Arabian Journal of Chemistry (2017) **10**, 82–90

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Synthesis and physicochemical studies of some new quinolinoxazine pentamethine cyanine dyes

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Received 7 October 2011; accepted 12 June 2012
Available online 21 June 2012

KEYWORDS

Quinolinoxazine;
Synthesis;
Electronic absorption spectra;
Fluorescence emission;
Solvatochromic behaviour

Abstract Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used in photography and as information storage in laser technology. A series of novel cyanine dyes were synthesized through the formylation of quinolinium[*b*,*c*]1,4-oxazine-chloride salt **1**. Reaction of compound 2-chloro-3-formyl-quinolinium[*b*,*c*]1,4-oxazine-chloride salt **2** with different molar ratios of 2(4)-methyl substituted heterocyclic in basic catalysis afforded the corresponding 2-chloroquinolinium[*b*,*c*]1,4-oxazine-chloride salt-3[2(4)]-dimethine (**3a**–**c**), quinolinium[*b*,*c*]-1,4-oxazinechloride salt-2,3[2(4)]-pentamethine (**4a**–**c**) and quinolino[*b*,*c*]1,4-oxazine-6yl[2(4)]-monomethine-/2,3[2(4)]-pentamethine cyanine dyes (**5a**–**c**) respectively. The structure of the dyes was characterized by elemental analysis, visible absorption, fluorescence emission, IR, ^{1}H-NMR and mass spectroscopy. The correlations between the structure and properties of these dyes have been studied. A comparison of the visible absorption maxima between compounds **3b**, 4b and **5b** showed that asymmetrical mono-pentamethine cyanine dye **5b** reveals a bathochromic shift than both dimethine **3b** and pentamethine cyanine dyes **4b**. This could be attributed to the more extensive π-conjugation and increasing number of methine groups in asymmetric pentamethine. All the observations and analytical spectra in this paper support the syntheses of new di-, penta- and mono-/pentamethine cyanine dyes. The absorption spectra of dyes were investigated in organic solvents. The results indicated that the excitation for their colour is a simple charge-transfer from oxygen atom of oxazine nucleus and/or nitrogen atom of pyridine (quinoline) nucleus to N-quaternary salts in di-, penta- and mono-/pentamethine cyanine dyes respectively. These dyes showed positive solvatochromism with increased solvent polarity, which depends on the structure and the type of dye.

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1. Introduction

There is growing interest in our group toward the synthesis of N-bridgehead heterocyclic compounds in view of their use in the synthesis of cyanine dyes (Abd El-Aal, 1998, 1999, 2006; Koraiem et al., 2002, 2006). Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used as data storage materials and organic semiconductor

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Peer review under responsibility of King Saud University

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http://dx.doi.org/10.1016/j.arabjc.2012.06.003
1878-5352
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materials (Mustroph and Stollenwerk, 2006; Spitler and Parkinson, 2009), in laser technology (Chatterjee et al., 1988; Yabushita et al., 2004; Shank and Ippen, 1973), and as spectral sensitizers in photography (Tani et al., 1992).

Quinoxazine compounds have a wide spectrum range of biological activities and pharmaceutical actions like kinase inhibitor activity and antibacterial activity (He et al., 2003; Seitz et al., 2002). In addition, quinoxazine compounds are electroluminescent materials (Thomas et al., 2005) and organic semiconductors (Brien et al., 1996).

This paper reported the synthesis of some novel N-bridgehead heterocycles dimethine, pentamethine, and mono/pentamethine cyanine dyes, and evaluated the structure–properties relationship of the new dyes on the basis of their visible absorption spectra/fluorescence emission in ethanol. Also, photophysics studies in different organic solvents are discussed, which might be used as photosensitizer dyes in different optical applications.

2. Experimental

All melting points are uncorrected. Elemental analysis was carried out at the Microanalytical center (Cairo-University). The IR (ν^{KBr}) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H-NMR spectra were recorded with a Bruker AMX-250 spectrometer. ^{1}H-NMR, spectra were measured with a Bruker AMX-400 spectrometer, with TMS as an internal standard. Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the wavelength range (350–700) on Shimadzu-1601VC UV/Visible automatic recording spectrophotometer with 1 cm quartz cell used for absorbance and spectra measurements, Faculty of Science, Suez. The fluorescence emission spectra were recorded within the wavelength range (480–600) on JASCO-FB6300 spectrofluorometer with 1 cm quartz cell emission and spectra measurements, Faculty of Science, Suez. The synthesis of quinolinium[*b*,*c*]-1,4-oxazine-2-one chloride salt **1**, was carried out according to Abd El-Aal (1998).

2.1. Synthesis of 2-chloro-3-formyl-quinolinium[b,c]-1,4-oxazine chloride salt 2

To a solution of compound **2** (3 g, 0.013 mol) in (10 mL) dry dimethylformamide and phosphorous oxychloride (5 mL, 0.033 mol) were added under stirring in an ice-bath. The second step was stirring at room temperature for 15 min. The solution was heated for 30 min, cooled and then poured into 400 mL ice-water. The solid product was collected and crystallized from petroleum ether 60–80 °C; m.p. > 300 °C, Yield = 80%.

Analytical data for $C_{12}H_7NO_2Cl$ (M.wt = 232.5).

Calcd.%; C = 61.94; H = 3.01; N = 6.02.

