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Dyes and Pigments 65 (2005) 183–189
DYES and PIGMENTS
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Synthesis and spectral properties of polymethine dyes derived from 5-methyl-11-phenyl-5*H*-indeno[2,1-*b*]quinoline

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Received 25 June 2004; received in revised form 24 July 2004; accepted 30 July 2004

Abstract

Based on the 5-methyl-11-phenyl-5*H*-indeno[2,1-*b*]quinoline nucleus, symmetric and unsymmetric cationoid polymethine dyes as well as merocyanines have been synthesized, and their absorption spectra have been studied. As shown, the absorption maxima are shifted with reference to the analogous oxa-compounds hypsochromically for symmetric or strongly asymmetric (containing the low-electron-donor second end residue) dyes, and bathochromically for slightly asymmetric (containing the high- or medium-electron-donor second end residue) dyes.

Keywords: Polymethine dyes; Pseudoazulenes

Our earlier research [1–5] was focused on the syntheses and spectral studies of polymethine dyes (PDs) derived from oxygen-containing pseudoazulene heterocyclic systems, viz., indeno[2,1-*b*]pyran and indeno[2,1-*b*]chromene. It is now of theoretical and practical interest to investigate the effect caused on the electronic absorption spectra of such PDs by the substitution of the nitrogen for oxygen atoms in their pseudoazulene end nuclei. To this end, we have chosen 5-methyl-11-phenyl-5*H*-indeno[2,1-*b*]quinoline, the most easily accessible compound among nitrogen-containing heterocyclic pseudoazulenes. According to the calculation performed for the relevant residue of the 5*H*-indeno[2,1-*b*]quinoline nucleus (at the 6-position) by the previously described method [6], its effective length ($L = 5.42$) is only slightly less and electron-donor ability ($\Phi_0 = 54°$) is much higher than the corresponding topological parameters for indeno[2,1-*b*]chromene [4]. The challenge is to trace how the energy level positions for the PDs concerned vary with their end-group parameter values.

To obtain 5-methyl-11-phenyl-6*H*-indeno[2,1-*b*]quinoline (**A**), we attempted to employ the known procedure [7]. It is, however, noteworthy that methylation of 11-phenyl-6*H*-indeno[2,1-*b*]quinoline with dimethyl sulfate does not yield salt **A**, contrary to what was reported in Ref. [7]; instead, a mixture of variously alkylated products is formed, as indicated by the ^{1}H NMR spectra. At the same time, methylation with methyl iodide (as described before for unsubstituted 6*H*-indeno[2,1-*b*]quinoline [8]) leads solely to the quaternization of

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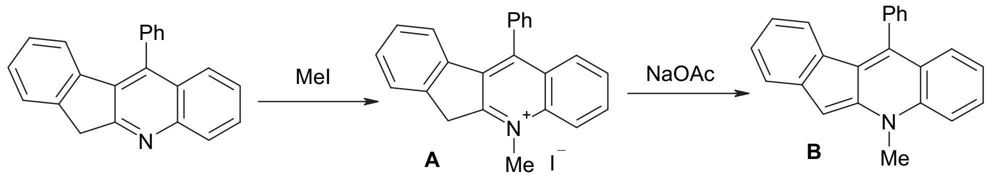
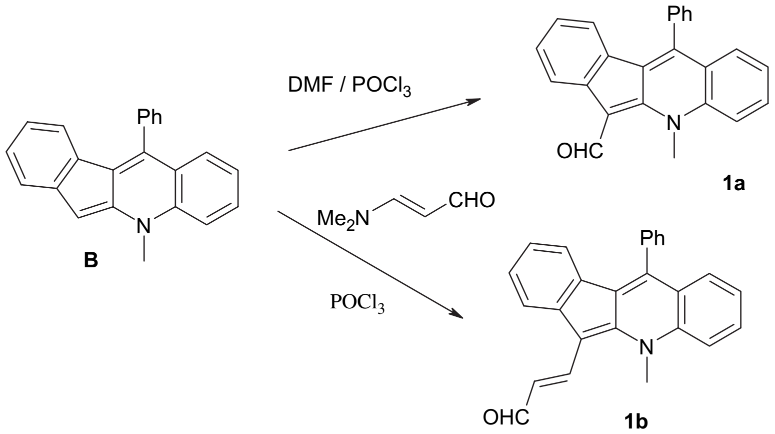
doi:10.1016/j.dyepig.2004.07.016

