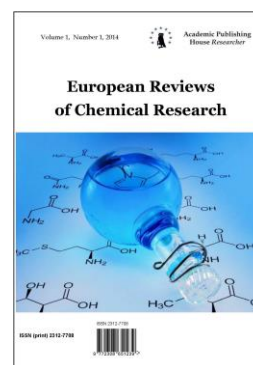


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Synthesis and Studies on New Dimethine and Tetramethine Cyanine Dyes

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Abstract

New dimethine cyanine dyes and tetramethine cyanine dyes having the nucleus of furo[(3,2-d; (3',2'-d)-bis pyrazole] were prepared. The electronic visible absorption spectra of all the synthesized cyanine dyes were investigated in 95 % ethanol solution to evaluate their spectral sensitization properties. Solvatochromism for some selected dyes were examined 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)] to evaluate their solvatochromic properties. Halochromism (acid-base properties) of some chosen dyes were measured in aqueous universal buffer solutions having varied pH values (1.75, 2.45, 4.65, 5.80, 7.88, 8.75, 10.58 and 12.60 units) to evaluate their halochromic characterization. Structural determination were carried out through elemental analysis, visible spectra, mass spectrometer, IR and ¹H NMR spectral data.

Keyword: synthesis, cyanine dyes, solvatochromism, halochromism, visible spectra, methine cyanine dyes.

1. Introduction

Enhanced attention has been focused on the chemistry of cyanine dyes (Arjonat et al., 2016; Shindy et al., 2012; Zhang et al., 2008; Park et al., 2013; Shindy et al., 2016; Deligeorgiev et al., 2007; Keisar et al., 2014; Soriano et al., 2016; Takasu et al., 2006; Park et al., 2013; Zhao et al., 2013; Shindy et al., 2016a; Shershof et al., 2013; Wang, Kim 2009; Komljenovic et al., 2016). This is because the multiplicity uses and applications of cyanine dyes in a diverse and a broad area (Liu et al., 2011; Owens et al., 2014; Matsuoka, 1990; Ansari et al., 2014; Shindy et al., 2014; Shindy, 2014; Shindy et al., 2014a; Shindy, 2015; Shindy, 2015a; Shindy et al., 2015; Shindy, 2016; Zhang et al., 2016; Chen et al., 2016). Their uses and applications includes but not limited to photographic sensitizers for silver halide emulsion in manufacturing technology of photosensitive material industry, photosensitizers for solar cells material, in modern optical technologies, photoconducting media, solvatochromic and halochromic probes, at diagnostics and treatment of cytological abnormalities, in fluorescent marker technology, in photorefractive media, information storage, optical disks as recording media, and in laser technology.

Taking in accounts and consideration the above applications and uses of cyanine dyes we prepared here new photosensitizers, solvatochromic and halochromic cyanine dyes as new synthesis contribution and spectroscopic investigation in this field and/or to may be used and/or

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applied in any of the mentioned uses and application of cyanine dyes particularly as photographic sensitizer for silver halide emulsion in photographic industry, as probes for determining solvent polarity in physical, physical organic and/or inorganic chemistry and as pH indicators in operations of acid/base titration in analytical chemistry.

2. Results and discussion:

2.1. Synthesis

Selenium dioxide oxidation of 4, 5-dimethyl-2, 7-diphenyl-furo [(3, 2-d), (3, 2-d)-bis pyrazole] (1) (Shindy et al., 2017) in 2:1 molar ratios, in dioxane as organic solvent achieved the 4,5-dicarbaldehyde compound (2), Scheme (1), Table (1). Further reaction of the 4,5-dicarbaldehyde compound (2) with iodoethane quaternary salts of α -picoline, quinaldine and/or γ -picoline in 1:2 molar ratios and in ethanol containing few mls of piperidine resulted the 4,5[(2(4))-bis dimethine cyanine dyes (3a-c), Scheme (1), Table (1).

Reaction of the 4,5-dicarbaldehyde compound (2) with acyl and/or substituted acyl such as acetaldehyde, acetone, acetophenone p-methoxyacetophenone, or p-nitroacetophenone, in 1:2 molar ratios, in ethanol containing piperidine gives the 4,5 (2)-bis (acyl ethenyl) as intermediate compounds (4a-e), Scheme (1), Table (2). Subsequent reactions of the intermediate compounds (4a-e) with 1-ethyl-2-methyl-quinolinium iodide quaternary salt in 1:2 molar ratios, in ethanol and in presence of few mls of piperidine produced the 4,5(2)-bis tetramethine cyanine dyes (5a-e), Scheme (1), Table (2).

The structures of the prepared compounds were identified through elemental analysis, visible spectra Tables (1, 2), mass spectrometer, IR (Wade, 1999) and ^1H NMR (Wade 1999a) spectral data, Table (3).

