-4-ium(quinolin-1-ium) in dye (**5b**) resulted in bathochromically shifted by (80nm) than (**5a**) [**5b**,  $\lambda_{\max}$  660, 570, 470, 435 nm,  $\epsilon_{\max}$ , 2400, 5400, 7800, 8800 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to the more extensive  $\pi$ -delocalization within benzene ring attached to pyridine ring in dye (**5b**). Substituting of **A (B)** =quinolin-4-ium (quinolin-1-ium) in dye (**5b**) by **A (B)** = quinolin-1-ium (quinolin-1-ium) in dye (**5c**) causes hypso- chromically shifted of 45nm than (**5b**) [**5c**,  $\lambda_{\max}$  512, 450 nm  $\epsilon_{\max}$ , 6800, 14000 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to an easier charge

transfer within extended  $\pi$ -delocalization of 4-ium salt rather than 1-ium **Table (3)**. Substituting **A (B)** =quinolin-4-ium (quinolin-1-ium) in dye **(5b)** by A (B) =quinolin-4-ium (pyridin-1-ium) in dye **(5d)** move the absorption bands towards bathochromic shift by 10nm than **(5b)**. [**5d**,  $\lambda_{\max}$  690, 595, 560, 400nm  $\epsilon_{\max}$ , 3200, 12800, 11400, 9600 mol<sup>-1</sup> cm<sup>2</sup>]. This is due to that inserting of ring causes the more extensive  $\pi$ -delocalization and extra conjugation, so the absorption takes place at longer wavelength, **Table (4)**.



#### Equation (2): Internal Charge Transfer Pathways of (5a-d and 7a-f)

The high absorption spectra of **(5a-d)** value range  $\lambda_{\max}$  n.m 510,445,415, 660,570,470,435,512, 450, 690,595,560,400  $\epsilon_{\max}$  (6000), (8000), (9600), (2400), (5400),(7800),(8800),(6800),(14000),(3200),(12800),(11400),(9600) mol<sup>-1</sup> cm<sup>2</sup> **Table (3)**, is due to the interpretation of multi **[ICT]** pathways of **(7a-d)** is due to the different orientation of the internal charge transfer for more directions, it is from the direction of multi **[ICT]** internal charges is from NH of piperidine nuclei as electron source towards heterocyclic quaternary salts as electron sink of zero methine cyanine type, as was represents with blue arrows colour or from NH of piperidine nuclei as electron source towards either naphtho quinone cyclic carbonyl, as was represents with green arrows colour or towards Benz indolizinium iodide, as was represents with red arrows colour as electron sink.

Meanwhile, the high absorption spectra of **(7a-f)** value range at  $\lambda_{\max}$  nm 390-620, 470-690, 400-645, 490-700, 355-480, 520,  $\epsilon_{\max}$  (1000, 36000, 50000, 50000, 7000, 13500, 5000, 7500, 3500, 5000, 5500, 7900, 7900)  $\text{mol}^{-1} \text{cm}^2$  **Table (3)**, is due to the interpretation of multi **[ICT]** of **(7a-d)** is due to the different orientation of the internal charge transfer for more directions, it is from the N-bridge head of indolizine nuclei as electron source either towards cyclic carbonyl group of quinoid as electron sink, as was represents with blue arrows colour, or towards heterocyclic quaternary salts as electron sink of mono methine cyanine type, as was represents with black arrows colour. The other direction of multi **[ICT]** internal charges is from NH of piperidine nuclei as electron source towards heterocyclic quaternary salts as electron sink of zero methine cyanine type, as was represents with red arrows colour or towards heterocyclic quaternary salts as electron sink of mono methine cyanine type, as was represents with green arrows colour. The calculations and computational studies including **HOMO-LOMO** of **(5a-d & 7a-f)** were under investigation to elucidate such activities by one of my colleagues in future.

