Novel Polyheterocyclic Cyanine Dyes: Synthesis, Photosensitiztion and Solvent/Electronic Transitions Correlation

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Abstract

Novel polyheterocyclic cyanine dyes covering aza-cyanine dyes and bis aza-cyanine dyes derived from 3,8-diethyl-2,7-diphenyl benzo [2,3-b; $\overline{2}$,$\overline{3}$-$\overline{b}$] bis furo[3,2-d] pyrazolium iodide quaternary salt were prepared. The electronic visible absorption spectra for all the synthesized cyanines were investigated in 95 % ethanol solution to evaluate their photosensitization/electronic transitions correlation. The cyanine dyes were thought to be better photosensitizers when they absorb the visible light to initiate the electronic transitions at higher wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently, the photosensitization of the cyanine dyes decreases when they absorb the visible light to initiate the electronic transitions at lower wavelength bands (hypsochromic shifted and/or blue shifted dyes). Solvent/electronic transitions correlation study for some selected cyanine dyes were carried out in pure solvents having different polarities [water (78.54), Dimethylformamide (36.70), ethanol (24.3), chloroform (4.806), benzene (2.28) and dioxane (2.209)] to evaluate their solute/solvent interaction properties (general and/or specific solvent effects). Structural identification were confirmed using elemental analysis, visible spectra, IR and ^{1}H NMR spectral data.

Keywords: cyanine dyes, aza-cyanine dyes, synthesis, photosensitization/electronic transitions correlation, visible spectra, solvent / electronic transitions correlation.

1. Introduction

Cyanine dyes (Shindy, 2017; Shindy, 2016; Shindy, 2018; Shindy et al., 2017; Shindy et al., 2017a; Solomon et al., 2014; Lynch et al., 2013; Shindy et al., 2012; Arjona et al., 2016; Shindy et al., 2015; Shindy, 2015; Shindy, Koraiem, 2008) have a wide range and various applications in different fields of science and technology. Their uses and applications include but not limited to spectral sensitizers for silver halide emulsions in photographic material industry for coloured and non coloured (black and white) films (cyanine dyes were originally used, and still are, to increase the sensitivity range of photographic emulsions, i. e. to increase the range of wavelengths which will form an image on the film) (Msaki, Tadashi, 1992; Mari, 1993; Tadashi, 1992; Nobuaki, 1995; Yoshio, Tadahire, 1999), as tools for lasers (Toshiyoshi et al., 2003; Tsutomu et al., 1994), as optical recording media (Toshio, 1992), optical filters (Hiroshi, 1999), optical information recording disk (Katsuji, Katsuhiko, 1991), as inks containing near-IR absorber for optically readable printing (Rivera et al., 2007), and for the development of integrated optochemical sensors

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(Clegg et al., 1992). In addition, cyanine dyes can also be very usefully employed for conformational studies via fluorescence energy transfer (Norman et al., 2000; Mortensen, Chui, 2002), agarose gel and capillary electrophoresis staining (Zhu et al., 1994), DNA analysis in polymerization chain reactions (Schwartz, Ulfelder, 1992; Bengtsson et al., 2003) and flow cytometry (Hirons et al., 1994), or as fluorescent probes for membrane fluidity (Kurihara et al., 1977; Armitage, O'Brien, 1992) and membrane potential studies (Reers et al., 1991) and as a probe for albumin and collagen in the extracellular matrix (Panova et al., 2007). Recently, cyanine dyes have been tested for therapeutic uses, and in the future time cyanine dyes may find very important applications in this field.

Taking in account and consideration these important, useful and interested applications of cyanine dyes, we prepared here new classes of photosensitizers and solvatochromic aza-cyanine dyes as new synthesis contribution and spectroscopic investigation in this field, and hoping that it may be find useful uses in any of the wide fields and various aspects of cyanine dyes applications, particularly as photosensitizers in photographic material industry for colored and non colored (black and white) films, as acid-base indicators in analytical chemistry, as probes for determining solvent polarity in solution chemistry and /or as anti-bacterial strains (bactericidals), anti-fungi strains (fungicidals) in pharmaceutical (pharmacological) industry.

