

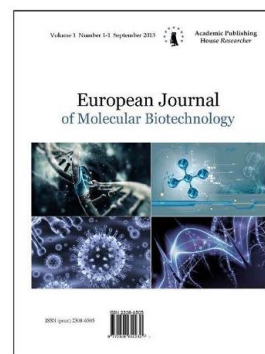
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## Synthesis, Spectral Sensitization, Solvatochromic and Halochromic Evaluation of New Monomethine and Trimethine Cyanine Dyes

H.A. Shindy <sup>a,\*</sup>, A.K. Khalafalla <sup>a</sup>, M.M. Goma <sup>a</sup>, A.H. Eed <sup>a</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Aswan University, Aswan 81528, Egypt

### Abstract

New heterocyclic starting material namely 4,5-dimethyl-2,7-diphenyl-furo[(3,2-d), (3, 2-d)] bis pyrazole were prepared and employed to synthesis of some novel monomethine cyanine dyes (simple cyanine dyes) and trimethine cyanine dyes (carbocyanine dyes). Spectral sensitization evaluation for all the synthesized cyanine dyes was carried out through investigating their electronic visible absorption spectra in 95% ethanol solution. Solvatochromic and/or hachromic evaluation for some selected dyes were carried out through examining their electronic visible absorption spectra in pure solvents having different polarities [Water (78.54), Dimethylformamide (36.70), Ethanol (24.3), Chloroform (4.806), Carbontetrachloride (2.238) and Dioxane (2.209)] and/or in aqueous universal buffer solutions having varied pH values (1.75, 2.45, 4.65, 5.80, 7.88, 8.75, 10.85 and 12.60 units), respectively. Structure determination were carried out via elemental analysis, visible spectra. Mass spectrometer, IR and <sup>1</sup>H NMR spectral data.

**Keywords:** Synthesis, cyanine dyes, visible spectra, halochromism, solvatochromism, carbocyanine dyes.

### 1. Introduction

Increased research interest in cyanine dyes chemistry (Shindy et al., 2012, Shindy et al, 2016, Shindy et al, 2015, Shindy et al., 2015a, Shindy, 2012, Shindy et al., 2014) essentially arises from their applications and uses in various research field (Shershof, et al., 2013, Leevy, et al., 2008, Zhang, et al., 2004 and Savitsky, et al. 2004, Li et al., 2006, Wang, et al., 2007, Licha, et al., 2000). Such as biochemistry, molecular biology, bio-medicine and structural biology. In addition, cyanine dyes are frequently used as reporter groups for labeling proteins, DNA sequencing, oligonucleotides and antibodies (Wang et al., 2009, Zhang et al., 2008, Peng et al., 2008, Pham et al., 2005, Chen et al., 2005, Zheng et al., 2002). Besides, these dyes attract much attention because of their application in a number of research area such as probes for the determination of solvent polarity, potential applications for colorimetric sensor (Bamfield, 2001, Janzen et al., 2006), as photographic sensitizers and in chemotherapy (Toutchkine et al., 2007, Wröblewska et al., 2005, Rösch et al., 2006, Würthner et al., 2006, Martins et al., 2006, Leng et al., 2005).

Taking in consideration the above benefits of cyanine dyes we prepared here new polyheterocyclic monomethine and trimethine cyanine dyes as new synthesis contribution, spectral sensitization, solvatochromic and halochromic evaluation to may be used and/or applied in any of the wide range applications of cyanine dyes, particularly as photographic sensitizers for silver

\* Corresponding author

E-mail addresses: [hashindy2@hotmail.com](mailto:hashindy2@hotmail.com) (H A. Shindy)

halide emulsion in photographic industry, as probes to determining solvent polarity in solution chemistry and/or as pH indicators in operations of acid/base titrations in analytical chemistry.

## 2. Results and discussion

### 2.1-Synthesis:

Reaction of 3-methyl-1-phenyl-5-pyrazolone (1) with 4-bromo-3-methyl-1-phenyl-5-pyrazolone (2) in equimolar ratios in ethanol containing pyridine achieved 4,5-dimethyl-2,7-diphenyl-furo[(3,2-d), (3,2-d)] bis pyrazole (3) as new heterocyclic starting material compound, Scheme (1).

Quaternization of (3) using excess of iodoethane resulted its 3,6-di iodoethane quaternary salt compound (4), Scheme (1).

Reaction of the quaternary salt (4) with 1-ethylpyridinium-4-yl salt, 1-ethyl quinolinium-4-yl salt and/or 2-ethyl isoquinolinium-1-yl salt in 1:2 molar ratios and in ethanol as organic solvent containing few mls of piperidine gives the 4,5-[4(1)]-bis monomethine cyanine dyes (5a-c), Scheme (1).

1:2 molar ratios of the quaternary salts (4) and triethylorthoformate (triethoxy methane) were reacted in ethanol containing piperidine and produced the intermediate compound (6). Further reaction of the intermediate compound (6) in 1:2 molar ratios with 1-ethyl pyridinium-2-yl salt, 1-ethyl quinolinium-2-yl salt and/or 1-ethyl pyridinium-4-yl salt in ethanol and in presence of piperidine achieved the 4,5-[2(4)]-bis trimethine cyanine dyes (7a-c), Scheme (1).

The structure of the prepared compounds were identified by elemental analysis (Tables 1, 2), visible spectra (Tables 1, 2), mass spectrometer, IR (Wade, 1999) and <sup>1</sup>H NMR (Wade, 1999a) spectral data (Table 3).