2.2. Spectral studies

Spectral sensitization evaluation studies for all the synthesized cyanine dyes were carried out through investigating their electronic visible absorption spectra in 95 % ethanol solution. The dyes were thought to be better spectral sensitizers when they absorb the visible light to initiate the electronic transitions at higher wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently, the spectral sensitization of the dyes decreases when they absorb the visible light to initiate the electronic transitions at lower wavelength bands (hypsochromic shifted and/or blue shifted dyes). So, 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 one is shorter than that of the latter one. In contrary, 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 one is longer than that of the latter one. Spectral sensitization evaluation study is very important in the case of cyanine dyes because the extensive uses of these dyes in photographic industry to increase the sensitivity range of silver halide emulsion by making an increase in the range of wavelength which form an image on the film.

The electronic visible absorption spectra of the 4,5-[2(4)] bis dimethine cyanine dyes (3a-c) in 95 % ethanol solution discloses bands in the visible region (440-540 nm). The positions of these bands and their molar extinction coefficients are remarkably effected by the types of the heterocyclic quaternary salts residue (A) and their linkage positions. So, substituting A=1-ethyl-pyridinium-2-yl salt by A=1-ethyl quinolinium-2-yl salt, transferring from dye (3a) to dye (3b) causes bathochromic shifts for absorption bands by (20 nm), Table (1). This can be attributed to increasing π -delocalization conjugation in the latter dye (3b) due to the presence of the additional benzene ring system in quinoline nucleus in correspondence to pyridine nucleus system in the former dye (3a). Changing the linkage position from 2-yl salt residue to 4-yl salt residue moving from dye (3a) to dye (3c) resulted bathochromic shifts for the absorption bands by (15 nm), Table (1). This can be related to increasing the length of the π -delocalization conjugation in the latter dye (3c) due to the presence of γ -picoline nucleus in correspondence to the α -picoline nucleus in the former dye (3a).

Additionally, the electronic visible absorption spectra of the 4,5(2)-bis tetramethine cyanine dyes (5a-e) in 95 % ethanol solution reveals displacements to give bathochromic and/or

hypsochromic shifted bands depending upon the nature of the substituents in the diene side chain (R). So, substituted R = H in dye (5a) by R = CH₃ and/or R = Ph to get dyes (5b) and/or (5c) causes strong red shifts for the absorption bands by (70 nm) and/or (50 nm), respectively (Table 2). This can be related to the electron donating character of the methyl group in dye (5b) and/or increasing conjugation in the dye (5c) due to the presence of phenyl ring system. Substituting R = C₆H₅ in dye (5c) by R = C₆H₄, p.OCH₃ and/or R = C₆H₄.pNO₂ to get dyes (5d) and/or (5e), produced bathochromic shifts and/or hypsochromic shifts for the absorption bands by (30 nm) and/or (10 nm), respectively, Table (2). This can be attributed to the strong electron donating character of the methoxy group in dye (5d) and the strong electron attracting character of the nitro group in dye (5e). Electron donating groups facilitate and increase the intensity of the electronic charge transfer to the quaternary quinolinium salt residue by pushing electrons and consequently red shifts occurs. Inversely electron attracting groups makes difficult and decreases the intensity of the electronic charge transfer to the quaternary quinolinium salt residue by pulling electrons and accordingly blue shifts occurs.

General comparison between the electronic visible absorption spectra of the dimethine cyanine dyes (3a-c) and the tetramethine cyanine dyes (5a-e) reveals that the latter dyes have red shifted bands than the former dyes, Tables (1, 2). This can be illustrated in the light of the increasing of the number of methine groups in the latter dyes, Scheme (1).

From this study we could conclude that:

The electronic visible absorption spectra of the 4,5[2(4)]-bis dimethine cyanine dyes (3a-c) and the 4,5(2)-bis tetramethine cyanine dyes (5a-e) underwent displacements to give bathochromic and/or hypsochromic absorption bands accompanied with increasing and/or decreasing the number and the intensity of the absorption bands depending upon the following factors:

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

quinaldine dyes > α -picoline dyes (for the dimethine cyanine dyes).

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

γ -picoline dyes > α -picoline dyes (for the dimethine cyanine dyes).

c-Nature of the substituents (R) in the diene side chain in the order of:

(I) CH₃ dyes > Ph dyes > H-dyes (for the tetramethine cyanine dyes).

(II) C₆H₄.pOCH₃ dyes > C₆H₅-dyes > C₆H₄.pNO₂ dyes (for the tetramethine cyanine dyes).

d-Increasing the number of the methine units in the order of:

tetramethine cyanine dyes > dimethine cyanine dyes.

2.3. Solvatochromic studies

Solvatochromic evaluation studies for some selected synthesized cyanine dyes (3b) and (5a) was carried out via examining of their electronic visible absorption spectra in pure solvents having different polarities. The dyes are thought 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 this 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 spectra of the dimethine cyanine dye (3b) and the tetramethine cyanine dye (5a) 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., 2014; Shindy, et al., 2014a) are recorded. The λ_{\max} (wavelength) and ϵ_{\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) it's clearly that the electronic visible absorption spectrum of the dyes (3b) and (5a) in ethanolic medium are characterized by the presence of two (dye 3b) and/or four (dye 5a) essential absorption bands. These bands can be assigned to intermolecular charge transfer transition (Shindy et al., 2014; Shindy et al., 2014a). These charge transfer is due to transfer of lone

pair of electrons from the N-phenyl 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-phenyl pyrazole nitrogen atom, Scheme (3) (A). This decreases slightly the electron density on the N-phenyl pyrazole nitrogen atom and consequently decreases to some extent the mobility of the attached π -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-phenyl pyrazole nitrogen atom forming intermolecular hydrogen band, Scheme (3) (B). This makes difficult the transfer of electronic charge from the N-phenyl 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.