2-Results and Discussion
2.1. Synthesis

Reaction of 3,8-diethyl-4,9-dimethyl -benzo [2,3-b; $\bar{2}$,$\bar{3}$-$\bar{b}$] bis furo[3,2-d] pyrazolium iodide quaternary salt (1) (Shindy, 2007) with equimolar ratios of the nitroso compounds (ρ.nitroso-phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) in ethanol as organic solvent and piperidine as a basic catalyst achieved the 4[2(1)]-aza-cyanine dyes (2a−c), Scheme (1).

In addition, reaction of 1 M ratios of the diquaternizsed compound (1) with 2 M ratios of the nitroso compounds (4-nitroso-phenol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol) in ethanol and in presence of few mls of piperidine resulted the 4,9 [2(1)]-bis aza-caynine dyes (3a-c), Scheme (1).

Chemical confirmations takes place through reaction of the 4[2(1)]-aza-cyanine dyes (2a-c) with equimolar ratios of the same nitroso compounds (ρ.nitroso-phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) in ethanol catalyzed by piperidine to produce the same 4,9 [2(1)]- bis aza-cyanine dyes (3a−c), characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data, Method (2), Scheme (1).

The structure of the prepared compounds was identified by elemental analysis (Table 1), visible spectra (Table 1) as well as IR (Wade, 1999) (Table 2) and ^{1}H NMR (Wade, 1999a) (Table 2) spectral data.

2.2. Synthesis mechanisms

The synthesis mechanism of the aza-cyanine dyes (2a-c) is suggested to proceeds as follows:

1-The first step in this mechanism involves the formation of the carbanion ion (a) via attacking of the basic catalyst piperidine to the active acidic methyl group of the heterocyclic quaternary salt, Scheme (2).

2-The second step involves nucleophilic attack of the carbanion ion (a) to the positively center of the ionized nitroso group to form the anion (b), Scheme (2).

3-The third step represents transfer of a proton from piperidine$^+$-H to the anion (b) yielding the intermediate compound (c), Scheme (2).

4-The fourth step involves the dehydration of the intermediate compound (c) by the action of piperidine and heating to form the required aza-cyanine dyes (d), Scheme (2).

The synthesis mechanism of the bis aza-cyanine dyes (3a-c) is suggested to proceeds in a way similar to that of the aza-cyanine dyes (2a-c).

2.3. Photosensitization / electronic transitions correlation

Photosensitization/electronic transitions correlation for all the synthesized cyanine dyes was carried out through examining their electronic visible absorption spectra in 95 % ethanol solution. The cyanine dyes were thought to be better photosensitizers when they absorb the visible light to initiate the electronic transitions at higher wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently, the photosensitization of the cyanine dyes decreases when they absorb the visible light to initiate the electronic transitions at lower wavelength bands (hypsochromic shifted and/or blue shifted dyes) (Shindy et al., 2002; Shindy et al., 2006; Shindy et al., 2015a;

Shindy et al., 2015b). So, we may say that the photosensitization of one cyanine 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. In contrary, we may say that the photosensitization of one cyanine 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. Studying the electronic visible spectra of cyanine dyes in 95 % ethanol solution is very important in the case of cyanine dyes because the extensive uses of these dyes as photographic sensitizers for silver halide emulsion in photosensitive material industry.

The visible electronic transitions spectra of the aza-cyanne (bis aza-cyanine) dyes 2a–c (3a–c) in 95 % ethanol solution discloses bands in the region 390–485 nm (405–500 nm), which their positions and molar extinction coefficients are influenced by the type of the substituents (X), the number of the electronic charge transfer pathways inside the dyes molecules, the number of the aza-methine units in the dyes structures and by the nature of the planarity of the dyes, Schemes (1), (3), Table (1).