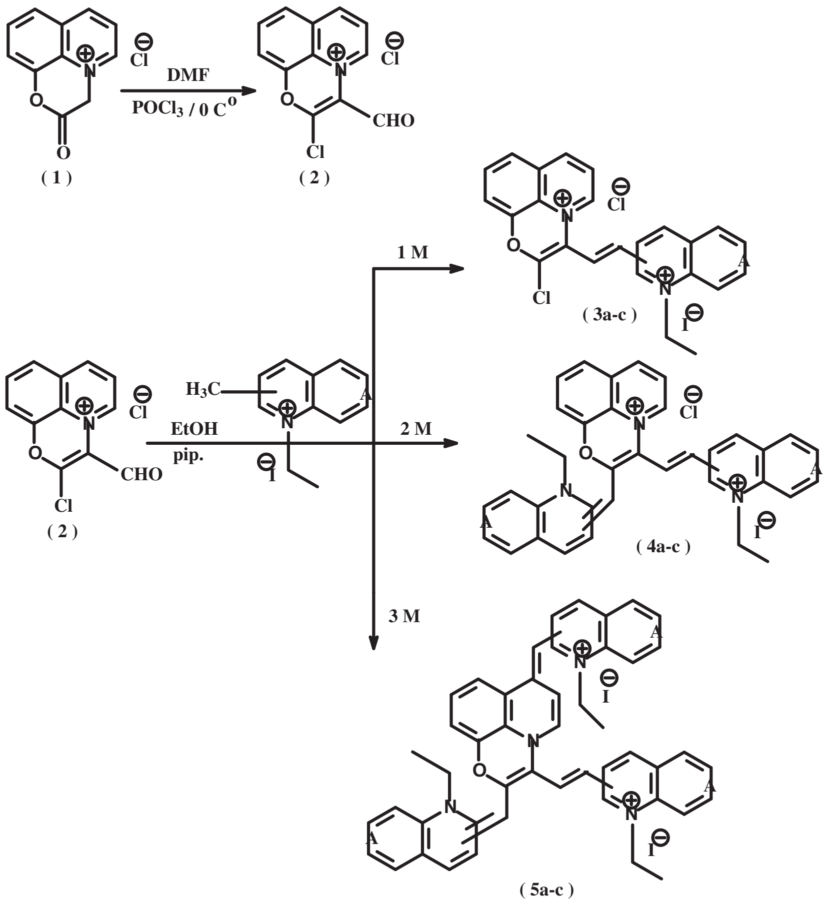
Found%; C = 61.79; H = 2.97; N = 5.87.

Table 1 Characterization data of 2-chloro-quinolinium[*b*,*c*]-1,4-oxazine chloride salt-3[2(4)]-dimethine (**3a-c**), quinolinium[*b*,*c*]-1,4-oxazine-chloride salt-2,3[2(4)]-pentamethine (**4a**–**c**) and quinolinium[*b*,*c*]-1,4-oxazine-6yl[2(4)]-monomethine-2,3[2(4)]-pentamethine (**5a**–**c**) cyanine dyes.

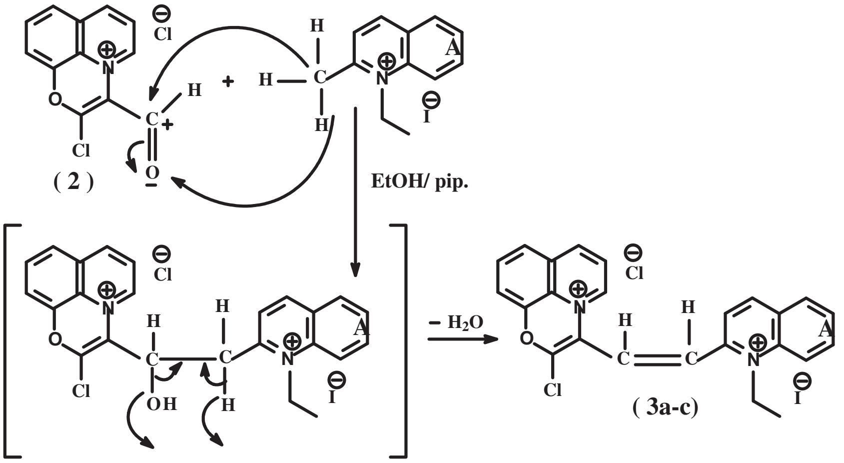
Comp. No.	M.P. °C	Yield %	Colour	Mol. formula (Mol. wt.)	Calcd.% (Found)%			Absorption spectra in EtOH	
					C	H	N	λ_{max} (nm)	$\varepsilon_{max} \times 10^3$ (L mol^{-1} cm^{-1})
3a	280	75	Reddish violet	$C_{20}H_{17}N_2OICl_2$	48.19	3.41	4.81	358	3.33
				(498)	(48.00)	(3.30)	(4.70)		
3b	> 300	89	Intense violet	$C_{24}H_{19}N_2OICl_2$	52.55	3.46	4.37	405sh	3.00
				(548)	(52.00)	(3.44)	(4.20)	432sh	2.90
								519sh	3.30
								560	5.80
								587	5.60
3c	> 300	80	Violet	$C_{20}H_{17}N_2OICl_2$	48.19	3.41	4.81	359	3.80
				(498)	(48.10)	(3.00)	(4.70)		
4a	> 300	76	Brownish violet	$C_{28}H_{27}N_3OICl$	57.58	4.26	7.19	478	1.30
				(583.50)	(57.50)	(4.00)	(7.15)		
4b	> 300	90	Intense violet	$C_{36}H_{31}N_3OICl$	63.20	4.53	6.14	485sh	11.00
				(683.50)	(63.00)	(4.40)	(6.00)	519	16.00
								561	19.00
								600sh	10.00
4c	> 300	78	Reddish violet	$C_{28}H_{27}N_3OICl$	57.58	4.62	7.19	488	1.50
				(583.50)	(57.00)	(4.50)	(7.15)		
5a	> 300	75	Reddish violet	$C_{36}H_{36}N_4OI_2$	54.40	4.53	7.10	467sh	1.55
				(794)	(54.00)	(4.40)	(6.96)		
5b	> 300	89	Intense violet	$C_{48}H_{42}N_4OI_2$	61.00	4.45	5.93	518sh	11.00
				(944)	59.90	(4.40)	(5.88)	560sh	16.00
								597	19.00
								696sh	2.70
5c	> 300	77	Violet	$C_{36}H_{36}N_4OI_2$	54.40	4.53	7.10	387sh	1.30
				(794)	(54.00)	(4.40)	(6.96)	485sh	1.60

*2.2. Synthesis of 2-chloro-quinolinium[b,c]-1,4-oxazine-3[2(4)]-dimethine cyanine dyes (**3a–c**)*

A mixture of equimolar amounts of compound **2**, (0.1 g, 0.0004 mol) and methyl substituted heterocyclic [α-(γ)-picoline and quinaldine ethyl iodide] (0.11 g, 0.0004 mol) were dissolved in ethanol (20 mL) in the presence of piperidine (0.7 mL) as basic catalyst. The reaction mixture was refluxed for 16 h. filtered hot, cooled and neutralized with acetic acid (0.3 mL). The precipitated solid, after dilution with water (5 mL) was collected and recrystallized from ethanol to give the corresponding compounds (**3a–c**).