From this investigation we can conclude that:

The solvatochromism of the examined cyanine dyes (3b) and (5a) 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).

2.4. Halochromic studies (acid-base properties)

Halochromic evaluation studies for some selected synthesized cyanine dyes (3b) and (5a) 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 dimethine cyanine dye (3b) and the bis tetramethine cyanine dye (5a) 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 important purpose of this study is to evaluate the halochromic properties of these dyes to may be used and/or applied as pH indicators in operations of 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., 2014; Shindy, et al., 2014a) and therefore more conjugation.

So, the electronic visible absorption spectra of the bis dimethine cyanine dye (3b) and the bis tetramethine cyanine dye (5a) in aqueous universal buffer solutions of varying pH values (1.75, 2.45, 4.65, 5.80, 7.88, 8.75, 10.58 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-phenyl pyrazole nitrogen atom undergoes to protonation in low pH media (acidic media). This leads to a criterion of positive

charge on the N-phenyl 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-phenyl 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 λ 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., 2014; Shindy et al., 2014a). The acid dissociation or protonation constants values of the dyes (3b) and (5a) are given in Table (6).

From this examination we could conclude that:

The halochromism of the bis dimethine cyanine dye (3b) and the bis tetramethine cyanine dye (5a) 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 higher pH media (basic media) due to the deprotonated and/or coloured structures of these dyes in this media.

3. Conclusion

1. The intensity of the colours of the 4,5-[2(4)]-bis dimethine cyanine dyes (3a-c) and the 4,5(2)-bis tetramethine cyanine dyes (5a-e) can be explained in the light of the two suggested mesomeric structures (A) and (B) producing a delocalized positive charge over the conjugated system, Scheme (2).

2. These cyanine dyes can be used as:

a. Photographic sensitizers in photosensitive material industry due to their spectral and/or photosensitization properties,

b. Indicators for solvent polarity in physical, physical organic and/or inorganic chemistry due to their solvatochromic properties and

c. Indicators in operations of acid-base titrations in analytical chemistry due to their halochromic properties.

3. Because cyanine dyes have multiplicity uses and applications in various fields of science, technology, engineering, pharmacology and medicine, this research paper might be very interesting and useful for the large heterogenous community groups of chemists, biologists, physicists, biotechnologists, pharmacologists and medical scientists.

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. ^1H 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-diformyl-2, 7-diphenyl-furo [(3, 2-d), (3, 2-d)-bis pyrazole] (2)

A pure crystallized sample of (1) (0.01 mol) and selenium dioxide (0.02 mol) were heated under reflux in dioxane (30 ml) for 16-18 hrs. The reaction mixtures were filtered on hot to remove selenium metal and the filtrate was cooled and precipitated by ice water mixture. The precipitated products were filtered, dried, collected, and crystallized from ethanol. To give the 4,5-dicarbaldehyde compound (2). The data are shown in Table (1).

4.2.2-Synthesis of 2, 7- diphenyl-furo [(3, 2-d), (3, 2-d) bis Pyrazole]- 4, 5 [2(4)]-bis- dimethine cyanine dyes (3a-c)

A mixtures of unimolar ratios (0.01 mol) of compound (2) and bimolar ratios (0.02 mol) of N-iodoethane quaternary salts of α -picoline, quinaldine, γ - picoline were heated under reflux in ethanol (30 ml) containing few mls of piperidine (1-2 mls) for 4-5 hrs. The reaction mixtures which attained colours from deep brown to deep violet at the end of refluxing was filtered while hot to remove any impurities, cooled and precipitated by dilution with ice water mixture. The precipitated products was filtered, washed with water several times, dried, collected and crystallized from ethanol. The data are summarized in Table (1)

4.2.3-Synthesis of 2, 7- diphenyl-furo [(3, 2-d), (3, 2-d)-bis pyrazole]-4, 5-bis (acyl ethenyl) as intermediate compounds (4a-e)

The 4,5-dicarbaldehyde compound (2) were heated under reflux with acyl and/or acyl derivatives (acetaldehyde, acetone, acetophenone, p-methoxyacetophenone, or p-nitroacetophenone) in 1:2 molar ratios in ethanol (30 ml) containing piperidine (1-2 ml) for 6 hrs. The reaction mixture, which changed from reddish colour to deep brown colour at the end of refluxing, was filtered while hot to remove any impurities, concentrated, cooled and precipitated by adding ice-water mixture to give the intermediate compounds (4a-e) which was crystallized from ethanol. The data were given in Table (2).