So, substituting X = 4-OH by X = 2-OH, 5,6-benz and/or 2-OH, 3,4-benz passing from phenol dyes 2a (3a) to naphthol dyes 2b,c (3b,c) imparted bathochromic shifts in addition to increasing the intensity of the bands. This can be attributed to increasing conjugation in the latter dyes due to the presence of the more π–delocalization naphthalene nucleus compared by the less π–delocalization benzene nucleus in the former dyes, Scheme (1), Table (1).

In addition, substituting X = 2-OH, 5,6-benz in β-naphthol dyes 2b (3b) by X = 2-OH, 3,4-benz to obtain α-naphthol dyes 2c (3c) resulted in red shifted and intensified absorption bands, Scheme (1), Table (1). These may be related to the higher planarity of the latter dyes which leads to easier mobility of the electronic charge transfer pathways to the positively charged heterocyclic pyrazolium iodide quaternary salts residue and consequently red shift occurs, Scheme (1), Table (1).

Besides, comparing the electronic visible absorption spectra of aza-cyanine dyes (2a–c) by their analogous bis aza-cyanine dyes (3a–c) reveals that the latter dyes possesses bathochromic shifted and intensified bands compared with the former dyes, Scheme (1), Table (1). This can be related to the following two factors: a-The presence of two electronic charge transfer pathways in the latter dyes (3a-c) in correspondence to one electronic charge transfer pathways in the former dyes (2a-c), Scheme (3). b-Increasing conjugation due to increasing the number of the aza-methine (-CH=N-) groups in the latter dyes (3a-c) compared to the former dyes (2a-c) by one aza-methine unit, Scheme (1).

2.4. Solvent/electronic transitions correlation:

Visible electronic transitions study in pure solvents having different polarities is very important in the case of cyanine dyes in order to select the best solvents to use of these dyes as photosensitizers when they are applied as photographic sensitizers in photographic material industry. In addition, this study bears to have a great practical importance in the case of cyanine dyes because the extensive uses of these dyes in the textile industry (Gaspar et al., 2008) and/or as probes for determining solvent polarity in physical, physical organic and/or solution chemistry (Green et al., 1992).

The visible electronic transitions spectra of the aza-cyanine dye.(2a) and the bis aza-cyanine dye (3a) in pure solvents of different dielectric constant viz water (78.54), DMF (36.70), ethanol (24.3), chloroform (4.806), benzene (2.28) and dioxane (2.209) (Shindy et al., 2012; Shindy, 2007) are recorded. The λ_{max} and ε_{max} values of the absorption bands due to different electronic transitions within the solute molecule in these solvents are represented in Table (3).

From Table (3), it's clearly that the visible electronic transition absorption spectra of the dyes in ethanolic medium are characterized by the presence of three essential absorption bands. These bands can be assigned to intermolecular charge transfer transitions (Shindy et al., 2012; Shindy, 2007). These charge transfer is due to transfer of lone pair of electrons from the phenolic hydroxyl oxygen atom (the electron donating and/or the basic center of the dyes) to the positively charged heterocyclic pyrazolium iodide quaternary salts residue (the electron accepting and/or the acidic center of the dyes) and vice versa, Scheme (3).

Careful examination of the results in Table (3) shows that, changing the solvent from ethanol to DMF caused a bathochromic shifts for the absorption bands of the dyes accompanied with increasing the intensity of the bands. This can be attributed to increasing the polarity of the solvent

due to increasing the dielectric constant of DMF related to ethanol (general solvent effects and/or positive solvatochromism).