### 2.2-Spectral sensitization evaluation:

Spectral sensitization evaluation for all the synthesized cyanine dyes was carried out through investigating their electronic visible absorption spectra in 95 % ethanol solution. The dyes are thought to be better spectral sensitizers when they absorb light at longer wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently the spectral sensitization of the dyes decrease when they absorb light at shorter wavelength bands (hypsochromic shifted and/or blue shifted dyes). So, we may say that the spectral sensitization of one dye is higher than the other one if the wavelength of the maximum absorption spectrum of the former is longer than that of the latter. Inversely, we may say that the spectral sensitization of one dye is lower than the other one if the wavelength of the maximum absorption spectrum of the former is shorter than that of the latter.

The electronic visible absorption spectra of the monomethine cyanine dyes (5a-c) in 95 % ethanol solution discloses bands in the visible region (380-440 nm). The positions of these bands and their molar extinction coefficient (molar absorptivity) are largely effected by the types of heterocyclic quaternary salts residue (A) and their linkage positions. So, substituting, A = 1-ethyl-pyridinium-4-yl salt by A = 1-ethyl-quinolinium-4-yl salt moving from dye (5a) to dye (5b) caused bathochromic shifts for the absorption bands by (20 nm), Scheme (1), Table (1). This can be attributed to increasing  $\pi$ -delocalization in the latter dye (5b) due to the presence of quinoline ring system in correspondence to pyridine ring system in the former dye (5a). Changing the linkage position from 1-ethyl-quinolinium-4-yl salt to 2-ethyl isoquinolinium-1-yl salt, transferring from dye (5b) to dye (5c) resulted a hypsochromic shifts for the absorption bands by (12 nm), Scheme (1), Table (1). This can be related to decreasing the length of the  $\pi$ -delocalization conjugation in latter dye (5c) due to the presence of isoquinoline ring system in correspondence to quinoline ring system in the former dye (5b).

Additionally, the electronic visible absorption spectra of the trimethine cyanine dyes (7a-c) in 95 % ethanol solution reveals bands in the visible range (438-620 nm). The positions of these bands underwent displacements to give bathochromic shifts (red shifts) and/or hypsochromic shifts (blue shifts) in addition to increasing and/or decreasing the number and the intensity of the absorption bands depending upon the type of the heterocyclic quaternary salt residue (A) and their linkage positions, Scheme (1), Table (2). So, substituting pyridinium salt residue in dye (7a) by quinolinium salt residue to get dye (7b) caused strong bathochromic shifts for the absorption bands by (140 nm) in addition to increasing the number of the absorption bands, Scheme (1), Table (2). This can be attributed to increasing conjugation in the latter dye (7b) due to the presence

quinaldine nucleus in corresponding to  $\alpha$ -picoline nucleus in the former dye (7a). Changing the linkage position from 2-yl salt residue in dye (7a) to 4-yl salt residue to obtain dye (7c) resulted bathochromic shifts (red shifts) for the bands by (60 nm) accompanied by increasing the number of the bands, Scheme (1), Table (2). This can be related to increasing the length of the conjugation in the latter dye (7c) due to the presence of  $\gamma$ -picoline nucleus in correspondence to  $\alpha$ -picoline nucleus in the former dye (7a).

General comparison for the electronic visible absorption spectra of the monomethine cyanine dyes (5a-c) with those of the trimethine cyanine dyes (7a-c) displayed that the latter dyes have bathochromically shifted bands than the former dyes, Tables (1, 2). This can be explained in the light of increasing the number of methine groups in the latter dyes, Scheme (1).

### 2.3-Solvatochromic evaluation:

Solvatochromic evaluation for some selected synthesized cyanine dyes (5b) and (7b) was carried out via examining of their electronic visible absorption spectra in pure solvents having different polarities. The dyes are though to be better solvatochromic dyes when they give a remarkable positive solvatochromism and/or negative solvatochromism in these solvents. Positive solvatochromism reveals bathochromic shifted (red shifted) absorption bands with increasing solvent polarity. Inversely, negative solvatochromism discloses hypsochromic shifted (blue shifted) bands with increasing solvent polarity. This study was carried out to select the best solvents to use of these dyes as photosensitizers when they are used and/or applied in photosensitive material industry. The other important purpose of these study is to evaluate the solvatochromic properties of these dyes to may be use and/or applied as probes for determining solvent polarity in physical, physical organic and/or inorganic chemistry.

So, the electronic visible absorption of the monomethine cyanine dye (5b) and the trimethine cyanine dyes (7b) in pure solvents of different polarities (different dielectric constant) namely water (78.54), DMF (36.70), ethanol (24.3), chloroform (4.806), carbontetrachloride (2.238) and dioxane (2.209) (Shindy, et al, 2015b, Shindy, et al, 2016a) are recorded. The  $\lambda_{\max}$  (wavelength) and  $\epsilon_{\max}$  (molar extinction coefficients) values of the absorption bands due different electronic transitions within the solute molecule in these solvents are represented in Table (4).

From Table (4) its clearly that the electronic visible absorption spectrum of the dyes (5b) and (7b) in ethanolic medium are characterized by the presence of two (dye 5b) and/or three (dye7b) essential absorption bands. These bands can be assigned to intermolecular charge transfer transition (Shindy, et al., 2015b, Shindy, et al., 2016a). These charge transfer is due to transfer of lone pair of electrons from the N-ethyl pyrazole nitrogen atom to the positively charged quaternary nitrogen atom of the quinolinium salt residue, Scheme (2).