4.2.4-Synthesis of 2, 7- diphenyl-furo [(3, 2-d), (3, 2-d) bis pyrazole]-4,5 (2)-bis tetramethine cyanine dyes (5a-e)

Piperidine (3-5 drops) was added to a mixture of an ethanolic solution (30 ml) of the intermediate compounds (4a- e) (0.01) and iodoethane quaternary salt quinaldine (0.02 mol). 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 (1×10^{-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 halochromism

The electronic visible absorption spectra of some selected synthesized cyanine dyes were investigated in pure organic solvents of spectroscopic grade (Shindy et al., 2014; Shindy et al., 2014a) 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 (1×10^{-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 (2) and (3a-c)

| Comp. No | Nature of product | | | Molecular formula (M.Wt.) | Analysis % | | | | | | Absorption spectra in 95 % ethanol solution | |
|----------|-------------------|-----------|-----------|--|------------|------|-------|-------|------|-------|---|---|
| | Colour | Yield (%) | M.P. (°C) | | Calculated | | | Found | | | λ_{max} (nm) | ϵ_{max} (mole \cdot l \cdot cm $^{-2}$) |
| | | | | | C | H | N | C | H | N | | |
| 2 | Red | 60 | 130 | C ₂₀ H ₁₂ N ₄ O ₃ (356) | 67.41 | 3.37 | 15.73 | 67.38 | 3.36 | 15.71 | --- | --- |
| 3a | Violet | 45 | 175 | C ₃₆ H ₃₂ N ₆ OI ₂ (818) | 52.81 | 3.91 | 10.26 | 52.80 | 3.88 | 10.24 | 440, 520 | 2275, 2279 |
| 3b | Deep violet | 63 | 170 | C ₄₄ H ₃₆ N ₆ OI ₂ (918) | 57.51 | 3.92 | 9.15 | 57.50 | 3.90 | 9.13 | 480, 540 | 2262, 2253 |
| 3c | Deep violet | 52 | 180 | C ₃₆ H ₃₂ N ₆ OI ₂ (818) | 52.81 | 3.91 | 10.26 | 52.80 | 3.88 | 10.24 | 460, 535 | 2242, 2251 |

Table 2. Characterization of the prepared compounds (4a-e) and (5a-e)

| Comp. No | Nature of product | | | Molecular formula (M.Wt.) | Analysis % | | | | | | Absorption spectra in 95 % ethanol solution | |
|----------|-------------------|-----------|-----------|---|------------|------|-------|-------|------|-------|---|---|
| | Colour | Yield (%) | M.P. (°C) | | Calculated | | | Found | | | λ_{max} (nm) | ϵ_{max} (mole \cdot l \cdot cm $^{-2}$) |
| | | | | | C | H | N | C | H | N | | |
| 4a | Deep red | 61 | 160 | C ₂₄ H ₁₆ N ₄ O ₃ (408) | 70.57 | 3.92 | 13.72 | 70.55 | 3.90 | 13.70 | --- | --- |
| 4b | Deep red | 50 | 175 | C ₂₆ H ₂₀ N ₄ O ₃ (436) | 71.55 | 4.58 | 12.84 | 71.53 | 4.52 | 12.82 | --- | --- |
| 4c | Deep red | 45 | 190 | C ₃₆ H ₂₄ N ₄ O ₃ (560) | 77.14 | 4.28 | 10.00 | 77.12 | 4.25 | 9.98 | --- | --- |
| 4d | Deep red | 55 | 195 | C ₃₈ H ₂₈ N ₄ O ₅ (620) | 73.54 | 4.51 | 12.90 | 73.52 | 4.50 | 12.89 | --- | --- |
| 4e | Deep red | 55 | 200 | C ₃₆ H ₂₂ N ₆ O ₇ (650) | 66.46 | 3.38 | 12.92 | 66.46 | 3.38 | 12.92 | --- | --- |
| 5a | Deep violet | 54 | 170 | C ₄₈ H ₄₀ N ₆ OI ₂ (970) | 59.38 | 4.12 | 8.65 | 59.36 | 4.10 | 8.64 | 450, 520, 540, 570 | 2276, 2229, 2127, 1332 |
| 5b | Deep violet | 51 | 165 | C ₅₀ H ₄₄ N ₆ OI ₂ (998) | 60.12 | 4.40 | 8.41 | 60.10 | 4.39 | 8.40 | 600, 640 | 2229, 1332 |
| 5c | Deep violet | 45 | 195 | C ₆₀ H ₄₈ N ₆ OI ₂ (1152) | 62.50 | 4.16 | 7.29 | 63.36 | 4.35 | 7.64 | 450, 550, 570, 620 | 2276, 2141, 1332, 723 |
| 5d | Deep violet | 55 | 180 | C ₆₂ H ₅₂ N ₆ O ₃ I ₂ (1182) | 62.94 | 3.39 | 7.10 | 62.94 | 3.39 | 7.10 | 545, 565, 610, 650 | 2277, 2046, 949, 577 |
| 5e | Deep violet | 55 | 190 | C ₆₀ H ₄₆ N ₈ O ₃ I ₂ (1212) | 59.40 | 3.79 | 9.24 | 59.38 | 3.78 | 9.23 | 540, 580, 600, 610 | 2211, 1317, 896, 892 |