### **3. EXPERIMENTAL**

All melting points are uncorrected. Elemental analysis were carried out at the micro analytical centre (Cairo-university). The IR spectra were determined with perkin elmer infrared 127B spectrophotometer (Cairo– University). The  $^1\text{H-NMR}$  spectra were recorded with EM-390 90 MHz NMR spectrophotometer. (Cairo– University). Mass spectra were recorded on a Hp Ms 6488 spectrometer. The visible were recorded on UV-visible recording spectrophotometer UV-240 and UV-160 A. Faculty of Science Aswan 4-(2-(3-amino-1, 4-di-oxo-1,4-di[H] naphthalen-2-yl)-2-oxo-ethyl)-1-ethyl-pyridin[quinolin-4(1)]-1-ium iodide **(1a-c)** was prepared in a way that described in prospective reference [12].

#### **3.1. Synthesis of 1-(2-(3-amino-1, 4-dioxo-1, 4-di [H]naphthalen-2-yl)-1-(1-ethyl-pyridin [quinolin-4(1)]-1-ium)-2-oxo-ethyl)-2-methyl-pyridin (quinolin)-1-ium iodide, (2a-c).**

An ethanolic solution of **(1a, b,** and 0.01mol) and 2-methyl-pyridin [quinoline]-bases (0.01mol) in iodine was refluxed for 3-5 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 give **(2a-c), Table (1).**

IR (KBr  $\text{cm}^{-1}$ ) of **(2b)** showed general absorption peaks at  $2890 \text{ cm}^{-1}$  (ylide anion),  $2921\text{-}2933 \text{ cm}^{-1}$  ( $\gamma$  H-Q-salt),  $3150\text{-}3000 \text{ cm}^{-1}$  ( $\gamma$  C-H,  $\gamma$  N-methyl-pyridinium iodide),  $1715\text{-}1730 \text{ cm}^{-1}$  ( $\gamma$  acyclic C=O),  $1600 \text{ cm}^{-1}$  ( $\gamma$  C=C conj. Cyclic),  $3350\text{-}3310 \text{ cm}^{-1}$ , ( $\gamma$  N-H, stretch primary amine), and ( $\gamma$  N-H str., pyridinium ion),  $1631\text{-}1625 \text{ cm}^{-1}$  ( $\gamma$  quaternary pyridine),  $1631\text{-}1625 \text{ cm}^{-1}$ . ( $\gamma$  pyridinium salts),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C str. pyridinium salts),  $1715 \text{ cm}^{-1}$  ( $\gamma$  quinoid cyclic C=O,  $3150\text{-}3000 \text{ cm}^{-1}$  ( $\gamma$  C-H.  $\gamma$  N-ethyl-pyridinium iodide),  $3037\text{-}3144 \text{ cm}^{-1}$  ( $\gamma$  pyridinium quaternary),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C str. pyridinium salts),  $3037\text{-}3144 \text{ cm}^{-1}$  (quaternary salts),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C-alkyl str. pyridinium salts), Characteristic strong  $1631\text{-}625 \text{ cm}^{-1}$  ( $\gamma$  C=N of heterocyclic quaternary nitrogen atom or ring vibrations of pyridinium ion) [13]...  $^1\text{H-NMR}$  (DMSO, 300 MHz) of selected **(2b)** showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  7.67-8.90 ppm (m, 6H, quinolin-4-ium),  $\delta$  8.10-9.11 ppm (m, 6H, quinolin-1-ium),  $\delta$  1.57 ppm (t, 3H,  $\text{CH}_3$ ),  $\delta$  4.80 ppm (q, 2H,  $\text{CH}_2$ ), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH),  $\delta$  2.92 ppm (s, 3H,  $\text{CH}_3$ ) &  $\delta$  4.79 ppm (s, 2H,  $\text{NH}_2$ ) [14,15].. Mass spectrum of **(2b)** reveals a molecular ion, peaks at  $m/z = 766$  and base peak at  $m/z = 200$  [16].