Scheme 1 (**3a–c**), (**4a–c**), (**5a–c**): A = 1-ethylpyridin-2-ium iodide (a); A = 1-ethylquinolin-2-ium iodide (b); A = 1-ethylpyridin-4-ium iodide (c).



Equation 1 (**3a–c**): A = 1-ethylpyridin-2-ium iodide; (a); A = 1-ethylquinolin-2-ium iodide (b); A = 1-ethylpyridin-4-ium iodide (c).

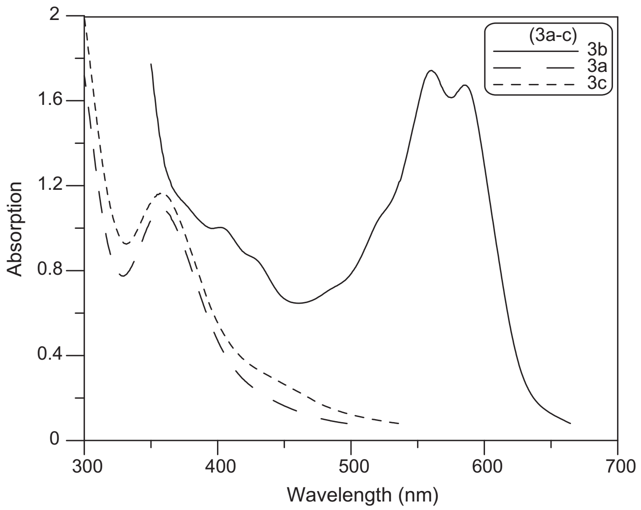


Figure 1 Absorption spectra of dimethine cyanine dyes (**3a**–**c**) in ethanol solution in (300–700 nm) wavelength range.

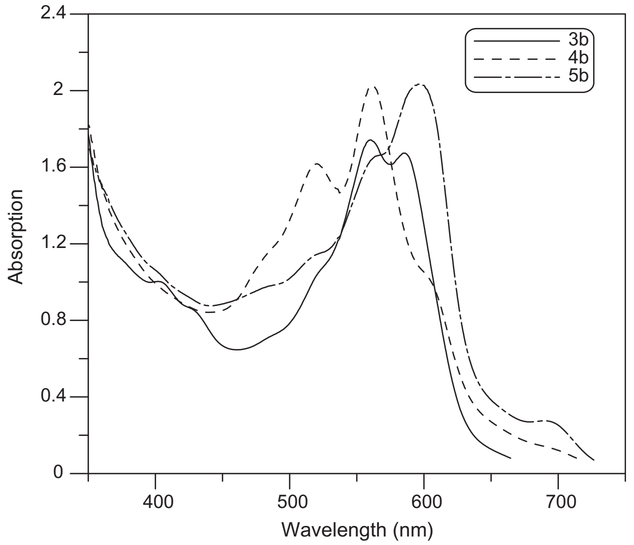


Figure 2 Absorption spectra of **3b**, **4b**, **5b** compounds in ethanol solution in (350–750 nm) wavelength range.

Characterization data are listed in Table 1.

Compound **3a**: IR (ν^{KBr}, cm^{-1}), at 3010 cm^{-1} (Ar-C–H, str.), 2980–2940 cm^{-1} (C_2H_5I, str.), 1600–1580 cm^{-1} (C=C ring, str.), 1430 cm^{-1} (C=N), 1090 cm^{-1} (Ar-Cl), 1050 cm^{-1} (C–O–C cyclic) and 805–785 cm^{-1} (=C–H bend. benzene ring), 748, 705 cm^{-1} (pyridine ring).

Compound **3a**: ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 7.02–8.01 (m, 12H, Ar-H + heter-H + CH=CH), 3.9 (q, 2H, CH_2–N+), 1.9 (t, 3H, CH_3).

Compound **3a**: Mass spectroscopy $M^+ + 4 = 502$.

Compound **3b**: IR (ν^{KBr}, cm^{-1}), at 3030 cm^{-1} (Ar-C–H, str.), 2970–2920 cm^{-1} (C_2H_5I, str.), 1600–1585 cm^{-1} (C=C ring, str.), 1435 cm^{-1} (C=N), 1085 cm^{-1} (Ar-Cl), 1080 cm^{-1}.

(C–O–C cyclic) and 795–745 cm^{-1} (=C–H bend. quinoline ring).

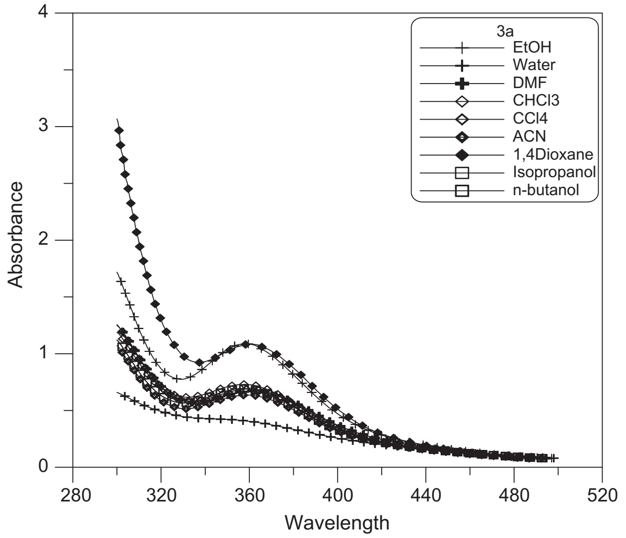


Figure 3 Absorption spectra of dimethine cyanine dye **3a** in different solvents.

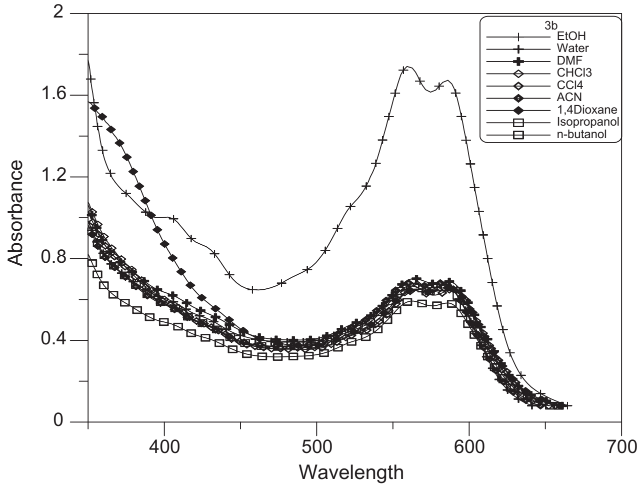


Figure 4 Absorption spectra of dimethine cyanine dye **3b** in different solvents.