Table 3. IR and ¹H NMR (mass) spectral data of the prepared compounds (2), (3b), (4a) and (5a).

| Comp. No | IR Spectrum (KBr, Cm ⁻¹) | ¹ H NMR Spectrum (DMSO, δ); & (Mass data) |
|----------|--|--|
| 2 | 687, 754 (monosubstituted phenyl). 1133 (C-O-C cyclic). 1326, 1367 (C-N). 1495, 1454 (C=N). 1621, 1593, 1547 (C=C). 1723 (CHO). | 7.2-8.2 (m, 10H, aromatic). 9.2 (s, 1H, CHO). M ⁺ : 356.16 |
| 3b | 694, 755 (monosubstituted phenyl). 878, 905 (o.disubstituted phenyl). 1158, 1083, 1046 (C-O-C cyclic). 1380, 1314 (C-N). 1496, 1442 (C=N). 1627, 1597 (C=C). 2925, 2857 (quaternary salt). | 0.9-2.3 (m, 6H, 2CH ₃ of quinolinium). 2.8-3.6 (m, 4H, 2CH ₂ of quinolinium). 7-8.8 (m, 26H, aromatic + heterocyclic + 4-CH=). |
| 4a | 690, 756 (monosubstituted phenyl). 1027, 1126 (C-O-C cyclic). 1366 (C-N). 1496, 1447 (C=N). 1625, 1598 (C=C). 1717 (CHO). | 7.2-8.6 (m, 14H, aromatic + 4-CH=). 9.2 (s, 2H, 2CHO). M ⁺ +1: 408.65 |
| 5a | 752 (monosubstituted phenyl). 876 (o.disubstituted phenyl). 1123, 1154 (C-O-C cyclic). 1382 (C-N). 1493, 1449 (C=N). 1627 (C=C). 2924, 2856 (quaternary salt). | 0.9-1.7 (t, 6H, 2CH ₃ of quinolinium). 3-3.4 (m, 4H, 2CH ₂ of quinolinium). 6.6-8.2 (m, 30H, aromatic + heterocyclic + 8-CH=). |

Table 4. Solvatochromism of the dyes (3b) and (5a) in pure solvents having different polarities

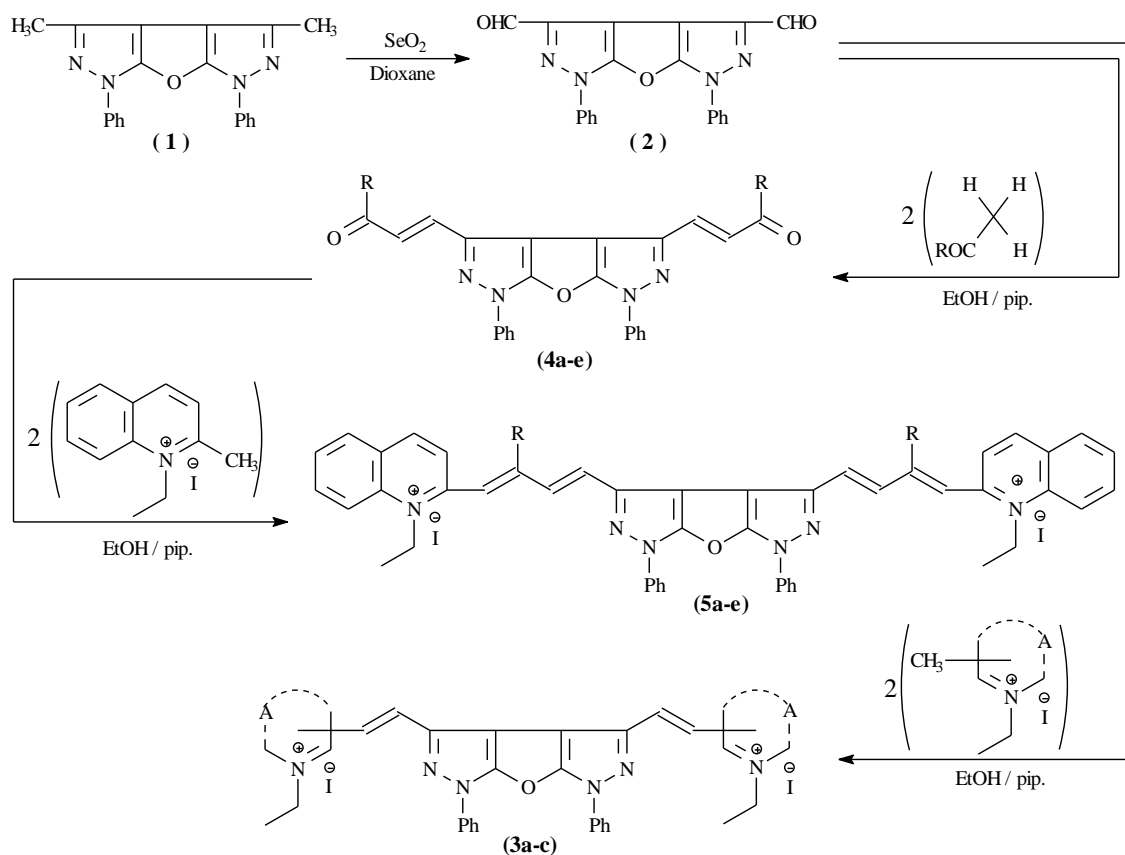
| Solvent Dye No. | H ₂ O | | EtOH | | DMF | | CHCl ₃ | | CCl ₄ | | Dioxane | |
|--------------------|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|
| | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) |
| 3b | 450 | 1795 | 480 | 2262 | 425 | 1686 | 450 | 1655 | 450 | 1655 | 450 | 1655 |
| | 480 | 2160 | 540 | 2253 | 460 | 1692 | 470 | 1672 | 550 | 1208 | 550 | 1270 |
| | 530 | 1922 | | | 580 | 1824 | 490 | 1599 | 565 | 1281 | 570 | 1223 |
| 5a | 450 | 1698 | 450 | 2276 | 420 | 935 | 430 | 1063 | 420 | 1595 | 430 | 1063 |
| | 490 | 2071 | 520 | 2229 | 450 | 1121 | 480 | 1008 | 460 | 1602 | 460 | 1008 |
| | 510 | 1833 | 540 | 2127 | 480 | 1179 | 570 | 891 | 480 | 1806 | 480 | 985 |
| | 560 | 1293 | 570 | 1332 | 560 | 880 | 635 | 513 | 550 | 1835 | 580 | 834 |
| | | | | | 580 | 864 | | | 640 | 774 | 645 | 450 |
| | | | | | 650 | 396 | | | | | | |