The data given in Table (4) show that the charge transfer band exhibits a hypsochromic shift in ethanol relative to DMF, dioxane, chloroform and carbontetrachloride. These effects may be attributed to the following factors:

a-The bathochromic shift in DMF relative to ethanol is a result of the increase in solvent polarity due to the increasing of dielectric constant of DMF relative to ethanol.

b-The hypsochromic shift occurs in ethanol relative to dioxane, chloroform and carbontetrachloride is a result of the solute solvent interaction through intermolecular hydrogen band formation between ethanol and the lone pair electrons of the N-ethyl pyrazole nitrogen atom, Scheme (3) (A). This decreases slightly the electron density on the N-ethyl pyrazole nitrogen atom and consequently decreases to some extent the mobility of the attached  $\pi$ -electrons over the conjugated system pathway to the positively charged quaternary nitrogen atom of the quinolinium salt residue, and consequently a hypsochromic shift occurs.

Also, from the data given in Table (4) it is observed that occurrence of unexpected hypsochromic shifts in water relative to ethanol and the other solvents. This can be mainly ascribed to the possible interaction of water molecules with the lone pair electrons of the N-ethyl pyrazole nitrogen atom, Scheme (3) (B). This makes difficult the transfer of electronic charge from the N-ethyl pyrazole nitrogen atom to the quaternary nitrogen atom of the heterocyclic quinolinium salt residue, and accordingly there is observed a hypsochromic shift in water relative to ethanol and the other solvents.

### 2.4-Halochromic evaluation:

Halochromic evaluation for some selected synthesized cyanine dyes (5b) and (7b) was carried out by investigating of their electronic visible absorption spectra in aqueous universal buffer solutions having varied pH values, Table (5). The dyes are thought to be better halochromic dyes when they give a noticeable positive halochromism and/or negative halochromism in these buffer solutions. Positive halochromism means occurrence of a bathochromic shifted (red shifted) absorption bands with changing solution pH of the buffer solution. In contrast negative halochromism means occurrence of a hypsochromic shifted (blue shifted) absorption bands with changing the pH of the buffer solution.

The solutions of the bis monomethine cyanine dyes (5b) and the bis trimethine cyanine dyes (7b) have a permanent cationic charge in basic media that then discharged on acidification. This prompted and encouraged us to study their spectral behaviour in different buffer solutions in order to select a suitable pH for use of these dyes as photosensitizers. The other purpose of this study is to evaluate the halochromic properties of these dyes to may be used and/or applied as pH indicators in acid / base titration in analytical chemistry. The acid dissociation or protonation constant of these dyes have been determined. The effect of the compounds as photosensitizers increases when they are present in the ionic form, which has a higher planarity (Shindy, et al., 2015b, Shindy, et al., 2016a) and therefore more conjugation.

So, the electronic visible absorption spectra of the bis monomethine cyanine dye (5b) and the bis trimethine cyanine dye (7b) in aqueous universal buffer solutions of varying pH values (1.75, 2.45, 4.65, 5.80, 7.88, 8.75, 10.85 and 12.60 units) showed bathochromic shifted bands at high pH media (alkaline media) and hypsochromic shifted bands at low pH media (acidic media). So, the mentioned dyes which has lone pair of electrons on the N-ethyl pyrazole nitrogen atom undergoes to protonation in low pH media (acidic media). This leads to a criterion of positive charge on the N-ethyl pyrazole nitrogen atom and consequently the electronic charge transfer pathways to the quaternary heterocyclic quinolinium salt residue will be difficult resulting in a hypsochromic shift for the absorption bands (protonated and/or colourless-yellow structure), Scheme (4) (A).

On increasing the pH of the media, the absorption bands are bathochromically shifted due to the deprotonation of the N-ethyl pyrazole nitrogen atom, and consequently the electronic charge transfer pathways to the quaternary heterocyclic quinolinium salt residue will be easier and facilitated resulting in a bathochromic shift for the absorption bands (deprotonated and/or coloured structure), Scheme (4) (B).

Several methods have been developed for the spectrophotometric determination of the dissociation constants of weak acids. The variation of absorbance with pH can be utilized. On plotting the absorbance at fixed  $\lambda$  vs. pH, S-shaped curves are obtained, Table (6). An all of the S-shaped curves obtained the horizontal portion to the left corresponds to the acidic form of the indicator, while the upper portion to the right corresponds to the basic form of the indicator, since the pka is defined as the pH value for which one half of the indicator is in the basic form and the other half is in the acidic form. This point is determined by intersection of the curve with a horizontal line midway between the left and right segments (Shindy, et al., 2015b, Shindy, et al., 2016a). The acid dissociation or protonation constants values of the dyes (5b) and (7b) are given in Table (6).

### 3. Conclusion

Following are major conclusions were extracted from the results discussed in this investigation:

1-The electronic visible absorption spectra of the 4,5-[4(1)]-bis monomethine (5a-c) and the 4,5-[2(4)]-bis trimethine (7a-c) cyanine dyes in 95 % ethanol underwent displacements to give bathochromic and/or hypsochromic shifts accompanied by increasing and/or decreasing the number and the intensity of the bands depending upon the following factors:

a-Types of the heterocyclic quaternary salt residue in the order of:

(I) quinolinium dyes > pyridinium dyes (for the bis monomethine cyanine dyes).

(II) quinaldinum dyes >  $\alpha$ -picolinium dyes (for the bis trimethine cyanine dyes).

b-Linkage positions of the heterocyclic quaternary salts in the order of:

(I)quinolinium dyes > isoquinolinium dyes (for the bis monomethine cyanine dyes).

(II)  $\gamma$ -picolinium dyes >  $\alpha$ -picolinium dyes (for the bis trimethine cyanine dyes).

c-Increasing number of the methine units in the order of:  
Trimethine cyanine dyes > monomethine cyanine dyes.

2-The intensity of the colours of the bis monomethine cyanine dyes (5a-c) and the bis trimethine cyanine dyes (7a-c) can be illustrated in the light of the two suggested mesomeric structures (A) and (B) producing a delocalized positive charge over the conjugated system, Scheme (2).

