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Synthesis and photophysics in organic solvents of mesosubstituted pentamethine and related metal complexes cyanine dyes

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Abstract

The reaction of a ratio of 1 mol of diacetylchloromethane with the heterocyclic nitrogen base afforded N-substituted heheterocyclidinium ylide halide **1a–1f.** Reaction of a ratio of 1 mol of **1a–1f** with 2 and 3 mol of 2(4)-methylheterocyclic quaternary salts in basic catalyst afforded meso-substituted pentamethine **2a–2f** and monomethine meso-substituted pentamethine **3a-3c** cyanine dyes respectively. Reaction of equimolar ratios of **6a–6e** with equi-(bi)- molar ratios of 2(4)-methylheterocyclic quaternary salts in basic medium afforded asymmetrical (symmetrical) meso-substituted mono-(bis) monomethine metal complex cyanine dyes **7** and **8a–8e**. Elemental analyses, IR and ^{1}H NMR spectral data confirmed the structures of newly synthesized compounds. The electronic absorption spectra of these dyes in ethanol and photophysics in different organic solvents are discussed.

Keywords: N-substituted heterocyclidinium ylide; Sensitizing; Meso-substituted; Metal complex

1. Introduction

Much work has been carried out on the synthesis of an assembled heterocyclic system to prepare and study the properties of different types of cyanine dyes [1–4]. Little attention has been focused on the synthesis of some cyanine dyes derived from heterocyclidinium quarternary salt moieties [5–7]. Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used as photography and information storage [8,9], in laser technology [10] and as photopolymerization initiator [11]. Cyanine dyes are cheap, easy to synthesize, and show very good optical properties, but their stability is not good. Since, the addition of transient metal chelate compounds as quenchers to cyanine dyes enhances their photostability and essentially inhibits their decolorization by light [12–14]. The stabilized cyanine dyes complex has a much higher resistance to light, heat and moisture than the mixture of the cation and the anion [15].

This paper reports the syntheses of meso-substituted pentamethine, merocyanine and new stabilized asymmetrical (symmetrical) mono-(bis)-monomethine metal complex cyanine dyes and evaluates the structure-properties relationships of the dyes on the basis of their visible absorption ethanol and photophysics in different organic solvents are discussed, IR and ^{1}H-NMR spectra.

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2. Results and discussion

The reaction of a ratio of 1 mol of diacetylchloromethane or diacetylmethane in presence of iodine with the heterocyclic nitrogen bases (pyridine,quinoline, isoquinoline, α- picoline, quinaldine and γ-picoline) [3] in non polar solvent afforded the corresponding N-substituted heheterocyclidinium ylide halide **1a–1f**. Elemental analyses (Table 3), IR and ^{1}H-NMR spectral data confirmed the structure of compounds **1a–1f**. Thus IR (ν^{KBr}) spectra of compound **1a** showed well define absorption bands at 1715 cm^{-1} (ν C=O), 3100 cm^{-1} (ν enolate OH bonded with C=O), 2920 cm $^{-1}$ (ν pyridinium ylide iodide). ^{1}H- NMR spectra ($CDCl_3$) for compound **1a** showed signals at δ 7.35–8.3 (m, 5H, pyridinium-H), 4.55 (s, 1H, enolate OH) and 2.3 (s, 6H, $2CH_3$). Interaction of a ratio of 1 mol amount of N-substituted heterocyclidinium ylide halide with 2 mol amounts of a 2(4)-methylheterocyclic quaternary salts (α-picoline, quinaldine and γ-picoline) in the presence of piperidine as basic catalyst afforded the corresponding compounds N-substituted heterocyclidinium pentamethine cyanine dyes **2a–2f**. Interaction of 1 mol amount of **1a–1c** (**2a–2c**) with 3 (1) mole amounts of a 2-methylquinolinium ethyliodide in basic catalyst afforded the corresponding *N*-heterocyclidinium monomethine-meso-substituted pentamethine cyanine dyes **3a–3c**. Scheme 1. Elemental analyses (Table 3), IR and ^{1}H-NMR spectral data confirmed the structure of compounds **2a–2f** and **3a–3c**. Thus IR (ν^{KBr}) spectra of compound **2a** general absorption bands at 2920–2960 cm^{-1} (ν ethyl iodide).^{1}H-NMR ($CDCl_3$) for compounds **2a** and **3a** showed signals at δ 3.9 (q, 2H, CH_2N^+), 1.9 (s, 6H, $2CH_3$), 1.5 (q, 2H, CH_2N) and 1.2 (t, 6H, $2CH_3$), characteristic signal at 6.5–7.9 (m, 19H, Ar-H; hetero-H; CH=) for compound **2a**, and 6.8–8.2 (m, 25H, Ar-H; hetero-H; CH=), for compound **3a**.