Table 5. Halochromism of the dyes (3b) and (5a) in aqueous universal buffer solutions having varied pH values

| pH Dye No. | Universal Buffers | | | | | | | | | | | | | | | |
|---------------|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|-------------------------|--|
| | 1.75 | | 2.45 | | 4.65 | | 5.8 | | 7.88 | | 8.75 | | 10.58 | | 12.6 | |
| | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) | λ_{max} (nm) | ϵ_{max} (mol ⁻¹ cm ²) |
| 3b | 430 | 2502 | 440 | 1194 | 440 | 1980 | 450 | 2468 | 450 | 1164 | 455 | 1281 | 455 | 1568 | 460 | 1233 |
| | 470 | 1631 | 474 | 1114 | 474 | 1489 | 478 | 1965 | 480 | 1197 | 480 | 1183 | 480 | 1526 | 480 | 1183 |
| | 585 | 957 | 587 | 734 | 589 | 754 | 590 | 832 | 592 | 757 | 593 | 717 | 595 | 957 | 598 | 836 |
| 5a | 460 | 1958 | 470 | 1428 | 470 | 1168 | 475 | 1067 | 475 | 1443 | 480 | 1119 | 485 | 1036 | 485 | 1165 |
| | 500 | 1467 | 505 | 1304 | 512 | 1052 | 515 | 1017 | 515 | 1017 | 510 | 1131 | 530 | 891 | 545 | 996 |
| | 615 | 725 | 620 | 481 | 622 | 634 | 628 | 583 | 630 | 711 | 635 | 673 | 638 | 465 | 640 | 412 |

Table 6. The variation of absorbance with pH at fixed λ for the dyes (3b) and (5a) in aqueous universal buffer solutions

| Dye | pH | | | | | | | | | PKa |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|--|-------------|
| | 1.75 | 2.45 | 4.65 | 5.8 | 7.88 | 8.75 | 10.58 | 12.6 | | |
| 3b $\lambda=480(\text{nm})$ | 1.574 | 1.012 | 1.234 | 1.804 | 1.099 | 1.086 | 1.401 | 1.081 | | 4.7 9.7 |
| 5a $\lambda=600(\text{nm})$ | 0.489 | 0.388 | 0.512 | 0.405 | 0.572 | 0.577 | 0.376 | 0.319 | | 4.5 10.4 |