Compound **3b**: ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 6.75–7.75 (m, 14H, Ar-H + heter-H + CH=CH), 4.1 (q, 2H, CH_2–N+), 1.75 (t, 3H, CH_3.

Compound **3b**: Mass spectroscopy $M^+ + 4 = 552$.

*2.3. Synthesis of quinolinium[b,c]-1,4-oxazine-chloride salt-2,3,[2(4)]-pentamethine cyanine dyes (**4a**–**c**)*

A mixture of compound **2**, (0.1 g, 0. 0004 mol) and bi molar amounts of methyl substituted heterocyclic [α-(γ)-picoline and quinaldine ethyl iodide] (0.22 g, 0.0008 mol) were fused in (2–3 mL) piperidine for 15 min. The reaction mixture was dissolved in ethanol and refluxed for 13 h, filtered hot, concentrated and dried to give compounds (**4a**–**c**). Characterization data are listed in Table 1.

Compound **4b**: IR (ν^{KBr}, cm^{-1}), at 3010 cm^{-1} (Ar-C–H, str.), 2960–2920 cm^{-1} (C_2H_5I, str.), 1600–1580 cm^{-1} (C=C

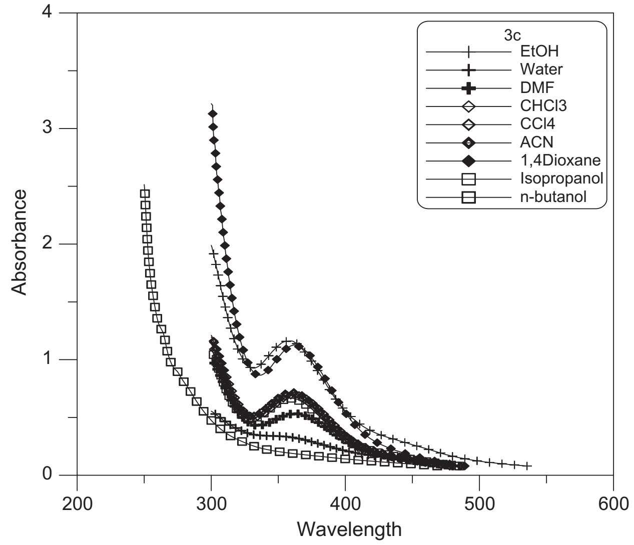


Figure 5 Absorption spectra of dimethine cyanine dye **3c** in different solvents.

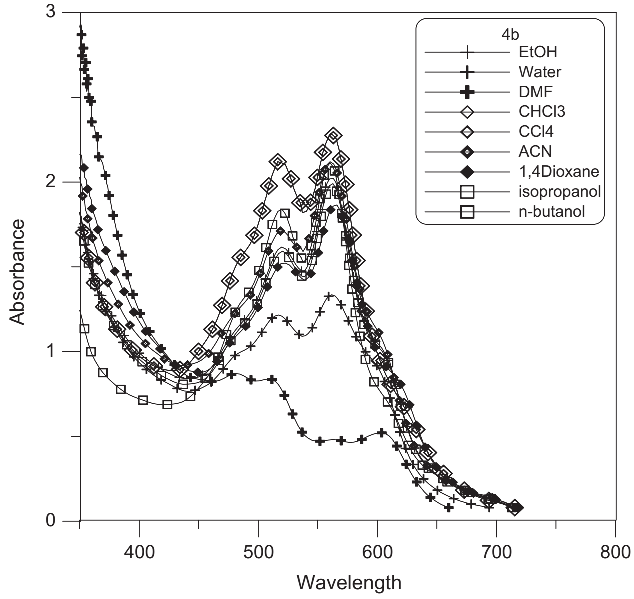


Figure 6 Absorption spectra of pentamethine cyanine dye **4b** in different solvents.

ring, str.), 1430 cm^{-1} (C=N), 1050 cm^{-1} (C–O–C cyclic) and 765–730 cm^{-1} (=C–H bend. quinoline ring).

Compound **4b:** ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 6.65–7.85 (m, 21H, Ar-H + heter-H + CH=CH), 4.3 (q, 2H, CH_2–N^+), 2.3 (q, CH_2–N),1.75 (t, 3H, CH_3), 1.02 (t, 3H, CH_3).

Compound **4b:** Mass spectroscopy $M^+ + 2 = 685$.

Compound **4c:** IR (ν^{KBr}, cm^{-1}), at 3030 cm^{-1} (Ar-C–H, str.), 2980–2940 cm^{-1} (C_2H_5I, str.), 1600–1585 cm^{-1} (C=C ring, str.), 1430 cm^{-1} (C=N), 1050 cm^{-1} (C–O–C cyclic) and 775–745 cm^{-1} (=C–H bend. quinoline ring), 745, 705 cm^{-1} (pyridine ring).

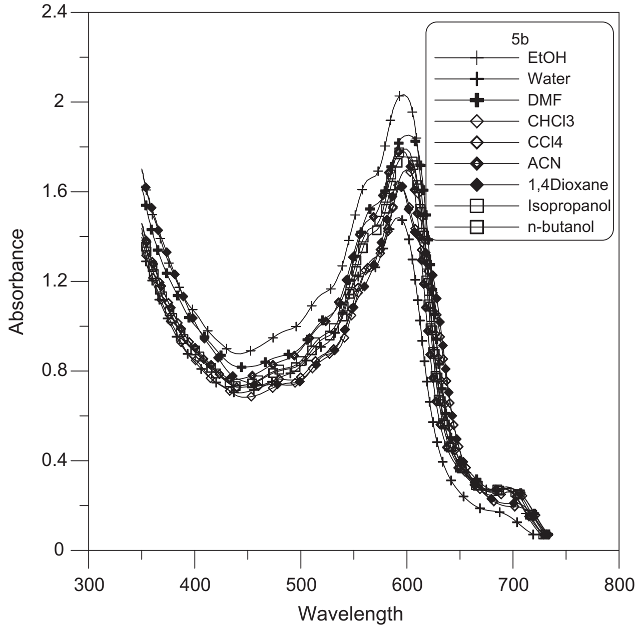


Figure 7 Absorption spectra of mono-pentamethine cyanine dye **5b** in different solvents.