Reaction of equimolar ratios of compounds **1a–1c** with equi(bi)-molar ratios of quinolinium ethyl iodide in basic catalyst afforded the asymmetrical (symmetrical) *N*-heterocyclidinium meso-substituted mero-(bis)-merocyanine dyes **4** and **5a–5c** respectively. Scheme 2 Elemental analyses (Table 3), IR and ^{1}H- NMR spectral data confirmed the structure of compounds **4** and **5a–5c**. Thus IR (ν^{KBr}) spectra of compound **5a** showed absorption bands at 1720 cm^{-1} (ν C=O) and 2960 cm^{-1} (ν ethyl iodide). ^{1}H-NMR ($CDCl_3$) for **5a** showed signanls at δ 6.8–8.1 (m, 19H, Ar-H; hetero-H; CH=), 4.1 (s, 1H, CH), 2.1 (q, 4H, CH_2N), 1.2 (t, 6H, $2CH_3$).

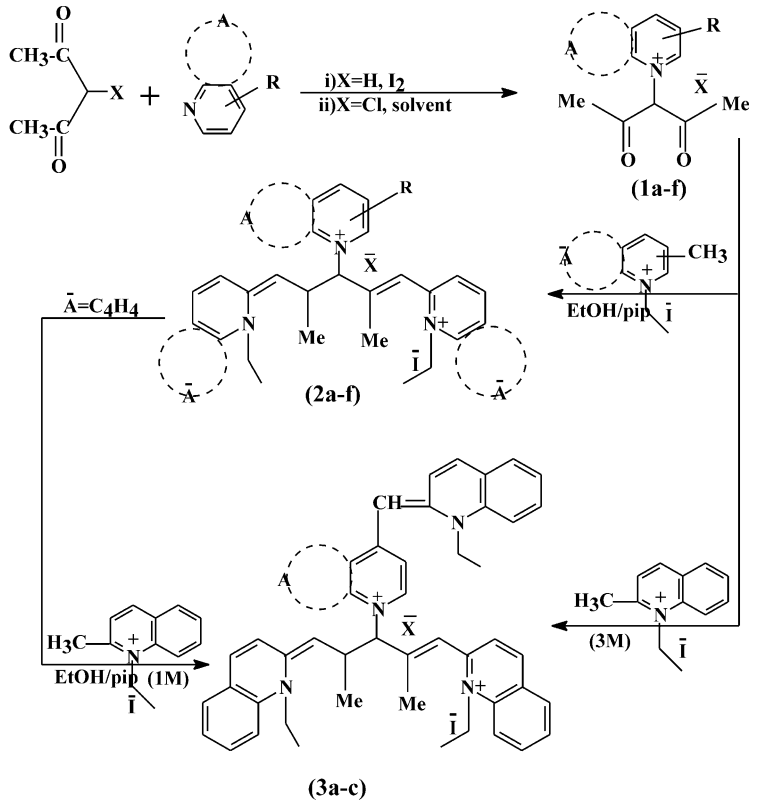
Reaction of equimolar ratios of compounds **1a–1c** with metal dichloride (copper, cobalt and nickel dichloride) in absolute ethanol gave the corresponding complexes **6a–6e** which consider as a key intermediate compounds in the synthesis of metal complex cyanine dyes. Thus, reaction of equimolar ratios of compounds **6a–6e** with equi (bi) molar ratios of the quaternary salts (pyridinium, quinolinium and isoqunolinium ethyl iodide) in thermal condition in presence of piperidine as basic catalyst. The reaction was proceeded through dehydrohalogenation reaction to give the corresponding asymmetrical (symmetrical) *N*-hetero-cyclidinium meso-substituted mono-(bis)-monomethine cyanine dyes metal complex **7** and **8a–8e** respectively. Scheme 2. Elemental analyses (Table 4), IR and ^{1}H- NMR spectral data confirmed the structure of compounds **6a–6e** and **8a–8e**. Thus IR (ν^{KBr}) spectra of compound 6a and 8a showed general absorption bands at 1715 cm^{-1} (νC=O) and 2960 cm^{-1} (ν ethyl iodide). ^{1}H-NMR ($CDCl_3$) for 6a showed signals at δ 7.4–8.3 (m, 7H,quinolinium), 2.3 (s, 6H, $2CH_3$) and for **8a** 6.7 (m, 17H, Ar-H; hetero-H; CH=), 2.1(q, 4H,two CH_2N), 1.3(t, 6H, two CH_3).