3-The solvatochromism of the examined cyanine dyes (5b) and (7b) in pure solvents having different polarities underwent displacements to give positive solvatochromism (occurrence of a bathochromic shift with increasing solvent polarity) and/or negative solvatochromism (occurrence of a hypsochromic shift with increasing solvent polarity) depending upon the following factors:

a-Increasing and/or decreasing the polarity (dielectric constant) of the solvents (General solvent effect).

b-Hydrogen bond and/or molecular complex formation between the solute (dyes molecules) and the solvent used (specific solvent effect).

4-The halochromism of the monomethine cyanine dye (5b) and the bis trimethine cyanine dye (7b) in aqueous universal buffer solutions having varying pH values underwent to give the following displacements changes in their absorption spectra wavelength bands:

a-Hypsochromic shifted bands in the lower pH media (acidic media) due to the protonated and/or colourless structures of the dyes in this media. b-Bathochromic shifted bands in the higher pH media (basic media) due to the deprotonated and/or coloured structures of these dyes in this media.

5-These cyanine dyes can be used as:

a-Photographic sensitizers for silver halide emulsion in photographic industry due to their spectral and/or photosensitization properties.

b-Indicators for solvent polarity in solution chemistry due to their solvatochromic properties.

c-Acid-base indicators in analytical chemistry due to their halochromic properties

## 4-Experimental

### 4.1-General:

All the melting points of the prepared compounds are measured using Electrothermal 15V, 45W 1 A9100 melting point apparatus, Chemistry department, Faculty of Science (Aswan University) and are uncorrected. Elemental analysis were carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Vario EL III Germany). Infrared spectra were measured with a FT/IR (4100 Jasco Japan), Cairo University. <sup>1</sup>H NMR Spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer (Cairo University). Mass Spectroscopy was recorded on Mas 1: GC-2010 Shimadzu Spectrometer (Cairo University). Electronic visible absorption spectra were carried out on Visible Spectrophotometer, Spectro 24 RS Labomed, INC, Chemistry department, Faculty of Science (Aswan University).

### 4.2-Synthesis:

#### 4.2.1-Synthesis of 4,5-dimethyl-2,7-diphenyl-furo [(3,2-d), (3,2-d) bis pyrazole] (3).

A mixture of equimolar ratios (0.01 mol) of 3-methyl-1-phenyl-5-pyrazolone (1) and 4-bromo-3-methyl-1-phenyl-5-Pyrazolone (2) was dissolved in ethanol (30 ml) containing pyridine (5-10 ml). The reaction mixture was heated under reflux for 6-8hrs, and changed its colour from reddish to deep brown at the end of refluxing. It was filtered while hot to remove any impurities and precipitated by ice-water mixture. The product were collected, dried and crystallized from ethanol. The results are listed in Table (1).

#### 4.2.2-Synthesis of 3, 6-diethyl 4, 5-dimetyl -2, 7-diphenyl-furo [(3, 2-d), (3, 2-d) bis pyrazolium] diiodide salts (4).

A pure crystallized sample of (3) (0.01 mol) and excess of bimolar ratios of iodoethane were heated in a sealed tube till complete fusion. The products were cooled, dissolved in ethanol (30 ml), and heated under reflux for 1 hour. The reaction mixtures were filtered while hot to remove impurities, concentrated and cooled. The precipitates were collected, dried, and crystallized using ethanol, see the data in Table (1).



#### 4.2.3-Synthesis of 3,6-diethyl-2,7-diphenyl-furo[(3, 2-d), (3,2-d) bis pyrazole]-4,5[4(1)]-bis monomethine cyanine dyes (5a-c).

A mixture of (4) (0.01 mol) and bimolar ratios of N-ethyl (pyridinium, quinolinium or isoquinolinium) salts were dissolved in ethanol (30 ml) containing piperidine (1-2 mls). The reaction mixtures were heated under reflux for 6 hrs. It was filtered off while hot to remove any impurities, cooled, and precipitated by dilution with ice-water mixture with continues shaking. The precipitates were filtered, washed with water several times, dried and crystallized from ethanol. The relevant data are given in Table (1).

#### 4.2.4-Synthesis of 3,6-diethyl-2,7-diphenyl-furo [(3, 2-d), (3,2-d) bis pyrazolium]-4,5[1,1-diethoxy ethyl] diiodide salt as intermediate compound (6).

1:2 molar ratios of the quaternary salt compound (4) and triethylorthoformate were heated under reflux in ethanol (30 ml) containing piperidine (1-2 mls) for 6 hrs, until it gave a permanent deep colour at the end of refluxing. The reaction mixture was filtered off while hot to remove impurities, concentrated to one half of its volume, cooled, and precipitated by cold water. The precipitates were filtered, washed with water several times, dried and crystallized from ethanol. The data were recorded in Table (2).

#### 4.2.5-Synthesis of 3,6- diethyl 2,7-diphenyl-furo[(3, 2-d), (3,2-d)) bis pyrazole] - 4, 5 [2 (4)] -bis trimethine cyanine dyes (7a - c).

A mixture of unimolar ratio (0.01 mol) of the intermediate compound (6) and bimolar ratio (0.02 mol) of N-ethyl (2-picolinium, quinaldinium, or 4-picolinium) iodide quaternary salts were dissolved in ethanol (30 ml) containing piperidine (1-2 mls). The reaction mixture was heated under reflux for 6 hrs, and attained highly violet colours at the end of refluxing. The mixture was filtered off while hot, precipitated by dilution with ice-water mixture with continues shaking. The precipitates were filtered off, washed with water several times dried and crystallized from ethanol. The data were registered in Table (2).