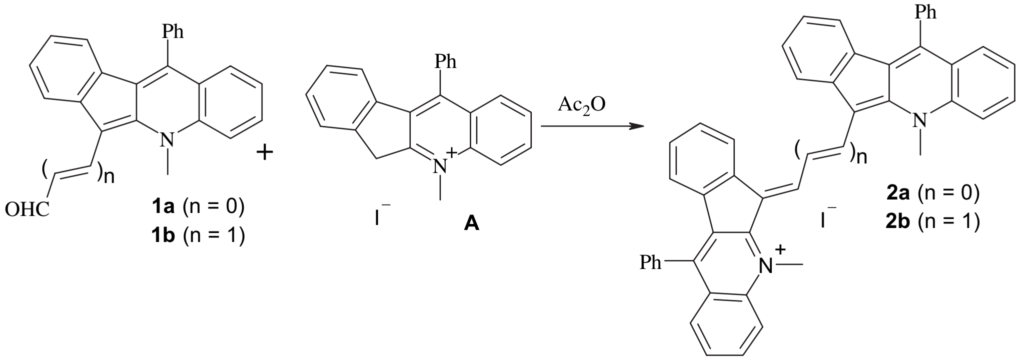
the nitrogen atom and hence to a significantly increased total yield of the desired salt **A**.

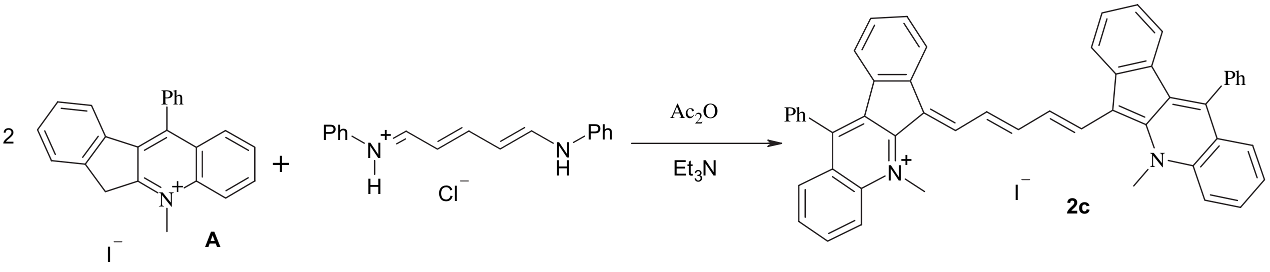


As starting substances for the synthesis of PDs, aldehydes **1a** and **1b** were prepared in high yields by the Vilsmeier–Haack formylation and vinylformylation, respectively.