The newly synthesized cyanine dyes are highly colored compounds and fairly soluble in polar organic solvents giving a fluorescence. These dyes are only sparingly soluble in non-polar solvents, soluble in conc. H_2SO_4 liberating iodine vapor on warming. Their ethanolic solution gave a violet color in alkaline medium that was discharged on acidification.

2.1. Structural effect of the newly synthesized cyanine dyes

The electronic absorption spectral features (λ_{max} and ε_{max} values) of the newly synthesized cyanine dyes **2a–2f, 3a–3c, 4, 5a–5c, 7** and **8a–8e** in ethanolic solution are depicted in Table 1. The visible

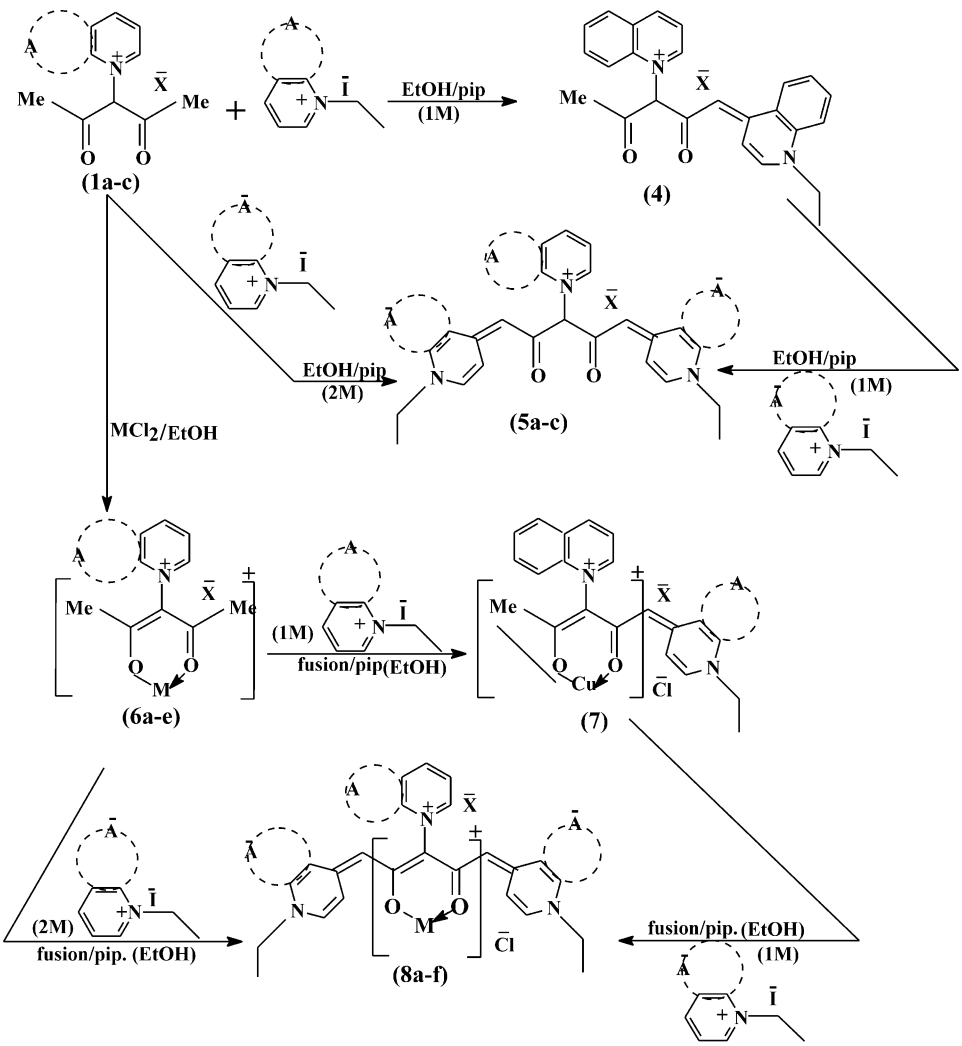
absorption spectra of meso-substituted pentamethine cyanine dyes **2a–2f** in 95% ethanol undergo bathochromic or hypsochromic shifts depending on the nature of the quaternary salts A, $\bar{A}$ and the substituent R. Dyes derived from *N*- quinolinium (quinolin-2-ium) salt either in A or $\bar{A}$ showed bathochromic shifts with an increasing the number of the absorption bands relative to those from *N*-pyridinium, *N*-isoquinolinium and pyridin-2(4)-ium salts. Thus, substitution of A = *N*-pyridinium salt moiety in compound **2a** by A = *N*-quinolinium salt moiety in compound **2b** brought about 5–15 nm accompanied by the appearance of a new band at 440 nm. Substituting A^- = 1-ethylpyridin-4-ium moiety in compound **2d** by A^- = 1-ethylquinolin-2-ium moiety in compound **2b** causes strong bathochromic shift by 105 nm accompanied by the