### **3.2. Synthesis of 1-(2-(1,4-dioxo-3-(prop-1-en-2-ylamino)-1,4-dihydro)naphthalen-2-yl)-1-(1-ethyl-pyridin[quinolin-4(1)]-1-ium-4-yl)-2-oxo-ethyl)-2-(2-oxo-propyl)pyridin (quinolin)-1-ium, (3a-d)**

A 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. The filtrate was concentrated and cooled concentrated to one third of its volume, cooled and precipitated by adding of ice-water mixture to give **(3a-d), Table (1)**. IR (KBr  $\text{cm}^{-1}$ ) of **(3b)** showed in addition to general absorption peaks cited for **(2b)**, characteristic absorption peaks at  $1712 \text{ cm}^{-1}$  ( $\gamma$   $\text{COCH}_3$ ),  $1640 \text{ cm}^{-1}$  ( $\gamma$  str. enolized acetyl carbonyl group), Characteristic strong  $1631\text{-}625 \text{ cm}^{-1}$  ( $\gamma$  C=N of heterocyclic quaternary nitrogen atom or ring vibrations of pyridinium ion),  $3120 \text{ cm}^{-1}$ , ( $\gamma$  N-H str., pyridinium ion),  $1631\text{-}1625 \text{ cm}^{-1}$  ( $\gamma$  quatern pyridine),  $1631\text{-}1625 \text{ cm}^{-1}$ . ( $\gamma$  pyridinium salts),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C str. pyridin-ium salts),  $1715 \text{ cm}^{-1}$  ( $\gamma$  quinoid cyclic C=O,  $3150\text{-}3000 \text{ cm}^{-1}$  ( $\gamma$  N-ethyl-pyridin-ium iodide),  $3037\text{-}3144 \text{ cm}^{-1}$  ( $\gamma$  2 bands pyridinium quaternary),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C str. pyridinium salts),  $3037\text{-}3144 \text{ cm}^{-1}$  (quaternary salts),  $1129\text{-}092 \text{ cm}^{-1}$  ( $\gamma$  exocyclic N-C-alkyl str. pyridinium salts) [13].  $^1\text{H-NMR}$  (DMSO, 300 MHz) of selected **(3b)** showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  7.67-8.90 ppm (m, 6H, quinolin-4-ium),

$\delta$  8.10-9.11 ppm (m, 6H, quinolin-1-ium),  $\delta$  1.57 ppm (t, 3H, CH<sub>3</sub>),  $\delta$  4.80 ppm (q, 2H, CH<sub>2</sub>), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH),  $\delta$  1.86-1.89 ppm (s, 3H, CH<sub>3</sub> of acetyl group) &  $\delta$  9.30 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H, CH<sub>2</sub>) [14,15]. Mass spectrum of (3b) reveals a molecular ion at  $m/z = 773$ , and base peak at  $m/z = 242.05$  [16].

### **3.3. Synthesis of Self-Assembly Heterocyclic [ICT] functional dye 6-acetyl-7-methyl-5, 14-dioxo-6, 14-di [H]-5H-benzo[g]indolizino [1, 2-c] quinolin-12-ium iodide-zero-13[4(1)] methine cyanine dyes, (4a-d),**