#### 4.3-Visible absorption spectra:

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95 % ethanol solution and recorded using 1cm Qz cell in Vis Spectrophotometer, Spectro 24RS Labomed, INC. A stock solution ( $1 \times 10^{-3}$ M) of the dyes was prepared and diluted to a suitable volume in order to obtain the desired lower concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

#### 4.4-Solvatochromism and halochromis:

The electronic visible absorption spectra of some selected synthesized cyanine dyes were investigated in pure organic solvents of spectroscopic grade (Shindy, et al., 2015b, Shindy, et al., 2016a) and different polarities and/or in aqueous universal buffer solutions having varying pH values and recorded using 1cm quartz cell in Vis Spectrophotometer Spectro 24 RS Labomed, INC. A stock solution ( $1 \times 10^{-3}$ M) of the dyes was prepared and diluted to a suitable volume using the suitable solvent and/or the buffer solution to obtain the required lower concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

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## Appendix

**Table 1.** Characterization of the prepared compounds (3), (4) and (5a-c)

Comp. No	Nature of product			Molecular formula (M.Wt.)	Analysis %						Absorption spectra in 95% ethanol solution	
	Colour	Yield (%)	M.P. (°C)		Calculated			Found			$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mole <sup>-1</sup> cm <sup>2</sup> )
					C	H	N	C	H	N		
3	Brown	65	190	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O (328)	73.17	4.87	17.07	73.15	4.85	17.04	---	-----
4	Deep brown	55	175	C <sub>24</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> (640)	45.0 0	4.06	8.75	44.9 8	4.04	8.73	-----	-----
5a	Red	45	160	C <sub>38</sub> H <sub>40</sub> N <sub>6</sub> O <sub>2</sub> (850)	53.6 4	4.70	9.88	53.6 2	4.68	9.86	380, 420	2286, 2278
5b	Deep red	59	140	C <sub>46</sub> H <sub>44</sub> N <sub>6</sub> O <sub>2</sub> (950)	58.10	4.36	8.84	58.0 0	4.34	8.82	400, 440	2286, 2242
5c	Deep red	53	155	C <sub>46</sub> H <sub>44</sub> N <sub>6</sub> O <sub>2</sub> (950)	58.10	4.36	8.84	58.0 0	4.34	8.82	395, 428	2267, 2246



**Table 2.** Characterization of the prepared compounds (6) and (7a-c)

Comp. No	Nature of product			Molecular formula (M.Wt.)	Analysis %						Absorption spectra in 95% ethanol solution	
	Colour	Yield (%)	M.P. (°C)		Calculated			Found			$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mole <sup>-1</sup> cm <sup>2</sup> )
					C	H	N	C	H	N		
6	Brown	62	150	C <sub>34</sub> H <sub>46</sub> N <sub>4</sub> O <sub>5</sub> I <sub>2</sub> (844)	48.34	5.45	6.63	48.32	5.44	6.60	---	---
7a	Violet	51	120	C <sub>40</sub> H <sub>44</sub> N <sub>6</sub> OI <sub>2</sub> (878)	54.66	5.01	9.56	54.63	5.00	9.54	438, 480	2276, 2225
7b	Deep violet	65	145	C <sub>50</sub> H <sub>48</sub> N <sub>6</sub> OI <sub>2</sub> (1002)	59.88	4.79	8.38	59.86	4.75	8.36	460, 560, 620	2275, 2244, 2220
7c	Deep violet	48	100	C <sub>40</sub> H <sub>44</sub> N <sub>6</sub> OI <sub>2</sub> (878)	54.66	5.01	9.56	54.63	5.00	9.54	440, 480, 540	2276, 2251, 2223

**Table 3.** IR and <sup>1</sup>H NMR (mass) spectral data of the prepared compounds (3), (4), (5b), (6) and (7b)

Comp. No	IR Spectrum (KBr, Cm <sup>-1</sup> )	<sup>1</sup> H NMR Spectrum (DMSO, $\delta$ ); & (Mass data)
3	687, 754 (monosubstituted phenyl). 1031, 1073, 1111, 1172 (C-O-C cyclic). 1328, 1367 (C-N). 1495, 1457 (C=N). 1617, 1594 (C=C).	2.2 (m, 6H, 2CH <sub>3</sub> of positions 4 and 5). 7.2-8 (m, 10H, aromatic). M <sup>+</sup> +1: 328.89
4	690, 756 (monosubstituted phenyl). 1034, 1072, 1119, 117 (C-O-C cyclic). 1362 (C-N) 1457, 1497 (C=N). 1597, 1551 (C=C). 2922 (quaternary salt).	2.2 (m, 6H, 2CH <sub>3</sub> of positions 4, 5). 2.3-2.4 (m, 6H, 2CH <sub>3</sub> of positions 3, 6). 3.5 (m, 4H, 2CH <sub>2</sub> of positions 3, 6). 7.2-8 (m, 10H, aromatic). M <sup>+</sup> : 640
5b	692, 757 (monosubstituted phenyl). 809, 833, 875 (o-disubstituted phenyl). 1025, 1119, 1164 (C-O-C cyclic). 1351 (C-N) 1489, 1525 (C=N). 1596 (C=C). 2924, 2855 (quaternary salt).	2.25 (m, 6H, 2CH <sub>3</sub> of positions 3, 6). 3.00 (s, 4H, 2CH <sub>2</sub> of positions 3, 6). 1.5 (m, 6H, 2CH <sub>3</sub> of quinolinium). 3.3 (s, 4H, 2CH <sub>2</sub> of quinolinium). 7-8.5 (m, 24H, aromatic + heterocyclic + 2-CH=).
6	756, 691 (monosubstituted phenyl). 1027, 1066, 1126, 1193 (C-O-C cyclic). 1358 (C-N). 1496, 1447 (C=N). 1596, 1553 (C=C). 2924, 2854 (quaternary salt).	1.35 (m, 12H, 4CH <sub>3</sub> of diethoxyethyl). 2.3-2.4 (m, 6H, 2CH <sub>3</sub> of positions 3, 6). 3.6 (m, 4H, 2CH <sub>2</sub> of positions 3, 6). 3.7 (m, 8H, 4CH <sub>2</sub> of diethoxyethyl). 3.8 (m, 4H, 2CH <sub>2</sub> of positions 4, 5). 4.2 (m, 2H, 2CH of positions 4, 5). 7-8.2 (m, 10H, aromatic). M <sup>+</sup> : 844.12
7b	600, 755 (monosubstituted phenyl). 876 (o-disubstituted phenyl). 1032, 1121, 1158 (C-O-C cyclic). 1437 (C=N). 1629 (C=C). 2926 (quaternary salt).	1.2-1.5 (m, 6H, 2CH <sub>3</sub> of positions 3, 6). 2.1-2.3 (m, 4H, 2CH <sub>2</sub> of positions 3, 6). 2.9-3 (m, 6H, 2CH <sub>3</sub> of quinolinium). 3.2-3.8 (b, 4H, 2CH <sub>2</sub> of quinolinium). 7-8.5 (m, 28H, aromatic + heterocyclic + 6-CH=).