Scheme 1. (**1a–1f**): a, R = H; A(X) = N-pyridinium; (iodide); b, R = H; A(X) = N-quinolinium; (iodide); c, R = H; A(X) = N-isoquinlinium;(iodide); d, R = 2-CH_3; A(X) = N-pyridinium, (chloride); e, R = 2-CH_3; A(X) = N-quinolinium; (chloride); f, R = 4-CH_3; A(X) = N-pyridinium, (chloride). Substituted in Scheme 1: (**2a–2f**): a, R = H; A(X) = N-pyridinium (iodide); A^- = 1-ethylquinolin-2-ium; b, R = H; A(X) = N-quinolinium (iodide); A^- = 1-ethylquinolin-2-ium; c, R = H; A(X) = N-isoquinlinium (iodide); A^- = 1-ethylquinolin-2-ium; d, R = H; A(X) = N-quinolinium (iodide); A^- = 1-ethylpyridin-4-ium; e, R = H; A(X) = N-quinolinium (chloride); A^- = 1-ethylpyridin-2-ium F, R = 2-CH_3; A(X) = N-quinolinium (chloride); A^- = 1-ethylpyridin-2-ium. (3a–3c):- a, A(X) = N-pyridinium; (iodide); b, A(X) = N-quinolinium; (iodide); c, A(X) = N-isoquinlinium; (iodide) Substituted in Scheme 1A: (5a–5c):- a, A(X) = N-pyridinium (iodide); A^- = N-ethylquinolin-4-ium; B, A(X) = N-quinolinium (iodide); A^- = N-ethylpyridin-4-ium; c, A(X) = N-isoquinolinium (iodide); A^- = N-ethylquinolin-4-ium. (6a–6e):- a, A(X) = N-quinolinium; (iodide); M = Cu; b, A(X) = N-quinolinium; (iodide); M = Ni; c, A(X) = N-quinolinium; (iodide); M = Co; d, A(X) = N-pyridinium; (iodide); M = Cu; e, A(X) = N-isoquinolinium; (iodide); M = Cu (8a-8e):- a, A(X) = N-quinolinium (iodide); A^- = N-ethylpyridin-4-ium; M = Cu b, A(X) = N-quinolinium (iodide); A^- = N-ethylquinolin-4-ium; M = Cu c, A(X) = N-quinolinium (iodide); A^- = N-ethylquinolin-1-ium; M = Cu d, A(X) = N-quinolinium (iodide); A^- = N-ethylquinolin-4-ium; M = Ni e, A(X) = N-quinolinium (iodide); A^- = N-ethylquinolin-4-ium, M = Co.

appearance of new two bands at 440 nm and shoulder at 685 nm respectively. This is due to the more extensive π-conjugation in quinoline moiety. Substituting R = CH_3 in compound **2f** by R = H in compound **2d** resulted in hypsochromic shift by 70 nm. This is may be attributed to increasing the conjugation through the hyperconjugative character of methyl group.

The visible absorption spectra of monomethine-meso substituted pentamethine cyanines **3a–3c** are more affected by the heterocyclic quaternary salts residue (A). Thus, substituting A = *N*-pyridinium moiety in compound **3a** by A = *N*-quinolinium moiety in compound **3b** resulted in bathochromic shift 10 nm to increasing π-conjugation. Similarly the electronic absorption spectra of meso-substituted bis merocyanine dyes **5a–5c** and bis-monomethine metal complex cyanine dyes **8a–8e** are influenced by heterocyclic quaternary salts residue A and $\bar{A}$. Thus, substituting A = *N*-isoquinolinium in compound **5c** by A = *N*-pyridinium moiety in compound **5a** causes bathochromic shift by 15 nm accompanied with appearance of new band at 510 nm. Substituting A^- = *N*-pyridinium moiety in compound **8a** by A^- = *N*-quinolinium moiety in compound **8b** resulted in bathochomic



Scheme 2.

shift by 5 nm. Also, Substituting $A^- = N$-isoquinolinium moiety in compound **8c** by $A^- = N$-quinolinium moiety in compound **8b** causes bathochromic shift by 85 nm. This is due to that 4-position is more extensive π-conjugation than 1-position.