An Ethanolic solution of (3a-d, 0.005 mol) in the presence of few mls. Piperidine was refluxed for 3 hours. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated and cooled concentrated to one third of its volume, cooled and precipitated by adding of ice-water mixture. to give (4a-d), Table (2). IR ( $\nu^{\text{KBr}} \text{ cm}^{-1}$ ) of (4b) showed in addition to the general absorption peaks at ( $\nu$  CH<sub>3</sub> Stretching Vibration), at 2890  $\text{cm}^{-1}$  ( $\nu$  ylide anion), 3150-3000  $\text{cm}^{-1}$  ( $\nu$  N-ethyl-pyridin-ium iodide), 1715  $\text{cm}^{-1}$  ( $\nu$  quinoid cyclic C=O), groups, characteristic absorption peaks at 1712  $\text{cm}^{-1}$  ( $\nu$  (NCOCH<sub>3</sub>), for (4b) & disappearance 1712  $\text{cm}^{-1}$  ( $\nu$  (NCOCH<sub>3</sub>) [13]. <sup>1</sup>H-NMR (DMSO, 300 MHz) of selected (4b) showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  7.94-9.01 ppm (m, 6H, quinolin-4-ium),  $\delta$  7.57-9.40 ppm (m, 6H, benzo [g]indolizine),  $\delta$  1.57 ppm (t, 3H, CH<sub>3</sub>),  $\delta$  4.80 ppm (q, 2H, CH<sub>2</sub>), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH),  $\delta$  1.91 ppm (s, 3H, CH<sub>3</sub> of acetyl group) &  $\delta$  9.30 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H, CH<sub>2</sub>),  $\delta$  2.26 ppm (s, 3H, CH<sub>3</sub>) [14,15]. Mass spectrum of (4b) reveals a molecular ion, peaks at  $m/z = 818$  and base peak at  $m/z = 760$  [16].

### **3.4. Synthesis of Self-Assembly Heterocyclic functional dye 13-(1-ethyl-pyridin-1-ium-4-yl)-7-methyl-5, 14-dioxo-6, 14-dihydro-5H-benzo[g] indolizino [1, 2-c] quinolin-12-ium iodide, (5a-d)**

An ethanolic solution of (4a-d, 0.005 mol) in presence of KOH or K<sub>2</sub>CO<sub>3</sub> or 1m M NaHSO<sub>3</sub> and use 0.1N HCl [13] was refluxed for 1 hour. The reaction mixture was filtrated from unreacted materials, concentrated and cooled; the solid product was collected and crystallized from ethanol to give (5a-d), Table (3). IR ( $\nu^{\text{KBr}} \text{ cm}^{-1}$ ) of (5b) showed in addition to the general absorption peaks at ( $\nu$  CH<sub>3</sub> Stretching Vibration), at 2890  $\text{cm}^{-1}$  ( $\nu$  ylide anion), 3150-3000  $\text{cm}^{-1}$  ( $\nu$  N-ethyl-pyridin-ium iodide), 1715  $\text{cm}^{-1}$  ( $\nu$  quinoid cyclic C=O), groups, characteristic appearance of absorption band at

3300-3500  $\text{cm}^{-1}$  ( $\nu_{\text{NH}}$ ) for **(5b)** [13].  $^1\text{H-NMR}$  (DMSO, 300 MHz) of selected **(5b)** showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  7.67-8.90 ppm (m, 6H, quinolin-4-ium),  $\delta$  7.57-9.40 ppm (m, 6H, benzo[g]indolizine),  $\delta$  1.57 ppm (t, 3H,  $\text{CH}_3$ ),  $\delta$  4.80 ppm (q, 2H,  $\text{CH}_2$ ), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH), &  $\delta$  5.93 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H,  $\text{CH}_2$ ),  $\delta$  2.26 ppm (s, 3H,  $\text{CH}_3$ ) [14,15]. Mass spectrum of **(5b)** reveals a molecular ion at  $m/z = 773$ , and base peak at  $m/z = 758$  [16].

### **3.5. Synthesis of 4-(6-acetyl-5, 14-dioxo-6, 14-di [Hbenzo[g]indolizino [1, 2-c] quinolin-7(5H) mono-[4(1)]-zero-13[4(1)] methine, (6a-f)**