**Table 4.** Solvatochromism of the dyes (5b) and (7b) in pure solvents having different polarities

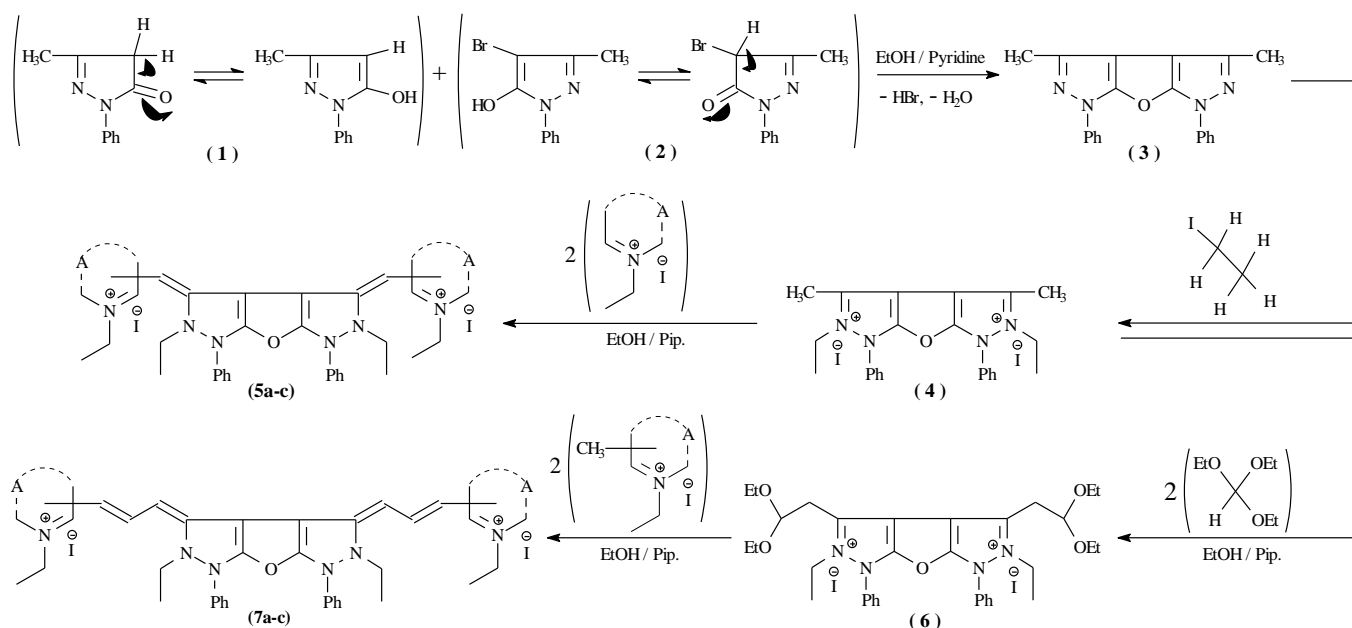
Solvent	H <sub>2</sub> O		EtOH		DMF		CHCl <sub>3</sub>		CCl <sub>4</sub>		Dioxane	
	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )
5b	410	1342	400	228	430	1366	420	1649	420	1764	420	1270
	430	1318	440	6	450	1398	450	1184	450	1784	450	1288
7b	430	1186	460	2275	430	1583	430	1094	420	1544	450	1140
	460	1309	560	2244	450	1550	470	1175	460	1550	480	1154
7b	555	877	620	222	550	1893	625	594	480	1721	580	828
				0	640	642			550	1820	635	374
									630	687		

**Table 5.** Halochromism of the dyes (5b) and (7b) in aqueous universal buffer solutions having varying pH values

pH	Universal Buffers															
	1.75		2.45		4.65		5.8		7.88		8.75		10.58		12.6	
Dye No.	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )
5b	400	2327	420	1707	425	1764	435	1644	440	2289	445	1248	445	2372	445	2471
	420	1971	435	1567	450	1910	460	1473	462	2234	468	1196	470	1857	474	2151
	540	713	555	1425	560	595	562	922	565	1036	570	802	572	877	575	946
7b	440	2007	450	1098	450	1467	450	2266	450	1815	450	1176	452	1069	455	1052
	480	1452	480	1143	482	1355	482	1804	485	1567	490	1023	495	1087	498	1043
	590	796	592	634	594	745	595	865	597	679	598	711	600	675	610	653