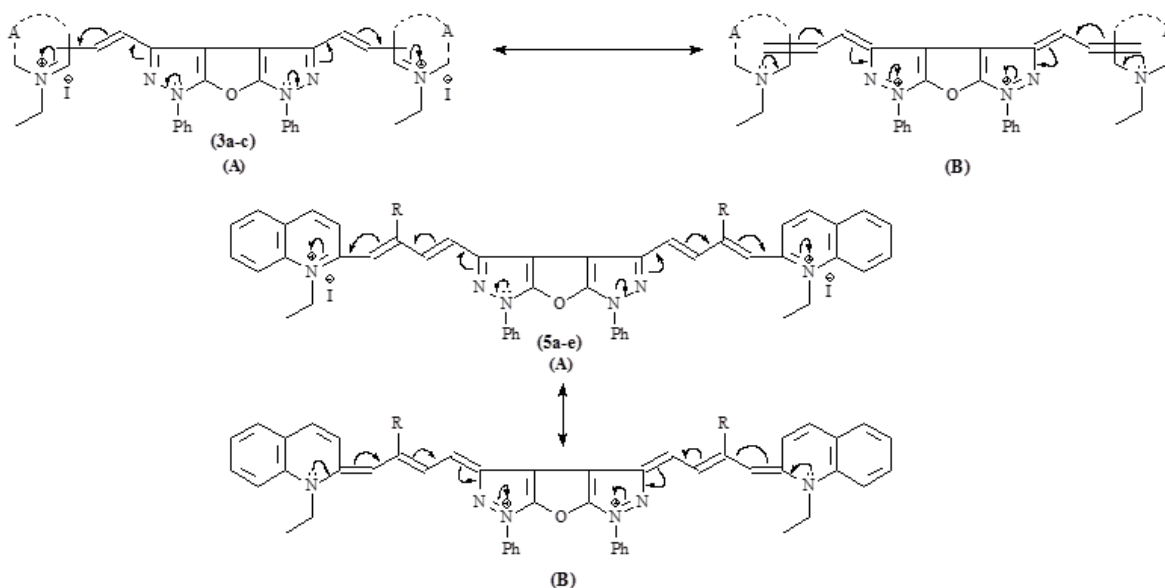


**Synthesis strategy of the prepared compounds (2), (3a-c), (4a-e) and (5a-e)
Scheme (1)**

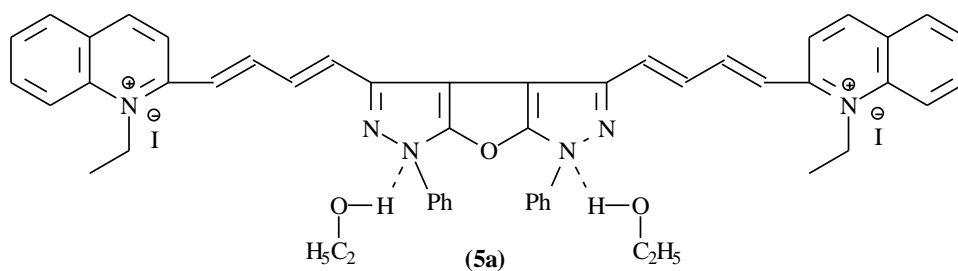
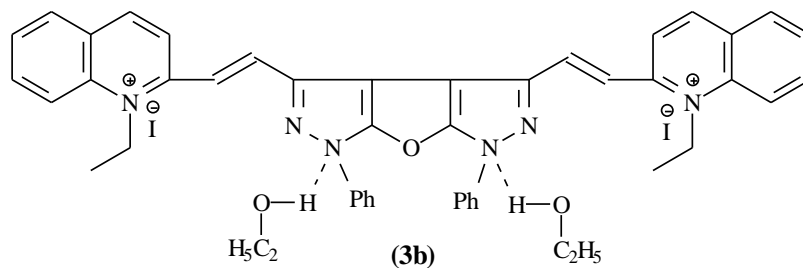
Substituents in Scheme (1):

(3a-c): A=1-ethyl pyridinium-2-yl salt (a); 1-ethyl quinolinium-2-yl salt (b); 1-ethyl pyridinium -4-yl salt (c).

(4a-e), (5a-e): R = H (a); CH₃ (b); C₆H₅ (c); C₆H_{4,p}.OCH₃ (d); C₆H_{4,p}.NO₂ (e).

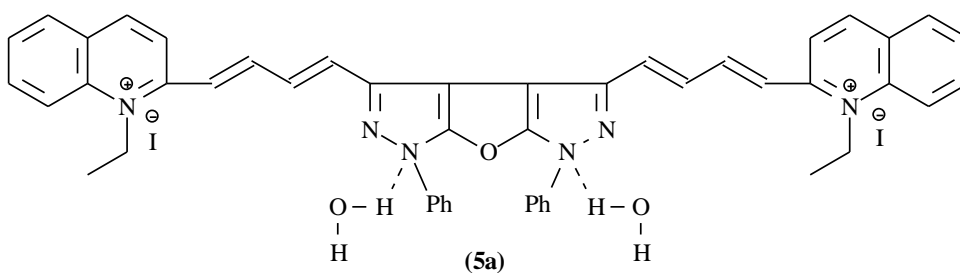
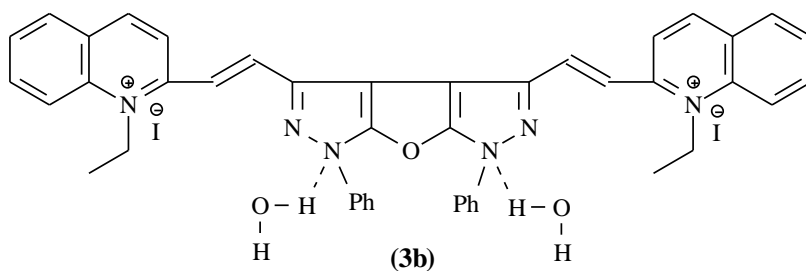