An Ethanolic solution of **(4a-d)**, 0.01 mol.) and pyridin [quinolin]-4(1)-ium-ethiodide salts (0.01 moles) in piperidine was refluxed on water bath for one hour. The reaction mixture was 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 to give **(6a-f)**, **Table [4]**. IR ( $\nu^{\text{KBr}}$   $\text{cm}^{-1}$ ) of **(6b)** showed in addition to the general absorption peaks at ( $\text{CH}_3$  Stretching Vibration),  $2890 \text{ cm}^{-1}$  ( $\nu$  ylide anion),  $3150\text{-}3000 \text{ cm}^{-1}$  ( $\nu$  N-ethyl-pyridin-ium iodide),  $1715 \text{ cm}^{-1}$  ( $\nu$  quinoid cyclic  $\text{C}=\text{O}$ ), characteristic absorption peaks at  $1712 \text{ cm}^{-1}$  ( $\nu$  NCO $\text{CH}_3$ ) for **(6b)** [13].  $^1\text{H-NMR}$  (DMSO, 300 MHz) of selected **(6b)** showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  7.67-8.90 ppm (m, 12H, quinolin-4-ium),  $\delta$  7.57-9.40 ppm (m, 6H, benzo[g]indolizine),  $\delta$  1.57 ppm (t, 3H,  $\text{CH}_3$ ),  $\delta$  4.80 ppm (q, 2H,  $\text{CH}_2$ ), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH), &  $\delta$  5.93 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H,  $\text{CH}_2$ ),  $\delta$  2.26 ppm (s, 3H,  $\text{CH}_3$ ),  $\delta$  1.91 ppm (s, 3H,  $\text{CH}_3$  of acetyl group),  $\delta$  5.99 ppm (s, 1H, =CH).  $^1\text{H-NMR}$  (DMSO, 300 MHz) of selected compound **(7b)** showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  8.10-9.08 ppm (m, 12H, quinolin-4-ium),  $\delta$  7.77-8.48 ppm (m, 6H, benzo[g]indolizine),  $\delta$  1.57 ppm (t, 3H,  $\text{CH}_3$ ),  $\delta$  4.80 ppm (q, 2H,  $\text{CH}_2$ ), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH), &  $\delta$  5.93 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H,  $\text{CH}_2$ ),  $\delta$  2.26 ppm (s, 3H,  $\text{CH}_3$ ),  $\delta$  1.91 ppm (s, 3H,  $\text{CH}_3$  of acetyl group),  $\delta$  6.03 ppm (s, 1H, =CH) [14,15]. The structure **(6b)** was consider most likely based on mass spectrum resulted in  $\text{M}^+$  peak at  $m/e = 971$  and base peak at  $m/e = 928$  which in agreement with the structure **(6b)** [16]



### **3.6. Synthesis of 5,14-dioxo-5,6,7,14-tetra[H]benzo[g]indolizino[1,2-c]quinolin-7(5H)mono-[4(1)]-zero-13[4(1)]methine (7a-f)**

An Ethanolic solution of (**5a-d**, 0.01 mol.) and pyridin [quinolin]-4(1)-ium-ethiodide salts (0.01 moles) in piperidine was refluxed on water bath for one hour. The reaction mixture was 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 to give (**7a-f**), **Table [4]**. IR ( $\nu^{\text{KBr}} \text{ cm}^{-1}$ ) of (**7b**) showed in addition to the general absorption peaks at ( $\text{CH}_3$  Stretching Vibration),  $2890 \text{ cm}^{-1}$  ( $\nu$  ylide anion),  $3150\text{-}3000 \text{ cm}^{-1}$  ( $\nu$  N-ethyl-pyridin-ium iodide),  $1715 \text{ cm}^{-1}$  ( $\nu$  quinoid cyclic C=O), characteristic absorption peaks disappearance  $1712 \text{ cm}^{-1}$  ( $\nu$  (NCOCH<sub>3</sub>) and appearance of absorption band at  $3300\text{-}3500 \text{ cm}^{-1}$  ( $\nu$ NH ) for (**7b**)[**13**]. <sup>1</sup>H-NMR (DMSO, 300 MHz) of selected compound (**7b**) showed in addition to the general signals at  $\delta$  7.60-7.72 ppm (m, 4H, Ar-H),  $\delta$  8.10-9.08 ppm (m, 12H, quinolin-4-ium),  $\delta$  7.77-8.48 ppm (m, 6H, benzo[g]indolizine),  $\delta$  1.57 ppm (t, 3H, CH<sub>3</sub>),  $\delta$  4.80 ppm (q, 2H, CH<sub>2</sub>), characteristic signal at  $\delta$  3.6 ppm (s, 1H, CH), &  $\delta$  5.93 ppm (s, 1H, NH),  $\delta$  3.71 ppm (s, 2H, CH<sub>2</sub>),  $\delta$  2.26 ppm (s, 3H, CH<sub>3</sub>),  $\delta$  1.91 ppm (s, 3H, CH<sub>3</sub> of acetyl group),  $\delta$  6.03 ppm (s, 1H, =CH)[**14,15**]. The structure (**7b**) was consider most likely based on mass spectrum resulted in Mass spectra of (**7b**) reveals a molecular ion [M] + peaks at  $m/z = 928$ , and base peak at  $m/z = 517$  [**16**]