It is obvious from the results in Table 1 that a correlation exists between the length of polymethine chain and the wavelengths of maxima absorption, i.e. the longer of the number methine group, the longer wavelength. However, as the length of the polymethine chain increases the dyes become less stable [16].

2.2. Photophysical properties of some selected cyanine dyes

Besides the structural parameters the λ_{max} and ε_{max} values are very sensitive to solvent interaction and polarity changes [17]. The dependence of the photophysical behaviour of cyanine dyes on the

Table 1
The electronic absorption spectra of mesosubstituted pentamethine cyanine dyes in 95% EtOH

Cyanine dyes 2a–f						
2a	**2b**	**2c**	**2d**	**2e**	**2f**	
			λ_{max} (nm) / log ε_{max} mol^{-1} cm^{-1}			
–	440(4.00)	–	480 (3.94)	460(3.83)	–	
570(4.21)	585(4.08)	540 (3.89)	–	–	550 (3.96)	
680(3.52)	685(3.40)	675(3.43)	–	–	–	
Cyanine dyes **3a**–**3c**, **4** and **5a**–**5c**						
3a	**3b**	**3c**	**4**	**5a**	**5b**	**5c**
–	–	–	450(3.92	450(4.09)	460(3.90)	435(4.70)
–	555(5.79)	–	520(3.65)	510(3.78)	525(3.72)	–
580(5.82)	590(5.98)	570(5.70)	–	–	–	–
Cyanine dyes **7** and **8a**–**8e**						
7	**8a**	**8b**	**8c**	**8d**	**8e**	
–	–	–	395(4.45)	–	–	
465(3.70)	475(3.95)	480(3.98)	–	455(3.75)	480(4.38)	

Table 2
Photophysical data of some selected newly synthesized cyanine dyes **2a**, **3c**, **5a**, and **8e**

Solvent	Dielectric constant (ε_r)	Viscosity (mN.S m^{-2})	**2a** λ_{max}[a]	**3c** λ_{max}	**5a** λ_{max}	**8e** λ_{max}
Water	80.10	1.002	558(—)	550	438(443)	465
Acetonitrile	37.50	0.375	562(670)	560	442(501)	470
Methanol	32.70	0.0544	564(675)	565	448(506)	476
Ethanol	24.55	1.078	570(680)	570	450(510)	480
Acetone	20.70	0.337	575(682)	573	454(512)	485
1-Propanol	20.33	2.237	580(687)	577	459(516)	493
1-Butanol	17.50	3.379	585(685)	586	464(521)	495
1-Pentanol	13.90	3.347	587(685)	588	466(526)	497
1-Hexanol	13.30	4.592	590(687)	593	472(529)	502
Chloroform	4.81	0.596	595(690)	598	483(535)	510

[a] [λ_{max}] Values refer to room temerature (25 °C). Solution concentrations are $1–5\times10^{-5}$ mol l^{-1}.