In addition, replacing the solvent of ethanol by chloroform, benzene and/or dioxane solvents reveals red shifted and intensified absorption bands for the dyes, Table (3). This can be related to solute–solvent interaction through intermolecular hydrogen bond formation between ethanol and the lone pair electrons of phenolic hydroxy oxygen atom (specific solvent effects and/or negative solvatochromism), Scheme (4). This decreases slightly the electron density on the phenolic hydroxy oxygen atom (the electron rich and/or the basic center of the dyes), and consequently decreases to some extent the mobility of the attached π-electrons over the conjugated system pathways to the positively charged heterocyclic pyrazolium iodide quaternary salts residue (the electron poor and/or the acidic center of the dyes), and so blue shifts occurs in ethanol related to chloroform, benzene and dioxane, Scheme (4).

Besides, it's was observed that the electronic visible absorption spectra bands of the dyes in: a-CHCl$_3$ reveals bathochromic shifted and intensified bands compared with their spectra bands in benzene and dioxane, Table (3). b-Benzene gives red shifted with increasing the intensity of the bands if compared with their spectra bands in dioxane, Table (3). This can be related to increasing the polarity of the solvents due to increasing the dielectric constants in the order of CHCl$_3$ > benzene > dioxane (general solvent effects and/or positive solvatochromism), Table (3).

Furthermore, it's also interest to notice that, the electronic visible absorption spectra of the dyes in water relative to the other solvents reveals a hypsochromic shifts for the absorption bands in addition to decreasing the number and intensity of the bands, Table (3). This can be ascribed to the possible interaction of water molecules with the lone pair electrons of the phenolic hydroxyl oxygen atom via formation of intermolecular hydrogen bonding (specific solvent effects and/or negative solvatochromism), Scheme (4). This makes difficult the transfer of the electronic charge from the phenolic hydroxyl oxygen atom (the electron releasing and/or the basic center of the dyes), to the heterocyclic pyrazolium iodide quaternary salts residue (the electron attracting and/or the acidic center of the dyes), and accordingly blue shifts occur in water related to other solvents, Table (3).

3. Conclusion
From this study it could be concluded that:

1. The higher photosensitization and/or the visible electronic transitions (longer wavelength bands and/or bathochromic shifted bands) of all the synthesized cyanine dyes in 95 % ethanol solution and/or in pure solvents of different polarities for some selected synthesized cyanine dyes increase by:

a. Increasing π–delocalization conjugation in the dyes molecules in the order of: naphthyl cyanine dyes > phenyl cyanine dyes in the sequence: α-naphthol and β-naphthol cyanine dyes > phenol cyanine dyes.

b. Increasing planarity of the dyes molecules in the order of: higher planarity cyanine dyes > lower planarity cyanine dyes in the sequence: α-naphthol cyanine dyes > β-naphthol cyanine dyes.

c. Increasing number of the electronic charge transfer pathways inside the dyes molecules in the order of: two electronic charge transfer pathways cyanine dyes > one electronic charge transfer pathways cyanine dyes in the sequence: bis aza-methine cyanine dyes > aza-methine cyanine dyes.

d. Increasing conjugation in the dyes molecules due to increasing the number of the aza-methine (-CH=N-) units in the dyes structures in the order of: bis aza-methine cyanine dyes > aza-methine cyanine dyes.

e. Increasing dielectric constant and/or polarity of the solvents in the order of: higher polarity solvents > lower polarity solvents in the sequence: i-DMF > EtOH, CHCl$_3$, Benzene and Dioxane. ii-CHCl$_3$ > Benzen and Dioxane. iii-Benzene > Dioxane.

f. Absence of Hydrogen bonding and/or molecular complex formation between the solvent and the solute (cyanine dyes molecules) in the order of: no hydrogen bond formation solvents > hydrogen bond formation solvents in the sequence: i-EtOH < CHCl$_3$, Benzene and Dioxane. ii-H$_2$O < DMF, EtOH, CHCl$_3$, Benzene and Dioxane.

2. The intensity of the colours and/or the electronic charge transfer pathways of the aza-cyanine dyes (2a-c) and the bis aza-cyanine dyes (3a-c) can be illustrated in the light of the

suggested two mesomeric electronic transitions structures, producing a delocalized positive charge over the conjugated chromophoric group system of the dyes, Scheme (3).