### **3.7. SPECTRAL BEHAVIOUR**

Spectral behaviours of the all syn the sized cyanine dyes in 95% ethanol were recorded using 1 cm cells. A stock solution (10<sup>-3</sup> M) of the dyes was diluted to appropriate volume in order to obtain the required concentrations

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**Table (1): Characterisation data for (2a-d & 3a-d).**

Comp. No.	Nature of product				Mol. Formula (M. wt)	Analytical analysis (%) Calcd (found)		
	Heterocyclic Substituent A(B)	m.p. °C	Yield %	Colour		C	H	N
2a	pyridin-4-ium (quinolin-1-ium)	290	65	Brown	C <sub>29</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 464	75.14 75.35	5.44 5.70	9.07 9.35
2b	quinolin-4-ium (quinolin-1-ium)	175	75	Black	C <sub>33</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 514	77.17 77.35	5.30 5.60	8.18 8.45
2c	quinolin-1-ium (quinolin-1-ium)	255	65	Buff	C <sub>33</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 514	77.17 77.45	5.30 5.56	8.18 8.45
2d	quinolin-4-ium (pyridin-1-ium)	195	70	Brownish Red	C <sub>29</sub> H <sub>25</sub> I <sub>2</sub> N <sub>3</sub> O <sub>3</sub> 717	48.56 48.66	3.51 3.67	5.86 5.99
3a	pyridin-4-ium (quinolin-1-ium)	> 300	75	Dark Brown	C <sub>34</sub> H <sub>31</sub> N <sub>3</sub> O <sub>5</sub> I <sub>2</sub> 562	72.71 72.87	5.56 5.75	7.48 7.76
3b	quinolin-4-ium (quinolin-1-ium)	195	70	Black	C <sub>38</sub> H <sub>33</sub> N <sub>3</sub> O <sub>5</sub> I <sub>2</sub> 612	74.62 74.87	5.44 5.65	6.87 6.99
3c	quinolin-1-ium (quinolin-1-ium)	> 300	80	Dark brown	C <sub>38</sub> H <sub>33</sub> N <sub>3</sub> O <sub>5</sub> I <sub>2</sub> 612	74.62 74.78	5.44 5.65	6.87 6.99
3d	quinolin-4-ium (pyridin-1-ium)	180	90	Brownish red	C <sub>34</sub> H <sub>31</sub> I <sub>2</sub> N <sub>3</sub> O <sub>5</sub> 815	50.08 50.35	3.83 4.00	5.15 5.35

Table (2): Characterisation data for (4a-d,5a-d):