**Table 6.** The variation of absorbance with pH at fixed  $\lambda$  for the dyes (5b) and (7b) in aqueous universal buffer solutions

Absorbance at fixed wavelength	Dye	pH								PKa
		1.75	2.45	4.65	5.8	7.88	8.75	10.58	12.6	
5b $\lambda=510(\text{nm})$		0.978	0.669	0.866	0.898	0.813	0.801	1.144	1.354	4.5 8.7
	7b $\lambda=590(\text{nm})$	0.796	0.634	0.745	0.865	0.679	0.711	0.466	0.49	4.6 10.2

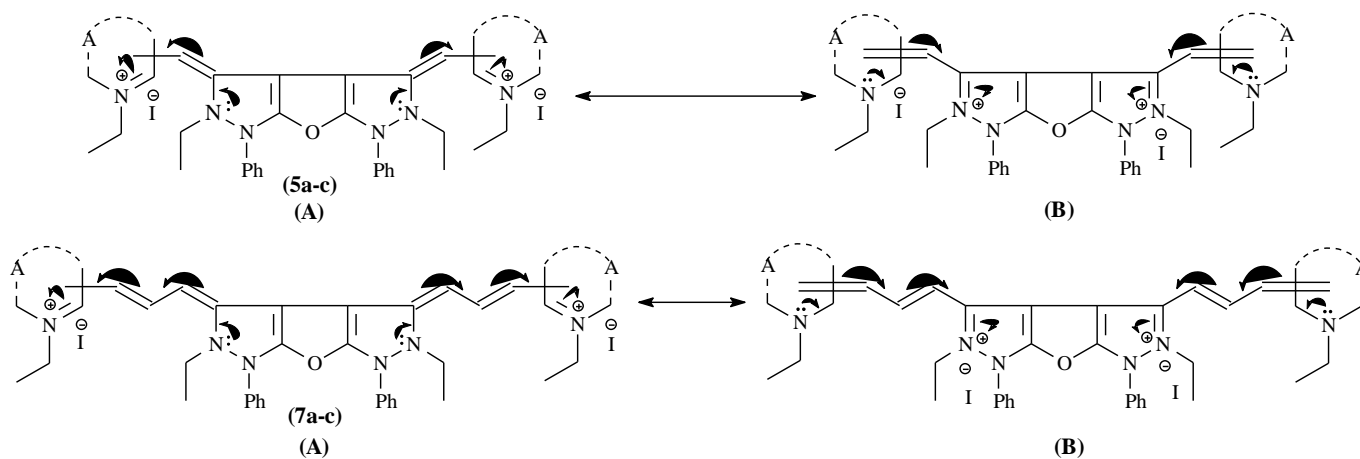


**Scheme 1. Synthesis strategy of the prepared compounds**

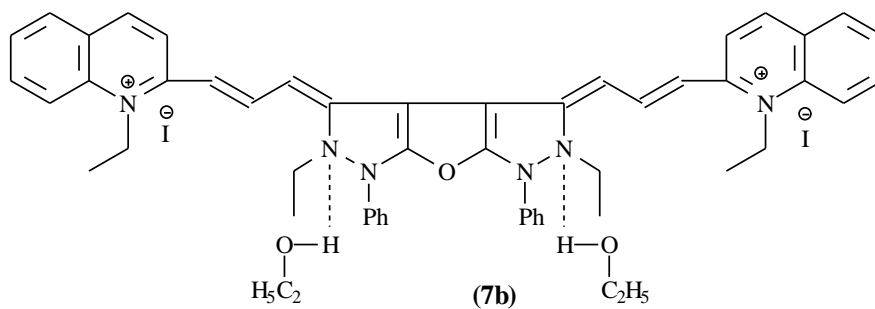
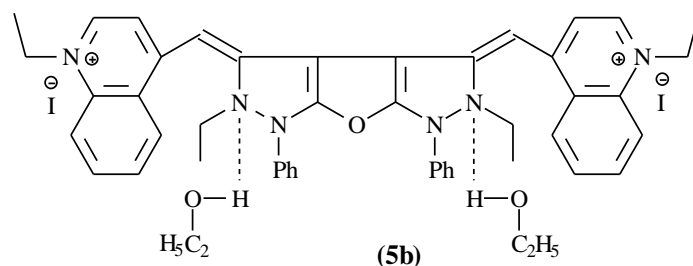
**Substitutes in Scheme (1):**

(5a-c): A=1-ethyl pyridinium-4-yl salt (a); 1-ethyl quinolinium-4-yl salt (b); 2-ethyl isoquinolinium-1-yl salt (c).

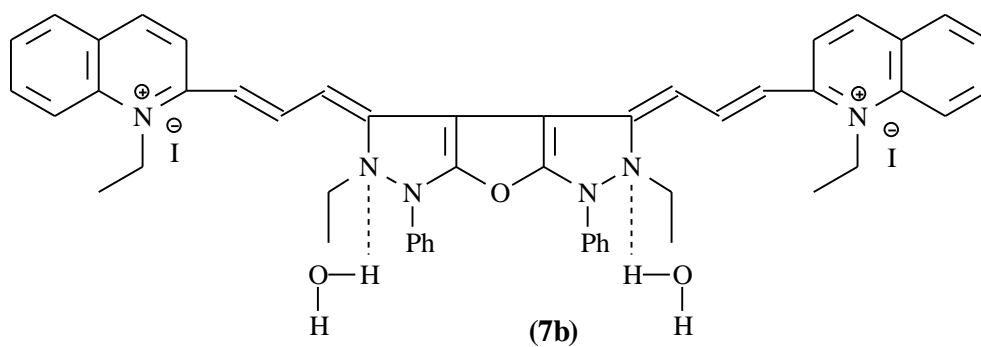
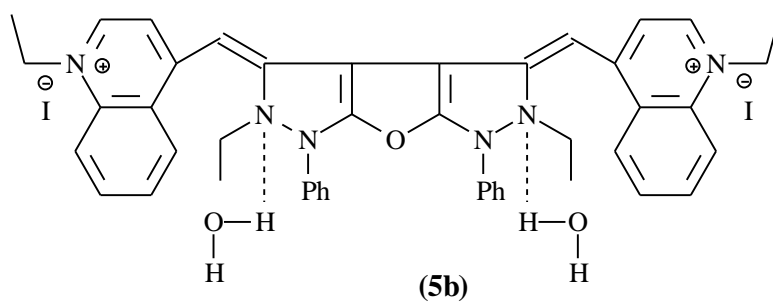
(7a-c): A=1-ethyl pyridinium-2-yl salt (a); 1-ethyl quinolinium-2-yl salt (b); 1-ethyl pyridinium-4-yl salt (c).