3. Because cyanine dyes have multi purposes uses and applications in various fields and different research area, this research paper is recommended not only for heterocyclic and/or cyanine dyes chemists but also for other scientists in other fields like biology, biotechnology, biochemistry, physics, engineering, pharmacology and, medicine. Also, this research paper is recommended for all whom interested in the light absorbing systems in their research, labeling of biomolecules and/or in the synthesis and characterization of complex organic compounds.

4. Expermental
4.1. General

All melting points are uncorrected. Elemental analyses were carried out at the Microanalytical Center of Cairo University (Cairo, Egypt) by an automatic analyzer (Heraeus). IR (KBr pellets) spectra were determined on a Perkin Elmer Infrared 127 spectrophotometer (Cairo University). ^{1}H NMR spectra were obtained using a varian Gemini NMR spectra 300 MHz spectrometers (Cairo University). Electronic visible absorption spectra were carried out on UV spectrophotometer (Department of Chemistry, Faculty of Science, Aswan University, Aswan, Egypt).

4.2. Synthesis
4.2.1-Synthesis of 3,8-diethyl-9-methyl-2,7-diphenyl-5,10-dione-benzo [2,3-b; $\overline{2},\overline{3}$-b] bis furo [3,2-d] pyrazolium iodid quaternary salt-4[2(1)]-aza-cyanine dyes (2a–c):

An equimolar ratios (0.01 mole) of the quaternary salt (1) and nitroso compounds (ρ.nitroso phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) were heated under reflux for 6-8 hours in ethanol (30 ml) and presence of piperidine (1-2 ml). The reaction mixture which attained from brown to deep brown colours at the end of refluxing were filtered while hot, concentrated, cooled and acidified by glacial acetic acid. The precipitates which appear by adding of cold water were filtered off, washed several times with water, air dried and crystallized from ethanol. The results were listed in Table (1).

4.2.2-Synthesis of 3,8-diethyl-2,7-diphenyl-5,10-dione-benzo [2,3-b; $\overline{2},\overline{3}$-b] bis furo [3,2-d] pyrazolium iodid quaternary salt-4,9[2(1)]-bis aza-cyanine dyes (3a–c):

Two different Methods were used to synthesize these cyanines:

Method (1): A mixture of 1 : 2 M ratios of (1) and nitroso compounds (ρ.nitroso phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) were allowed to boil under reflux for 6-8 hours in ethanol (30 ml) containing piperidine (1-2 ml). The reaction mixture which attained from brown to deep brown colours at the end of refluxing were filtered off while hot, concentrated, cooled and acidified by glacial acetic acid. The precipitates were collected and crystallized from ethanol. The results were summarized in Table (1).

Method (2): An equimolar ratios (0.01 mole) of the aza-cyanine dyes (2a–c) and nitroso compounds (ρ.nitroso phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) were dissolved in ethanol (30 ml), then piperidine (1-2 ml) was added. The reaction mixture was allowed to heat under reflux for about 6-8 hours and attained a permanent brown to deep brown colours at the end of refluxing. It was filtered while hot, concentrated, cooled and acidified by acetic acid. The precipitated products which separated by water were collected and crystallized from ethanol to give the same bis aza-cyanine dyes (3a–c) obtained by Method 1. See Table (1).

4.3. Photosensitization and solvent / electronic transitions correlation:

The organic solvents were of spectroscopic grade or were purified according to recommended methods (Shindy et. al., 2012; Shindy, 2007). The electronic visible absorption spectra of the dyes were recorded on UV-VIS recording spectrophotometer using 1 cm quartz cells. The stock solution were about 1x10^{-3} m. Lower molarities were obtained by an accurate dilutions. The spectra were recoded immediately to eliminate as much as possible the effect of time.