Comp. No.	Nature of Product				Mol. Formula (M. wt)	Analytical Analysis (%) Calcd (found)			Absorption spectra In 95 % EtOH	
	Heterocyclic Substituent A(B)	m.p. °C	Yield %	Colour		C	H	N	$\lambda_{\max}$ n. m	$\epsilon_{\max}$ mol <sup>-1</sup> cm <sup>2</sup>
4a	A=pyridin-4-ium- (quinolin-1-ium)	230	65	Brownish red	C <sub>33</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 512	77.48 77.75	4.93 5.05	8.21 8.45	455 370	2000 4000
4b	A=quinolin-4-ium- (quinolin-1-ium)	285	70	Deep red	C <sub>37</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 562	79.13 79.35	4.85 4.97	7.48 7.65	465 375	8800 8400
4c	A=quinolin-1-ium- (quinolin-1-ium)	195	55	Deep red	C <sub>37</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 562	79.13 79.45	4.85 4.98	7.48 7.67	460 373	4000 7400
4d	A=quinolin-4-ium- (pyridin-1-ium)	270	65	Brownish red	C <sub>33</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> 512	77.48 77.75	4.93 5.08	8.21 8.45	475	13200
5a	A=pyridin-4-ium- (quinolin-1-ium)	280	75	Dark brown	C <sub>31</sub> H <sub>23</sub> I <sub>2</sub> N <sub>3</sub> O <sub>2</sub> 723	51.47 51.67	3.21 3.45	5.81 5.94	510 445 415	(6000) (8000) (9600)
5b	A=quinolin-4-ium- (quinolin-1-ium)	>300	80	Deep Violet	C <sub>35</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> 520	80.91 81.00	4.85 5.05	8.09 8.35	660 570 470 435	(2400) (5400) (7800) (8800)
5c	A=quinolin-1-ium- (quinolin-1-ium)	290	70	Brown	C <sub>35</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> 520	80.91 81.00	4.85 5.08	8.09 8.34	512 450	(6800) (14000)
5d	A=quinolin-4-ium- (pyridin-1-ium)	>300	65	Dark Blue	C <sub>31</sub> H <sub>23</sub> I <sub>2</sub> N <sub>3</sub> O <sub>2</sub> 723	51.47 51.67	3.21 3.55	5.81 5.99	690 595 560 400	(3200) (12800) (11400) (9600)