**Colour intensity illustration of the synthesized cyanine dyes (3a-c) and (5a-e)
Scheme (2)**



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

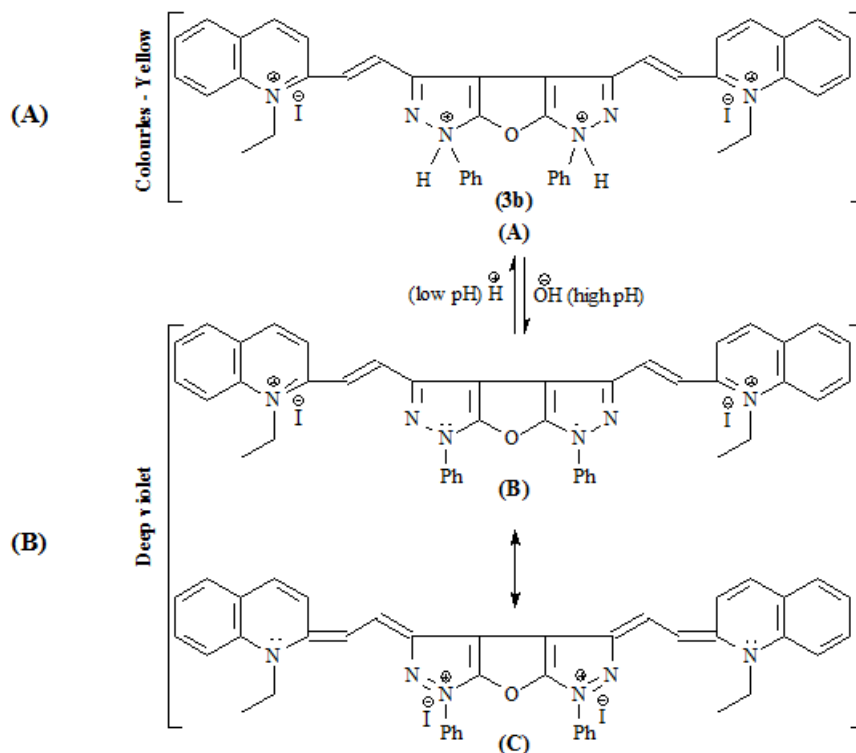
Scheme (3) (A)



Hydrogen bond formation between the cyanine dyes (3b), (5a) and water molecules (specific solvent effect)

Scheme (3) (B)

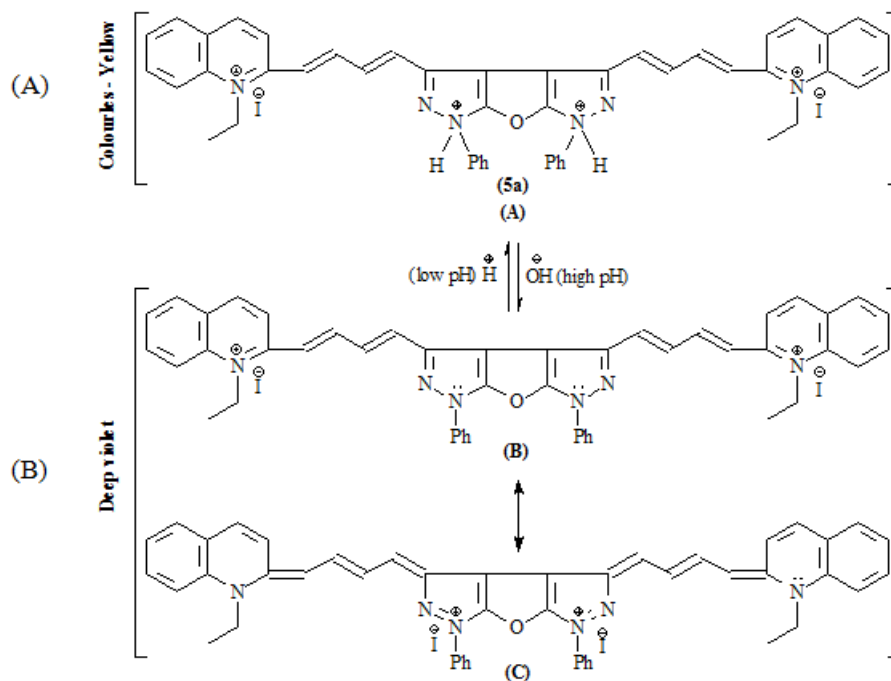
Effect of pH on discoloration efficiency of the cyanine dye (3b)



Decolourization (protonation) and colourization (deprotonation) of the cyanine dye (3b) in acid and base media, respectively (acido-basic equilibrium).

Scheme (4)

Effect of pH on discoloration efficiency of the cyanine dye (5a)



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

Scheme (4) Continue