5. Current future developments

The current and the future research developments aim to provide novel synthetic methods for the preparation of different classes of highly antimicrobial active, Anti-tumor, p-H sensitive, highly photographic sensitizers, non toxic, high stability, light fastness, near IR (Infrared), fluorescent, anti corrosion, strong labeled DNA and extra conjugated cyanine dyes. Such as oxadiazine cyanine dyes, thiazole cyanine dyes, metal stabilized cyanine dyes, pentamethine cyanine dyes, hexamethine cyanine dyes, heptamethine cyanine dyes, octamethine cyanine dyes, nonamethine cyanine dyes, undecamethine cyanine dyes and tridecamethine cyanine dyes.

6. Conflict of interest

There is no conflict of interest.

7. Acknowledgement

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Appendix

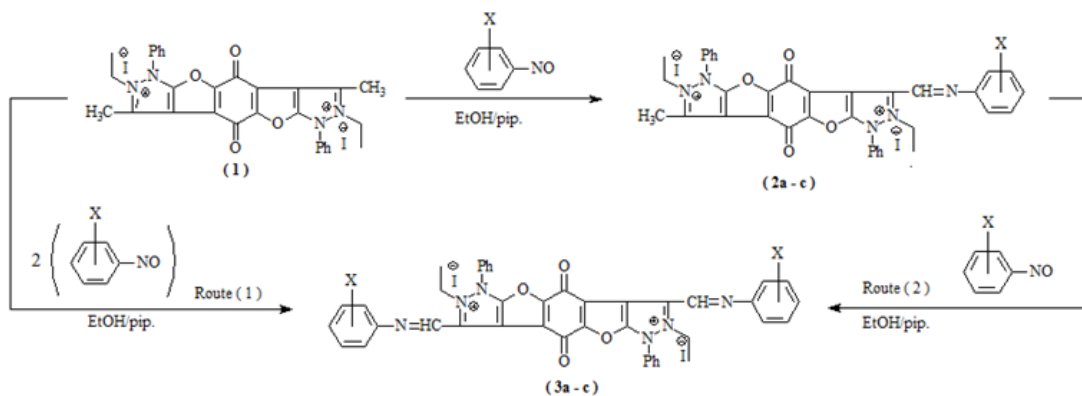**Table 1.** Characterization of the aza-cyanine (2a-c) and the bis aza-cyanine (3a-c) dyes

Comp. No.	Nature of products			Molecular formula (M. wt)	Analysis % calcd (found)			Visible electronic transitions in 95 % ethanol	
	m.p. °C	Yield %	Colour of crystals		C	H	N	λ_{max} (nm)	ε_{max} (mol^{-1}cm^2)
2a	168-170	93	Deep brown	$C_{36}H_{29}O_5N_5I_2$ (865)	49.94 (49.85)	3.35 (3.21)	8.09 (7.94)	390,425,475	13000,12100,11510
2b	173-175	82	Deep brown	$C_{40}H_{31}O_5N_5I_2$ (915)	52.46 (52.33)	3.39 (3.29)	7.65 (7.59)	395,430,480	14100,13020,12001
2c	188-190	95	Deep brown	$C_{40}H_{31}O_5N_5I_2$ (915)	52.46 (52.33)	3.39 (3.21)	7.65 (7.56)	400,435,485	16100,15010,17120
3a	178-180	80	Deep brown	$C_{42}H_{32}O_6N_6I_2$ (970)	51.95 (51.89)	3.29 (3.10)	8.65 (8.62)	405,440,490	18100,19200,11220
3b	218-220	85	Brown	$C_{50}H_{36}O_6N_6I_2$ (1070)	56.07 (56.00)	3.36 (3.34)	7.85 (7.81)	410,445,495	19121,21000,20000
3c	208-210	90	Deep brown	$C_{50}H_{36}O_6N_6I_2$ (1070)	56.07 (55.96)	3.36 (3.26)	7.85 (7.78)	415,450,500	20000,22000,27001