**Table (3): Characterisation data (6a-f & 7a-f)**

Comp. No.	Nature of Product				Mol. Formula (M.wt)	Analytical Analysis % Calcd (Found)			Absorption Spectra in 95% EtOH		
	Heterocyclic Substituent A[A' (B)]	M.P °C	Yield %	Colour		C	H	N	$\lambda_{\max}$ n.m	$\epsilon_{\max}$ mol <sup>-1</sup> cm <sup>2</sup>	Absorption Range $\lambda_{\max}$ n.m
6a	pyridin-4-ium[quinolin-4-ium(quinolin-1-ium)]	280	65	Deep red	C <sub>40</sub> H <sub>32</sub> I <sub>2</sub> N <sub>4</sub> O <sub>3</sub> 870	55.19 55.54	3.71 3.86	6.44 6.67	610 380	(1800) (9800)	380-610
6b	quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)]	230	63	Violet	C <sub>48</sub> H <sub>36</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> 716	80.43 80.67	5.06 5.45	7.82 7.98	690 575 460	(2000) (6000) (4200)	460-690
6c	quinolin-1-ium[quinolin-4-ium(quinolin-1-ium)]	235	75	Brownish red	C <sub>48</sub> H <sub>36</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> 716	80.43 80.65	5.06 5.56	7.82 7.98	635 <sup>sh</sup> 465 390	(2500) (2000) (7000)	390-635 <sup>sh</sup>
6d	quinolin-4-ium,[quinolin-4-ium(pyridin-1-ium)]	260	70	Deep violet	C <sub>44</sub> H <sub>34</sub> I <sub>2</sub> N <sub>4</sub> O <sub>3</sub> 920	57.41 57.68	3.72 3.85	6.09 6.35	700 600 470	(2600) (4600) (10800)	470-700
6e	quinolin-4-ium[pyridin-4-ium(quinolin-1-ium)]	195	80	Brownish red	C <sub>44</sub> H <sub>34</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> 666	79.26 79.45	5.14 5.46	8.40 8.55	470 335	(3500) (5500)	335-470
6f	quinolin-4-ium[quinolin-1-ium(quinolin-1-ium)]	125	75	Shiny Red	C <sub>48</sub> H <sub>36</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> 716	80.43 80.67	5.06 5.45	7.82 7.99	500	(13000)	500
7a	pyridin-4-ium[quinolin-4-ium(quinolin-1-ium)]	105	65	Deep Red	C <sub>42</sub> H <sub>32</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> 878	57.42 57.55	3.67 3.83	6.38 6.56	620 390	(1000)	390-620
7b	quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)]	235	60	Brownish red	C <sub>46</sub> H <sub>34</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> 674	81.88 81.98	5.08 5.35	8.30 8.45	690 585 470	(36000) (50000) (50000)	470-690
7c	quinolin-1-ium[quinolin-4-ium(quinolin-1-ium)]	230	60	Red	C <sub>46</sub> H <sub>34</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> 675	81.88 81.98	5.08 5.36	8.30 8.56	645 <sup>sh</sup> 475 400	(7000) (13500)	400-645 <sup>sh</sup>
7d	quinolin-4-ium,[quinolin-4-ium(pyridin-1-ium)]	220	65	Brownish red	C <sub>42</sub> H <sub>32</sub> N <sub>4</sub> O <sub>2</sub> I <sub>2</sub> 625	80.75 80.87	5.16 5.35	8.97 9.05	700 620 490	(5000) (7500)	490-700
7e	quinolin-4-ium[pyridin-4-ium(quinolin-1-ium)]	250	55	Pink	C <sub>42</sub> H <sub>32</sub> N <sub>4</sub> O <sub>2</sub> I <sub>2</sub> 625	80.75 80.89	5.16 5.45	8.97 9.05	480 355	(3500) (5000)	355-480
7f	quinolin-4-ium[quinolin-1-ium(quinolin-1-ium)]	160	80	Deep Red	C <sub>46</sub> H <sub>34</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> 675	81.88 81.98	5.08 5.25	8.30 8.55	520	(5500) (7900) (7900)	520

**Table (4) : Comparison of Absorption Spectra in EtOH of (5a-d & 7a-f)**

Comp. No.	Heterocyclic Substituent A(B)	Absorption Spectra of in 95% EtOH		
		$\lambda_{\max}$ n.m	$\epsilon_{\max}$ mol <sup>-1</sup> cm <sup>2</sup>	Range $\lambda_{\max}$ n.m
5a	A=pyridin-4-ium-(quinolin-1-ium)	510,445,415	(6000),(8000) (9600)	415-510
5b	A=quinolin-4-ium-(quinolin-1-ium)	660,570,470,435	(2400),(5400) (7800),(8800)	435-660
5c	A=quinolin-1-ium-(quinolin-1-ium)	512, 450	(6800),(14000)	450-512
5d	A=quinolin-4-ium-(pyridin-1-ium)	690,595,560,400	(3200),(12800) (11400),(9600)	400-690
7a	A=pyridin-4-ium[quinolin-4-ium(quinolin-1-ium)]	620 390	(1000)	390-620
7b	A=quinolin-4-ium[quinolin-4-ium(quinolin-1-ium)]	690,585 470	(36000), (50000) (50000)	470-690
7c	A=quinolin-1-ium[quinolin-4-ium(quinolin-1-ium)]	645 <sup>sh</sup> ,475 400	(7000),(13500)	400-645 <sup>sh</sup>
7d	A=quinolin-4-ium,[quinolin-4-ium(pyridin-1-ium)]	700,620 490	(5000), (7500)	490-700
7e	A=quinolin-4-ium[pyridin-4-ium(quinolin-1-ium)]	480,355	(3500), (5000)	355-480
7f	A=quinolin-4-ium[quinolin-1-ium(quinolin-1-ium)]	520	(5500), (7900) (7900)	520