Table 3
Characterization data of mesosubstituted cyanine dyes

Compound no.	Molecular formula (mol wt)	Calcd.% found%			Yield %	m.p. °C	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H-NMR($CDCl_3$) δ Assignment
		C	H	N				
1a	$C_{10}H_{12}NO_2I$ (305)	39.34 39.83	3.93 4.16	4.59 4.49	90	260–2	1715 (C=O) 3100 (OH) 2920 (C_2H_5I)	7.35–8.3 (m, 5H, het-H), 4.55 (s, 1H, enolate OH) 2.3 (s, 6H, 2 CH_3–)
1b	$C_{14}H_{14}NO_2I$ (355)	47.32 47.77	4.07 4.11	3.56 3.53	97	105–7		
1c	$C_{14}H_{14}NO_2I$ (355)	47.32 47.63	4.07 4.01	3.56 3.73	85	120–2	1720 (C=O) 3100 (OH) 2940 (C_2H_5I)	7.5–8.5 (m, 7H, het-H), 4.6 (s, 1H, enolate OH) 2.1 (s, 6H, 2 CH_3-)
1d	$C_{11}H_{14}NO_2Cl$ (227.5)	58.02 57.75	6.15 6.43	6.15 6.17	77	137–9		
1e	$C_{15}H_{16}NO_2Cl$ (277.5)	64.86 64.93	5.77 5.35	5.05 4.95	95	235	1720 (C=O) 3300 (OH) 2980–2940 (C_2H_5I)	7.5–8.3 (m, 6H, het-H), 4.5 (s, 1H, enolate OH) 2.3 (s, 6H, 2 CH_3-) 1.5 (s, 3H, CH_3)
1f	$C_{11}H_{14}NO_2Cl$ (227.5)	58.02 57.79	6.15 6.53	6.15 6.27	83	146–8		
2a	$C_{34}H_{35}N_3I_2$ (739)	55.21 55.09	4.74 4.23	5.68 5.33	89	220–2	2980 (C_2H_5I) 1585 (CH=CH)	6.5–7.9 (m, 19H, Ar.-H,het.-H, CH=) 3.9 (q, 2H, CH_2- N^+), 1.9 (s, 6H,2CH_3) 1.5 (q, 2H, CH_2-N), 1.2 (t, 6H, 2CH_3)
2b	$C_{38}H_{37}N_3I_2$ (789)	57.80 58.09	4.96 4.75	5.32 5.43	87	275–7		
2c	$C_{38}H_{37}N_3I_2$ (789)	57.80 57.53	4.96 5.13	5.32 5.27	93	192–4	2980 (C_2H_5I) 1585 (CH=CH)	6.8–7.9 (m, 21H, Ar.-H,het.-H, CH=) 4.1 (q, 2H, CH_2- N^+), 1.8 (s, 6H,2CH_3) 1.6 (q, 2H, CH_2-N), 1.1 (t, 6H, 2CH_3)
2d	$C_{30}H_{33}N_3I_2$ (689)	52.25 52.45	4.79 4.98	6.10 5.97	65	177–9		
2e	$C_{30}H_{33}N_3ClI$ (597.5)	60.25 60.13	5.25 5.17	7.03 6.91	95	135–7	2980–2940 (C_2H_5I) 1585 (CH=CH)	6.5–7.8 (m, 17H, Ar.-H,het.-H, CH=) 4.1 (q, 2H, CH_2- N^+), 1.9 (s, 6H,2CH_3) 1.5 (q, 2H, CH_2-N), 1.09 (t, 6H, 2CH_3)
2f	$C_{31}H_{35}N_3ClI$ (611.5)	60.31	5.67	6.73				
3a	$C_{46}H_{48}N_4I_2$ (910)	60.66 60.55	5.27 5.23	6.15 6.33	78	230–2	2980–2940 (C_2H_5I) 1585 (CH=CH)	6.7–8.3 (m, 27H, Ar.-H,het.-H, CH=) 3.9 (q, 2H, CH_2- N^+), 2.1 (s, 6H,2CH_3) 1.7 (q, 4H, CH_2-N), 1.2 (t, 9H, 2CH_3)
3b	$C_{50}H_{50}N_4I_2$ (960)	62.50 62.87	5.21 4.90	5.83 6.11	88	243–5		
3c	$C_{58}H_{50}N_4I_2$ (960)	62.50 62.37	5.21 5.21	5.83 6.01	81	270–2	2980–2940 (C_2H_5I) 1585 (CH=CH)	6.7–8.3 (m, 29H, Ar.-H,het.-H, CH=) 4.1 (q, 2H, CH_2- N^+), 1.9 (s, 6H,2CH_3) 1.6 (q, 4H, CH_2-N), 1.2 (t, 9H, 2CH_3)
4	$C_{25}H_{23}N_2O_2I$ (510)	58.82 58.98	4.51 4.29	5.49 5.63	91	181–3	1720 (C=O) 1585 (CH=CH)	6.8–8.5 (m,14H, Ar-H, heter-H, CH=) 3.5 (s,1H, CH-), 2.3 (s, 3H, CH_3) 1.5 (q, 2H, CH_2N), 1.2 (t, 3H, CH_3)

medium property permits their use as fluorescent probes in microheterogeneous system [19,20]. The results presented in Table 2 suggest that the absorption spectra of the selected dyes depend on the nature of the solvent. In solvents of high dielectric constant (ε_r) the absorption maxima show a hypsochromic shift effect, while in solvents of low ε_r the absorption maxima show a bathochromic shift effect [18]. It is obvious from Table 2 that the position of the maximum of **3c** shifted 48 nm from water to Chloroform as the dielectric constants decreased. Solvent viscosity has been shown to have a crucial influence on the fast nonradiative processes in cyanine dyes leading to photoisomerization, due to a frictional effect on the rotational motion [21,22–24]. We can see from Table 2 in alcoholic solvents, the position of the absorption maximum of dye **8e** shifted 26 nm