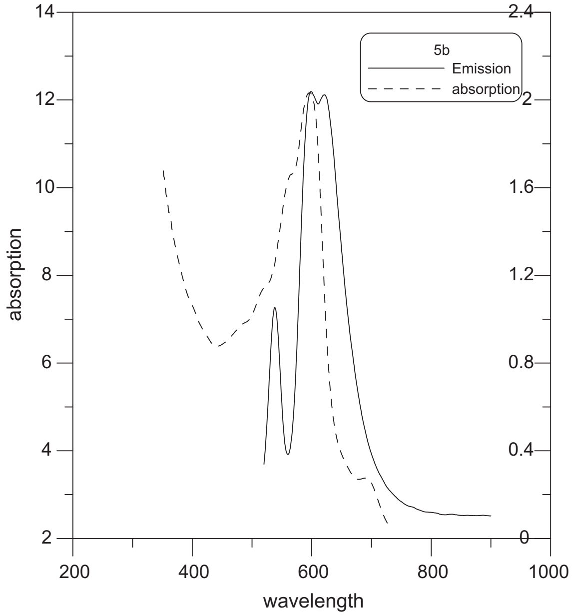


Figure 8 Absorption and emission ($\lambda_{ex} = 630$) spectra of **5b**.

Compound **4c:** ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 6.75–8.15 (m, 17H, Ar-H + heter-H + CH=CH), 4.25 (q, 2H, CH_2–N^+), 2.1 (q, CH_2–N), 1.65 (t, 3H, CH_3), 1.10 (t, 3H, CH_3).

Compound **4c:** Mass spectroscopy $M^+ + 2 = 635$.

*2.4. Synthesis of quinolino[b,c]-1,4-oxazine-6yl[2(4)]-monomethine-2,3[2(4)]-pentamethine cyanine dyes (**5a–c**)*

A mixture of compound **2**, (0.1 g, 0. 0004 mol) and tri molar amounts of methyl substituted heterocyclic [α-(γ)-picoline

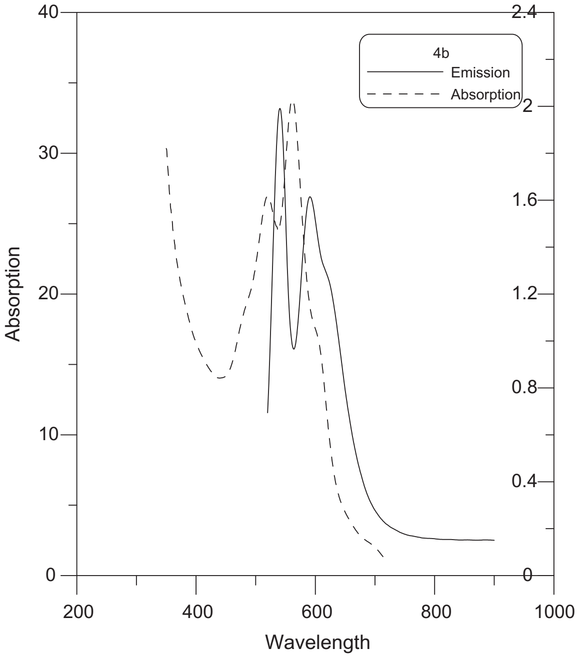


Figure 9 Absorption and emission (λ_{ex} = 600) spectra of **4b**.

and quinaldine ethyl iodide] (0.33 g, 0.001 mol) were dissolved in ethanol (20 mL) in presence of piperidine (0.7 mL) and refluxed for 16 h. The products were similarly obtained using the same method for compounds **4a–c** to give compounds **5a–c**. Characterization data are listed in Table 1.

Compound **5a:** IR (ν^{KBr}, cm^{-1}), at 3030 cm^{-1} (Ar-C–H, str.), 2980–2940 cm^{-1} (C_2H_5I, str.), 1600–1585 cm^{-1} (C=C ring, str.), 1430 cm^{-1} (C=N), 1050 cm^{-1} (C–O–C cyclic) and 785–750 cm^{-1} (=C–H bend. quinoline ring), 745, 705 cm^{-1} (pyridine ring).

Compound **5a:** ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 6.55–8.05 (m, 21H, Ar-H + heter-H + CH=CH), 4.25 (q, 4H, CH_2–N^+), 2.1 (q, 2H, CH_2–N), 1.75 (t, 6H, CH_3), 1.10 (t, 3H, CH_3).

Compound **5a:** Mass spectroscopy $M^+ + 1$ = 795.

Compound **5b:** IR (ν^{KBr}, cm^{-1}), at 3010 cm^{-1} (Ar-C–H, str.), 2970–2930 cm^{-1} (C_2H_5I, str.), 1600–1585 cm^{-1} (C=C ring, str.), 1435 cm^{-1} (C=N), 1050 cm^{-1} (C–O–C cyclic) and 785–740 cm^{-1} (=C–H bend. quinoline ring).

Compound **5b:** ^{1}H-NMR (DMSO, 300 MHz) spectra reveal signals at δ 6.50–7.95 (m, 27H, Ar-H + heter-H + CH=CH), 4.3 (q, 2H, CH_2–N^+), 2.15 (q, CH_2-N), 1.65 (t, 3H, CH_3), 1.02 (t, 3H, CH_3).

Compound **5b:** Mass spectroscopy $M^+ + 1$ = 945.

3. Results and discussion

All titled synthesized cyanine dyes (**3a–c**), (**4a–c**) and (**5a–c**), were started by the preparation of 2-chloro-3-formyl quinolinium[*b*,*c*]-1,4-oxazine-chloride salt **2** which was prepared via the Vilsmeier reaction through treating the compounds **1** (Abd El-Aal, 1998) with phosphorous oxychloride in dimethylformamide at 0 °C Scheme1.

The structure of compound **2** was established on analytical and spectral data. IR spectra showed characterization absorption bands at 3010 cm^{-1} (aromatic C–H, str.), 2780 cm^{-1} (aldehydic C–H, str.), 1700 cm^{-1} (CHO), 1605 cm^{-1} (C=C ring, str.), 1090 cm^{-1} (Ar-Cl), 1050 cm^{-1} (C–O–C cyclic) and 745 cm^{-1} (=C–H bend. For disubst. benzene ring). ^{1}H-NMR (DMSO, 300 MHz) spectra (Wade, 1999) reveal signals at δ = 6.8–7.9 ppm (m, 6H, Ar-H), and at δ = 9.5 ppm (s, 1H, CHO) for compound **2**. Mass spectroscopy of the compound **2** M^+ = 233.5.