Table 2. IR and ¹H NMR spectral data of the prepared compounds

Comp. No.	IR (KBr, cm^{-1})	¹H NMR (DMSO, δ)
2a	649, 693 (monosubstituted benzene). 756, 850 (p.disubstituted benzene). 1024, 1123, 1188 (C–O–C cyclic). 1308, 1362 (C–N). 1623 (C=O quinone). 1597 (C=C). 1497, 1555 (C=N). 2922, 2852 (quaternary salts). 3425 (OH phenolic).	0.7-1.8 (m, 9H, 2 CH$_3$ of positions 3, 8 + 1 CH$_3$ of position 9). 3-4.3 (b, 4H, 2 CH$_2$ of positions 3, 8) 6.9 -8.4 (m, 16H, aromatic + 1 OH + 1 -CH=).
3a	649, 693 (monosubstituted benzene). 756, 851 (p.disubstituted benzene). 1023, 1122, 1187 (C–O–C cyclic). 1308, 1361 (C–N). 1624 (C=O quinone). 1597 (C=C). 1496, 1553 (C=N). 2927, 2853 (quaternary salts). 3425 (OH phenolic).	0.7-1.8 (t, 6H, 2 CH$_3$ of positions 3, 8). 2.9-4.3 (m, 4H, 2 CH$_2$ of positions 3, 8). 6.8-8.4 (m, 22H, aromatic + 2 OH + 2 -CH=).

Table 3. Solvent/electronic transitions correlation study of some selected aza-cyanine dye (2a) and bis aza-cyanine dye (3a) in pure solvents

Comp. No.	Water		Ethanol		DMF		Chloroform		Benzene		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)
2a	370	12400	390	13000	420	15001	415	14000	405	13500	400	13400
	415	13500	425	12100	455	16100	450	15200	440	15000	430	14500
	--	--	475	11510	510	12510	505	12900	500	12800	490	12600
3a	370	20001	395	18100	420	20220	410	16010	405	14010	400	12100
	425	20201	430	19200	450	21570	440	15200	435	13010	425	11010
	--	--	480	11220	600	12100	590	11000	585	10300	485	10201

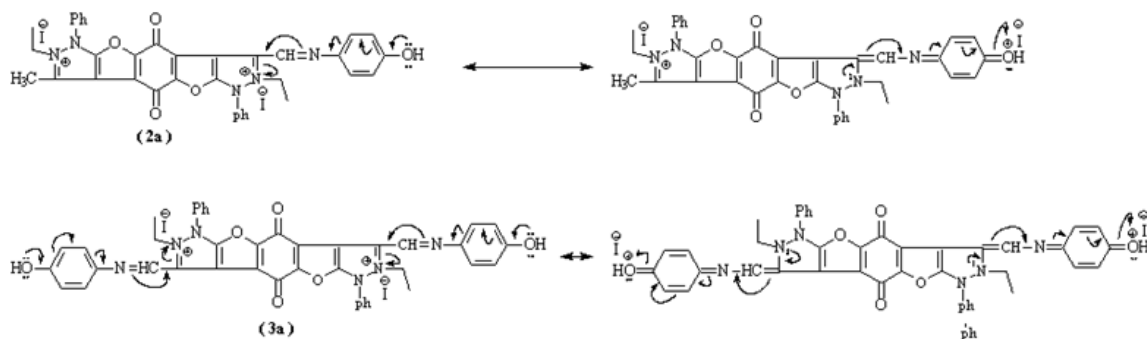(2a - c); (3a - c): X = 4-OH (a); 2-OH, 5,6-benz (b); 2-OH, 3,4-benz (c).