Table 4
Characterization data of mesosubstituted cyanine dyes

Compound no.	Molecular formula (mol wt)	Calcd.%, found%			Yield %	m.p. °C	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H-NMR($CDCl_3$) δ Assignment
		C	H	N				
5a	$C_{32}H_{30}N_3O_2I$ (615)	62.44 62.83	4.88 4.71	6.83 7.01	85	205–207	1720 (C=O) 2960 (C_2H_5I) 1585 (CH=CH)	6.8–8.1 (m, 19H, Ar-H,het-H, CH=) 2.1 (q, 4H, $2CH_2$-N), 4.1 (s,1H, CH), 1.3 (t, 6H, $2CH_3$-)
5b	$C_{28}H_{28}N_3O_2$ I (665)	64.69 64.77	4.81 5.01	6.32 6.53	91	187–189		
5c	$C_{36}H_{32}N_3O_2$ I (665)	64.69 64.95	4.81 4.59	6.32 6.63	93	176–178	1730 (C=O) 2940 (C_2H_5I) 1585 (CH=CH)	6.9–8.3 (m, 21H, Ar-H,het-H, CH=) 1.9 (q, 4H, $2CH_2$-N), 4.3 (s,1H, CH) 1.2 (t, 6H, $2CH_3$-)
6a	$C_{14}H_{13}NO_2ClICu$ (453)	37.09 36.85	2.87 3.03	3.09 3.17	75	165–167	1715 (C=O)	7.4–8.3 (m, 7H, het.-H), 2.3 (s, 6H, $2CH_3$)
6b	$C_{14}H_{13}NO_2ClINi$ (448.2)	37.48 37.33	2.90 3.15	3.12 3.25	85	158		
6c	$C_{14}H_{13}NO_2ClICo$ (448.4)	37.47 37.69	2.90 2.83	3.12 3.27	73	205–207		
6d	$C_{10}H_{11}NO_2ClICu$ (403)	29.78 30.09	2.73 2.83	3.47 3.33	82	190–192	1720 (C=O)	7.3–8.1 (m, 5H, het.-H), 2.1 (s, 6H, $2CH_3$)
6e	$C_{14}H_{13}NO_2ClICu$ (453)	37.09 37.29	2.87 3.05	3.09 3.23	85	170–172		
7	$C_{25}H_{22}N_2O_2ClICu$ (607)	49.42 49.57	3.62 3.43	4.61 4.27	76	160–162	2960 (C_2H_5I) 1715 (C=O) 1585 (CH=CH)	6.7–8.2 (m, 14H, Ar.-H,het.-H, CH=) 1.5 (q, 2H, CH_2-N), 1.9 (s,3H, CH_3) 1.1 (t, 3H, CH_3-)
8a	$C_{28}H_{27}N_3O_2ClICu$ (663)	50.68 50.41	4.07 4.37	6.34 6.13	83	77–79	2960 (C_2H_5I) 1715 (C=O) 1585 (CH=CH)	6.7–8.5 (m, 17H, Ar.-H,het.-H, CH=) 2.1 (q, 4H, $2CH_2$-N), 1.2 (t, 6H, CH_3-)
8b	$C_{36}H_{31}N_3O_2ClICu$ (763)	56.62 56.67	4.06 4.27	5.51 5.34	95	158	2980–2940 (C_2H_5I) 1720 (C=O) 1585 (CH=CH)	6.6–8.1 (m, 21H, Ar.-H,het.-H, CH=) 1.9 (q, 4H, $2CH_2$-N), 1.1(t, 6H, $2CH_3$-)
8c	$C_{36}H_{31}N_3O_2ClICu$ (763)	56.62 56.47	4.06 4.21	5.51 5.44	81	106–108		
8d	$C_{36}H_{31}N_3O_2ClINi$ (758.2)	56.98 57.23	4.09 4.25	5.54 5.67	92	95		
8e	$C_{36}H_{31}N_3O_2ClICo$ (758.4)	56.96 57.13	4.09 4.29	5.54 5.37	96	130–132		

form methanol to1-hexanol as the viscosity of solvent increased. Also, it is obvious that the location of the maximum absorption is influenced by the solvent viscosity at same dielectric constant. Thus, the location of the maximum absrption of dye **2a** shifted 5 nm on going from 1-propanol to 1-butanol and dye **5a** shifted 6 nm on going from 1-pentanol to 1-hexanol. This is due to increasing the solvent viscosity.