**Scheme 2. Colour intensity illustration of the synthesized cyanine dyes (5a-c) and (7a-c)**

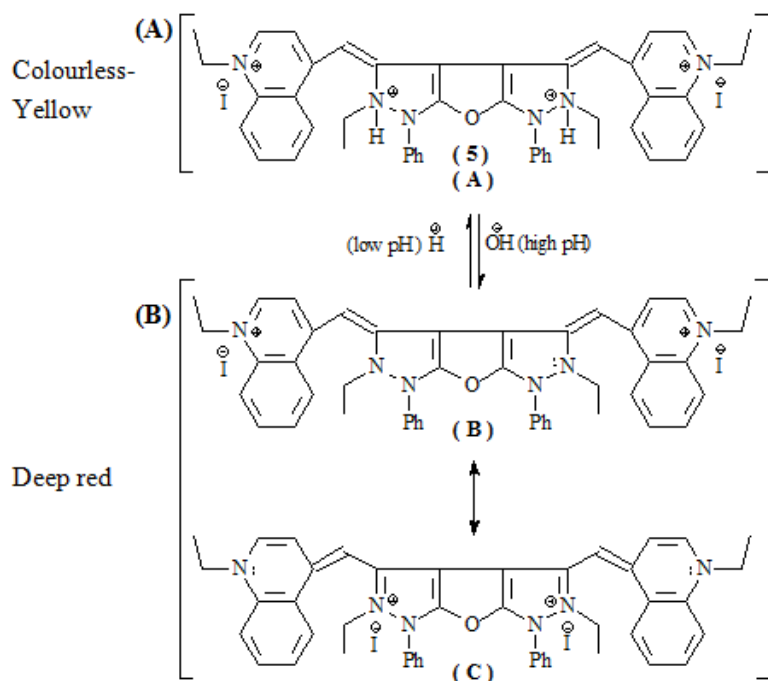


**Scheme (3) (A).** Hydrogen bond formation between the cyanine dyes (5b), (7b) and ethanol molecules (specific solvent effect).

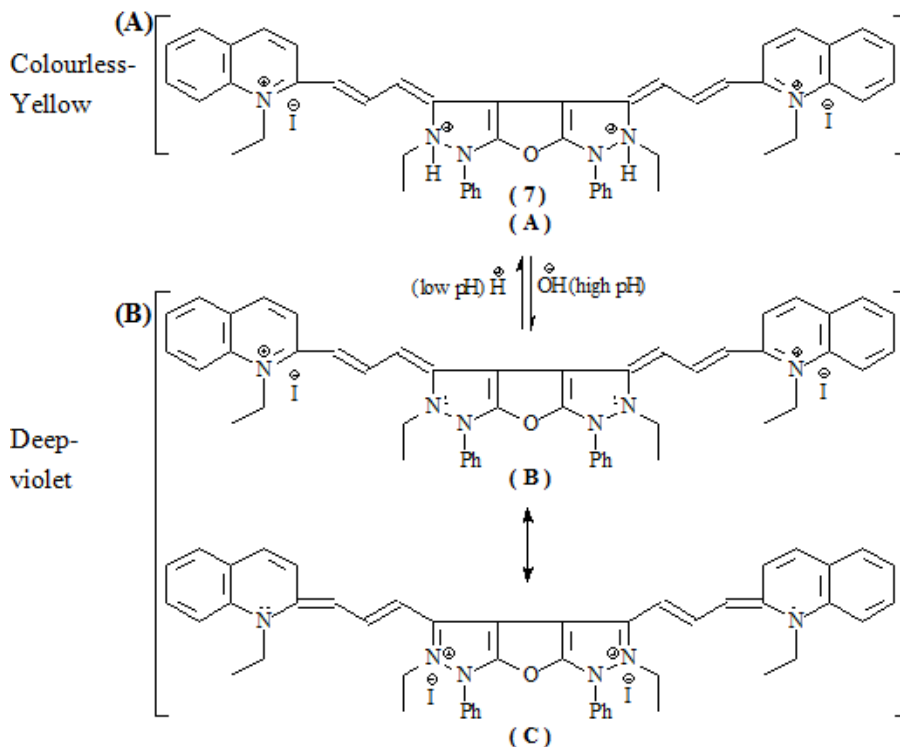


**Scheme (3) (B).** Hydrogen bond formation between the cyanine dyes (5b), (7b) and water molecules (specific solvent effect)

## Effects of pH media on the colour change of the cyanine dye (5b)



**Scheme (4).** Decolourization (protonation) and colourization (deprotonation) of the cyanine dye (5b) in acid and base media, respectively (acido-basic equilibrium).



**Scheme (4) Continue.** Decolourization (protonation) and colourization (deprotonation) of the cyanine dye (7b) in acid and base media, respectively (acido-basic equilibrium)