Scheme (1)

Synthesis strategy of the prepared aza-cyanine dyes (2a-c) and bis aza-cyanine dyes (3a-c)
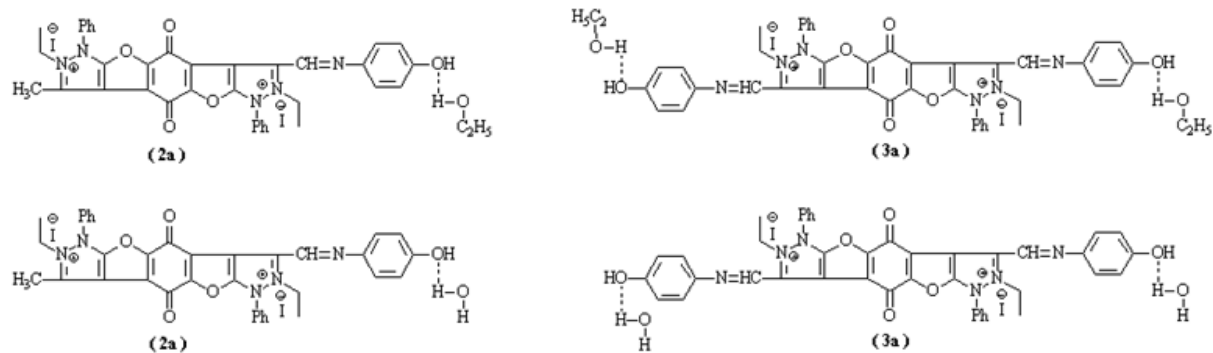
X = 4.OH; 2.OH, 5,6-benz; 2.OH,3,4-benz.
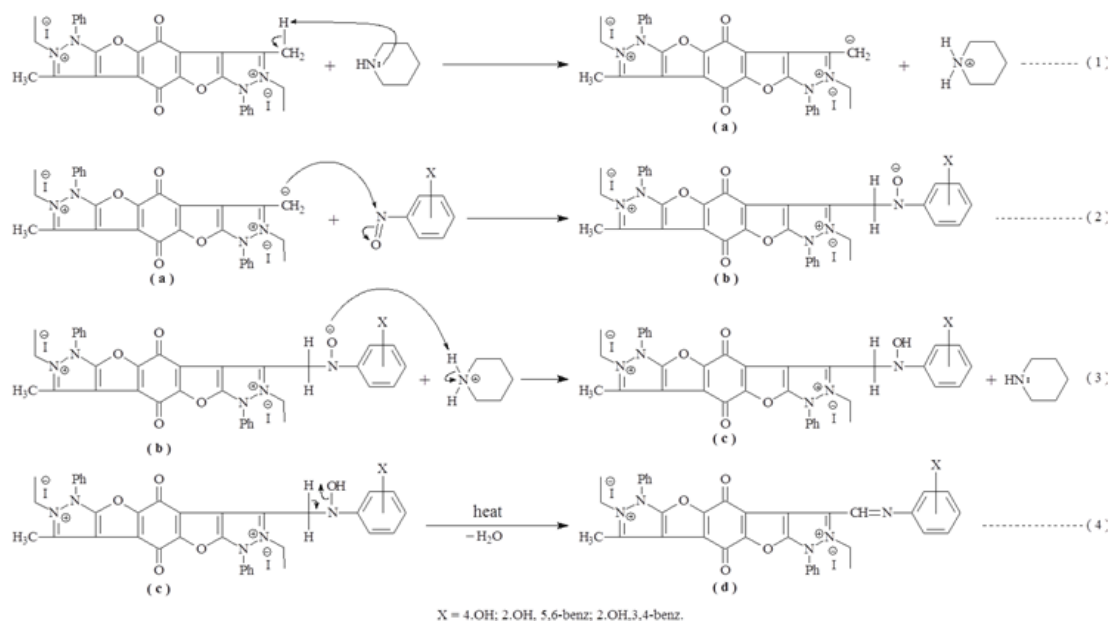
Scheme (2)

Synthesis mechanism of the aza-cyanine dyes (2a-c)

Scheme (3)

The colour intensity and/or the electronic charge transfer pathways illustration of the synthesized aza-cyanine dye (2a) and bis aza-cyanine dye (3a)

Scheme (4)

Hydrogen bond formation between the aza-cyanine dye (2a) and bis aza-cyanine dye (3a) with ethanol and water molecules (specific solvent effect)