Reaction of **2** with equimolar ratios of 2-(4)-ethyl-substituted heterocyclic quaternary salts afforded the corresponding 2-chloro-quinolinium[*b*,*c*]-1,4-oxazine chloride salt-3[2(4)]-

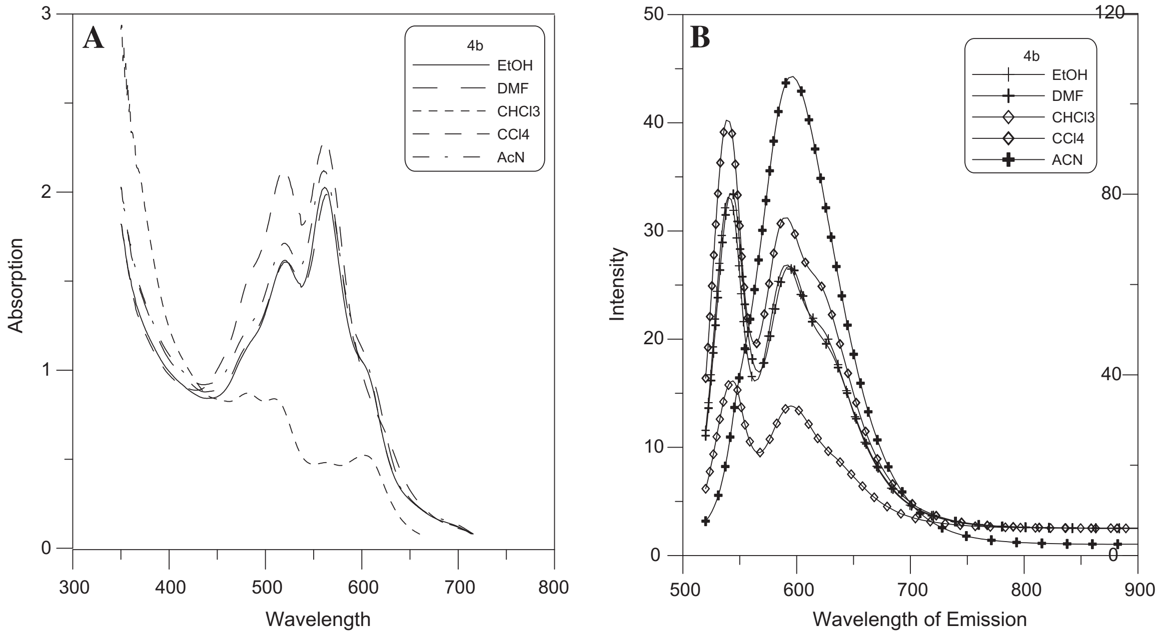


Figure 10 Emission (λ_{ex} = 600 nm) A and absorption B spectra of **4b** (2×10^{-5} mol/L).

dimethine cyanine dyes (**3a–c**). The reaction sequence is as shown in Scheme1.

The formation of 3[2(4)]-dimethine cyanine dyes (**3a–c**), was suggested to proceed through nucleophilic addition reaction of the active methyl of 2(4)-ethyl heterocyclic quaternary salt to the carbonyl group of compounds **2** followed by dehydration processes according to the following (Eq. (1):

The structure of the compounds (**3a–c**) was confirmed by analytical and spectral data, reported in Table 1.

Reaction of compound **2** with bimolar ratios of 2-(4)-ethyl-substituted heterocyclic quaternary salts afforded the corresponding quinolinium[*b*,*c*]-1,4-oxazine-chloride salt-2,3[2(4)]-pentamethine cyanine dyes (**4a–c**). The reaction sequence is as shown in Scheme 1.

The formation of 2,3[2(4)]-pentamethine cyanine dyes (**4a–c**), was suggested to proceed through nucleophilic addition reaction of the active methyl group of 2(4)-ethyl heterocyclic quaternary salt to the carbonyl group of compounds **2** followed by dehydration and dehydrohalogenation processes to give compounds (**4a–c**). The reaction was confirmed chemically by the interaction of compounds (**3a–c**) with equimolar ratios of 2-(4)-ethyl-substituted heterocyclic quaternary salts which give the same compounds (**4a–c**).

The structure of compounds (**4a–c**) was confirmed by analytical and spectral data, reported in Table 1.

Reaction of compound **2** with trimolar ratios of 2-(4)-methyl-substituted heterocyclic quaternary salts afforded the corresponding quinolino[*b*,*c*]-1,4-oxazine-6yl [2(4)]-monomethine-2,3[2(4)]-pentamethine cyanine dyes (**5a–c**). The reaction sequence is as shown in Scheme 1. The reaction was suggested to proceed through nucleophilic addition reaction of the active methyl group of 2(4)-ethyl heterocyclic quaternary salt to the carbonyl group of compound **2** and oxidative elimination followed by dehydrohalogenation process to give compounds (**5a–c**).

The structure of compounds (**5a–c**) was confirmed by analytical and spectral data, reported in Table 1.

The 2-chloroquinolinium[*b*,*c*]-1,4-oxazine chloride salt-3[2(4)]-dimethine (**3a–c**), quinolinium[*b*,*c*]1,4-oxazine-chloride salt-2,3[2(4)]-pentamethine (**4a–c**) and quino-linium[*b*,*c*]-1, 4-oxazine-6yl[2(4)]-monomethine-2,3[2(4)]-pentamethine cyanine dyes (**5a–c**) cyanine dyes are highly coloured compounds. Their colour in ethanol ranges from brownish-violet to intense violet, easily (partially) soluble in polar and nonpolar organic solvents exhibiting coloured solutions (red/violet) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. They are soluble in concentrated H_2SO_4 acid liberating iodine vapour on warming. Their ethanolic solutions give permanent colours in basic media, which reversibly discharged on acidification. They possess interachargable colours solution (brownish-violet/intense violet → yellow) in basic and acidic media.