The relation between the structure of the newly synthesized cyanine dyes of different polymethine and substituents and their photophysical properties are found to vary systematically with the nature of solvents. The photophysical properties newly synthesized cyanine dyes are affected by both dielectric constant and the viscosity of solvents. They are shown to change greatly on going from water to chloform (bathochromic shift) depending upon the decreasing in the dielectric constant and increasing in the viscosity of solvents. It is obvious from Table 2 that monomethine meso-substituted pentamethine **3c** is more affected (more bathochromic shift) by the change in both the dielectric constant and the viscosity of solvents than merocyanine **5a**, bis-monomethine metal complex **8e** and meso-substituted pentamethine cyanine dyes **2a.**

The results obtained show that the newly cyanine dyes can be applied as a probe for viscosity and polarity in studies of microheterogeneous media.

3. Experimental

Melting points (m.p.) were recorded on Gallenkamp melting point apparatus and uncorrected. Elemental analyses were carried out at the micro analytical center at Cairo University. Infrared were determined on a Perkin Elmer Infrared 1650 FT-IR instrument, visible spectra (300–700 nm) were recorded on a Shimadzu-UV-visible-240 spectrophotometer. ^{1}H-NMR spectra were recorded on an EM-390 90 MHz NMR spectrometer.

All reagnts were obtained from Aldrich Chemical Company, and solvents were obtained from BDH Chemical Company.

Synthesis methods of the new starting material and cyanine dyes were carried out according to references [3,4].

*3.1. Synthesis of N-substituted heterocyclidinium ylide halide **1a–1f***

3.1.1. Method (A)

To heterocyclic nitrogen base (pyridine, quimoline, isoquinoline, 2(4)-methylpyridine and 2-methylquinoline) (0.01 mol) in dry benzene (30 ml) at room temprature, diacetylchlomethane solution (0.01 mol) was added portion wise with stirring. After complete addition the mixture was allowed to stand for 30 min. The crystalline products were isolated by suction and recrystallized from ethanol.

3.1.2. Method (B)

A mixture of diacetylmethane (0.01 mol), iodine (0.01 mol) was dissolved in dry benzene (30 ml) and pyridine (quinoline and isoquinoline) (0.01 mol) was added. The reaction mixture was refluxed on water bath for one h. the crystalline products were isolated after evaporated the solvent and recrystallized from ethanol. Characterization data are listed in Table 3.

*3.2. Synthesis of N-substituted heterocyclidinium meso-substituted pentamethine cyanine dyes **2a–2f***

A mixture of compounds **1a–1f** (0.01 mol) and 2(4)-methylheterocyclic quaternary salts (α- or γ-picoline and quinaldine ethyl iodide) (0.01 mol) were dissolved in absolute ethanol (20 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 10–12 h. filtered hot, concentrated and cooled. The precipitated products after dilution with water were collected and crystallized from methanol. Relevant data are listed in Table 3.

3.3. Synthesis of N-substituted heterocyclidinium monomethine meso-substituted pentamethine cyanine dyes 3a–3c

A mixture of compounds **1a–1c** (0.01 mol) and quinaldine ethyl iodide (0.03 mol), the products

were obtained essentially using the same method as for **2a–2f**. Characterization data are given in Table 3.

3.4. Synthesis of asymmetrical (symmetrical) N-heterocyclidinium meso-substituted mero-(bis)-merocyanine dyes *4* and *5a–5c*

A mixture of **1a–1c** (0.01 mol) and quinolinium ethy iodide 0.01 mol (0.02 mol), the products were obtained essentially using the same method as for **2a–2f**. Characterization data are given in Table 4

3.5. Synthesis of N-heterocyclidinium ylide halide metal complex *6a–6e*

A mixture of compounds **1a–1c** (0.01 mol) and metal dichloride (copper, cobalt and nickel) (0.01 mol) were dissolved in absolute ethanol (30 ml). The reaction mixture was refluxed for 1–3 h, filtered hot and concentrated. The precipitated products were isolated and recrystallized from methanol. Relevant data are listed in Table 4.

3.6. Synthesis of asymmetrical (symmetrical) N-heterocyclidinium meso-substituted mono-(bis)-monomethine cyanine dyes 7 and *8a–8e*

A mixture of compounds **6a–6e** (0.01 mol) and N-quaternary salts (pyridinium, quinolinium and isoquinolinium ethy iodide) 0.01 mol (0.02 mol) under thermal condition (sand bath) and piperidine (5–7 drops) was added. The reaction mixture was heated to 30 min, cooled, triturated with ethanol (30 ml) and refluxed for 1 h. Filtered hot, concentrated and cooled, the precipitated products were isolated after dilution with water and collected. Characterization data are listed in Table 4.

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