3.1. Relation between structure and electronic absorption spectra of novel cyanine dyes

3.1.1. Electronic absorption spectra in ethanol

Electronic absorption spectra features (λ_{max} and ε_{max} values) of newly synthesized cyanine dyes (**3a–c**) Fig. 1, (**4a–c**) and (**5a–c**) in ethanol (alchromic behaviour) solution are shown in Table 1. The visible absorption maxima of newly synthesized cyanine dyes in ethanol undergo a bathochromic shift or hypsochromic shift depending on the nature of heterocyclic quaternary residue A and the number of methine groups. Thus, substitution of A = N-ethylpyridin-2-ium in compound **3a** by A = N-ethylquinolin-2-ium in compound **3b** resulted in a bathochromic shift of 46 nm with increasing number of absorption bands at 519, 559 and 587, which is due to the increasing π-conjugation in quinolin-2-ium moiety. Similarly, increasing the number of methine groups in pentamethine compound **4b** with

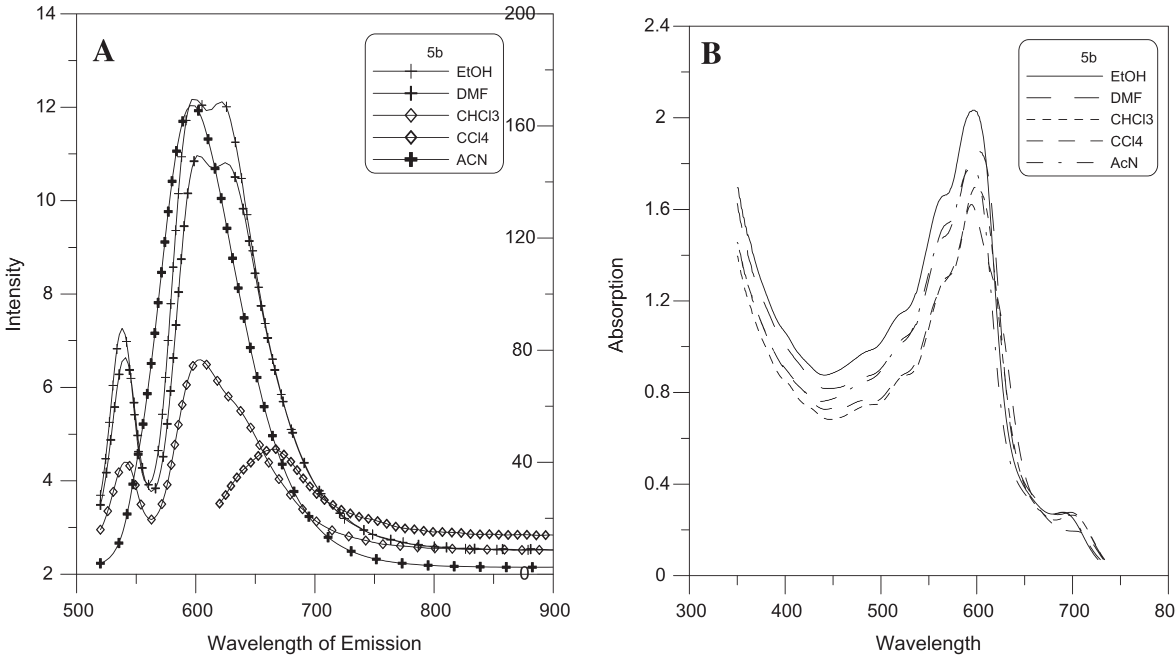


Figure 11 Emission (λ_{ex} = 630 nm) A and absorption B spectra of **5b** (2×10^{-5} mol/L).

Table 2 Values of absorption λ_{max} (nm) and extinction coefficients ε_{max} (10^3/L mol^{-1}scm^{-1}) of compounds **3a**, **3b**, **3c**, **4a**, **4b**, **4c**, **5b** in pure organic solvents.

Compd. No.	Water $\lambda_{max}{}^{a}$ $(\varepsilon_{max})^{b}$	DMF λ_{max} (ε_{max})	EtOH λ_{max} (ε_{max})	CH_3CN λ_{max} (ε_{max})	$CHCl_3$ λ_{max} (ε_{max})	2-PrOH λ_{max} (ε_{max})	*n*-ButOH λ_{max} (ε_{max})	Dioxane λ_{max} (ε_{max})	CCl_4 λ_{max} (ε_{max})
3a	353(1.43)	363(2.20)	358(3.33)	359(2.10)	358(2.30)	358(2.40)	366(6.20)	361(3.33)	361(3.30)
3b	405sh(2.00)	409sh(2.10)	405sh(3.30)	–	–	–	–	–	–
	432sh(1.70)	436sh(1.80)	432sh(2.90)	–	–	–	–	–	–
	519sh(1.50)	521 sh(1.60)	519sh(3.30)	560(2.33)	570(2.20)	560(2.20)	563(1.90)	562(2.10)	563(2.00)
	559(2.10)	562(2.30)	559(5.80)	583(2.23)	589(2.10)	585(2.20)	585(1.93)	589(2.13)	591(2.13)
	587(2.20)	587(2.30)	587(5.60)						
3c	355(1.10)	363(1.73)	359(3.80)	362(2.36)	361(2.26)	361(2.20)	364(2.60)	363(3.90)	363(2.26)
4a	463(1.40)	472(1.10)	478(1.30)	470(1.20)	484(1.10)	473(1.10)	476(1.60)	472(1.20)	476(1.20)
4b	480sh(9.40)	481sh(11.00)	485sh(11.00)	477sh(12.00)	481(8.30)	482sh(10.00)	482sh(12.00)	481sh(11.00)	479sh(14.80)
	517(12.00)	521(16.00)	519(16.00)	519(17.00)	511(8.30)	519(15.00)	520(17.80)	519(15.00)	517(21.00)
	562(13.00)	564(19.80)	561(19.60)	561(21.00)	562(4.70)	562(19.60)	563(20.00)	564(18.00)	566(22.00)
	597sh(9.70)	597sh(10.00)	597sh(10.00)	597sh(10.00)	597sh(5.10)	597sh(10.00)	597sh(7.00)	597sh(9.00)	597sh(7.00)
4c	473(1.30)	484(1.30)	488(1.50)	484(1.30)	494(1.10)	486(0.75)	490(0.75)	480(1.00)	468(1.10)
5b	512sh(8.80)	519sh(9.00)	518sh(11.00)	518sh(9.70)	519sh(8.70)	516sh(9.00)	520sh(9.30)	511sh(8.00)	521sh(7.40)
	556sh(11.90)	562sh(14.80)	560sh(16.00)	556sh(14.50)	562(12.50)	560sh(13.70)	565sh(13.70)	555sh(10.00)	561sh(7.40)
	592(14.50)	599(18.00)	597(19.70)	594(17.00)	597(16.60)	598(17.40)	598(17.40)	592(16.00)	594(12.00)
	–	–	–	–	–	–	–	617(13.50)	617sh(15.70)
	680sh(1.70)	700sh(2.70)	696sh(2.70)	694sh(2.70)	702sh(2.50)	699sh(2.70)	699sh(2.70)	704sh(2.10)	708sh(1.90)

Where a = λ_{max}/nm and b = $\varepsilon_{max} \times 10^3$/L mol^{-1} cm^{-1}.

Table 3 Data of the electronic absorption spectra (λ_{max}), fluorescence spectra (emission) and stock shifts in different solvents for compounds **4b** and **5b**.

Compd.	DMF			EtOH			ACN			$CHCl_3$			CCl_4		
	λ_{abs}	λ_{emis}	St. Shift	λ_{abs}	λ_{emis}	St. Shift	λ_{abs}	$\lambda_{emis.}$	St. Shift	λ_{abs}	λ_{emis}	St. Shift	λ_{abs}	λ_{em}	St. Shift
4b	481sh	–	–	485sh	–	–	477sh	–	–	481	–	–	479sh	–	–
	521	543	22	519	542	23	519	541	22	511	–	–	517	542	25
	564	599	35	561	600	39	561	597	36	562sh	601	39	566	595	29
	605sh	627sh	22	600sh	624sh	24	600sh	622sh	22	605	–	–	605sh	630	25
5b	519sh	543sh	24	518sh	535sh	17	477sh	–	–	481sh	–	–	521sh	545sh	24
	562sh	604sh	42	560sh	601sh	39	519sh	–	–	511sh	–	–	561sh	–	13
	599	624	25	597	625	28	591	664	73	595	604	9	594	610sh	16
	700sh	–	–	696sh	–	–	600sh	–	–	605sh	–	–	617sh	635sh	18
													708sh	–	–

respect to dimethine compound **3b** resulted in a bathochromic shift of 80 nm and appearing of shoulder at 600 nm as shown in Fig. 2. This could be attributed to the more extensive π-conjugation in pentamethine than dimethine moieties.

A comparison of the visible absorption maxima between compounds **3b**, **4b** and **5b** showed that asymmetrical mono-pentamethine cyanine dye **5b** reveals a bathochromic shift than both dimethine **3b** and pentamethine cyanine dyes **4b**. This could be attributed to the more extensive π-conjugation and increasing number of methine groups in asymmetric pentamethine Fig. 2.

*3.1.2. Solvatochromic behaviour of some selected cyanine dyes **3a**, **3b**, **3c**, **4b**, **5b***

The UV–Vis spectra of some newly synthesized dyes in several common solvents were determined. All the data were collected at room temperature and measured at a concentration of approximately 10^{-4} mol/L. The $\lambda_{\max}$ and $\varepsilon_{\max}$ of the dyes in different solvents are presented in Table 2. As indicated in the table, the $\lambda_{\max}$ ranges from 358 to 591 nm for dyes (**3a**–**c**) and from 478 to 605 nm in (**4a**–**c**) and from 467 to 700 nm in (**5a**–**c**) in different solvents. At the same time, the $\varepsilon_{\max}$ values were in the range of 1100–5600 L mol^{-1} cm^{-1}, 1000–22,000 L mol^{-1} cm^{-1} and 1100–18,000 L mol^{-1} cm^{-1} for (**3a**–**c**), (**4a**–**c**) and (**5a**–**c**) respectively. The order of the $\lambda_{\max}$ for dyes (**3a**–**c**) is **3b** > **3c** > **3a** as shown in Figs. 3–5 respectively. This is due to increasing conjugation in the dyes.

The electronic absorption spectra of **4a** and **4c** cyanine dyes showed a positive solvatochromism with increasing solvent polarity, which depends on the structure and the type of dye. The visible absorption spectra of cyanine dyes **3b**, **4b** and **5b** in pure solvents showed a negative solvatochromism with increasing polarity as shown in Figs. 4, 6 and 7 respectively, which depends on the type of dye. Because the ground state is more stabilized than the excited state due to solvation by solvents of higher polarity, absorption bands in the range 591–708 nm in polar solvents decrease to range 587–696 nm in nonpolar solvent. This finding clearly indicates that the absorption bands of these dyes undergo bathochromic or hypsochromic shifts according to increasing or decreasing conjugation in the dye molecules.

*3.1.3. Emission spectra of some selected new synthesized dyes **4b**,**5b***

Fluorescence emission spectra of compounds **4b** and **5b** in EtOH were measured at an excitation wavelength of 600–630 nm and are shown in Figs. 7 and 8. It can be found that compounds **4b** and **5b** exhibit strong fluorescence intensity. The fluorescence emission wavelengths of these compounds were around 595–630 nm. The absorption maxima of **4b** and **5b** in EtOH showed a bathochromic shift Fig. 9.

3.1.4. Fluoro-solvatochromism

The fluorescence maxima of **4b** showed a negative solvatochromism when going from carbon tetrachloride to dimethylformamide for longer wavelength at 630 nm and a positive solvatochromism when going from carbon tetrachloride to dimethylformamide for shorter wavelength at 595 nm Fig. 10. Meanwhile the fluorescence maxima of **5b** showed a positive solvatochromism when going from carbon tetrachloride to dimethylformamide Fig. 11. The λ_{abs}, λ_{emiss} and stock shifts of the dyes in different solvents are listed in Table 3. This maybe attributed to that fluorescence maxima affected by the type of cyanine dye.

4. Conclusions

All the observations and analytical spectra in this paper support the syntheses of new di-, penta- and mono-/pentamethine cyanine dyes. The absorption spectra of dyes were investigated in organic solvents. The results indicated that the excitation for their colour is a simple charge-transfer from oxygen atom of oxazine nucleus and/or nitrogen atom of pyridine (quinoline) nucleus to N-quaternary salts in di-, penta- and mono-/pentamethine cyanine dyes respectively. These dyes showed a positive solvatochromism with increased solvent polarity, which depends on the structure and the type of dye. Fluorescence emission spectra of some selected compounds in EtOH and the Stock shift were measured.

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