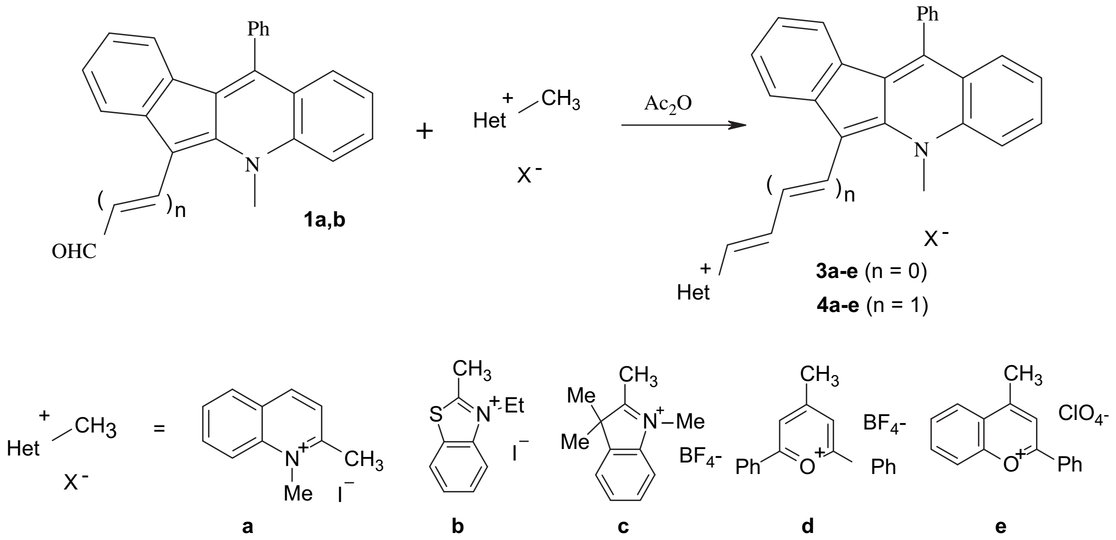


Aldehydes **1a** and **1b** were reacted with salt **A** in acetanhydride to produce symmetric PDs **2a** and **2b**, respectively. Pentamethine dye **2c** was synthesized by the reaction between 2 mol of salt **A** and 1 mol of *N*-(5-phenylimino-1,3-pentadienyl)aniline hydrochloride in acetanhydride in the presence of triethylamine.

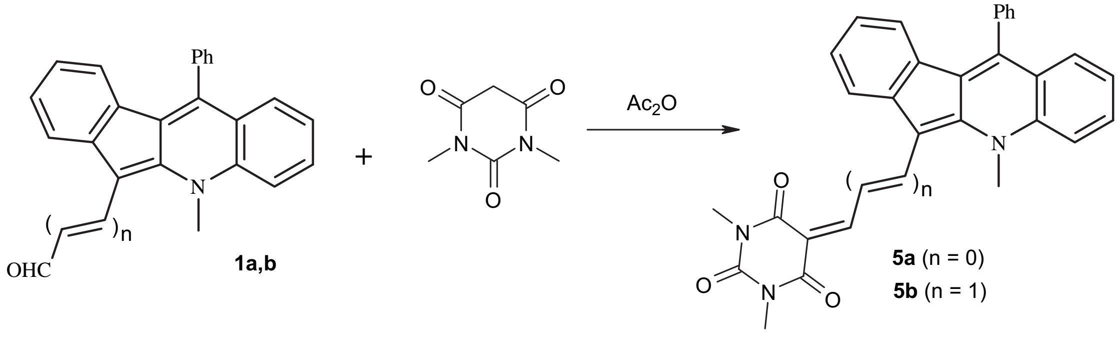




The reaction of aldehydes **1a** and **1b** with methyl-substituted onium salts of heterocycles **a**–**e** was used to afford unsymmetric PDs.



It was also instructive to obtain the merocyanines containing the 5-methyl-11-phenyl-5*H*-indeno[2,1-*b*]quinoline nucleus with the aim to compare their spectral properties with those of the merocyanines synthesized by us before on the basis of indeno[2,1-*b*]pyran and indeno[2,1-*b*]chromene [5]. Merocyanines **5a** and **5b** were prepared reacting aldehydes **1a** and **1b**, respectively, with 1,3-dimethylbarbituric acid.



The absorption spectra of symmetric PDs **2a**–**c** derived from 5-methyl-11-phenyl-5*H*-indeno[2,1-*b*]quinoline exhibit an intensive band in the visible region, with the maximum found at 659 nm ($n = 0$), 726 nm ($n = 1$), and 831 nm ($n = 2$); a number of weak bands lacking pronounced maxima also appear in the region 400–600 nm (see Fig. 1). This spectral picture is much the same as for the analogous symmetric PDs derived from the oxygen-containing pseudoazulene heterocyclic systems [1–5], with the difference that the absorption maxima of the aza-compounds are shifted hypsochromically by 55 and 76 nm, respectively. In passing from PDs **2a** to **2b**, the vinylene shift of 67 nm is much less than the normal value (100 nm), which may be attributable to a bathochromically shifted absorption of **2a** resulting from strong steric hindrances in its molecules [9]. It should be noted that the lesser vinylene shift for the nitrogen-containing than for oxygen-containing PDs (88 nm [3,4]) suggests stronger steric hindrances in the former case. This inference is also supported by simulating the structure of monomethine **2a** in terms of molecular mechanics. The vinylene shift observed in passing from **2b** to **2c** amounts to 105 nm.

Unsymmetric PDs **3a**–**e** and **4a**–**e** can be classified in two groups according to the topological parameters L and Φ_0 of their second heterocyclic residue **a**–**e**. If the corresponding values of the effective length L are comparatively small and the electron-donor ability Φ_0 is high to medium, as is the case with the PDs **a**–**c**, two absorption bands are observed in the visible region, the long-wavelength (first) band being more intensive than the short-wavelength (second) one (see Table 1 and Fig. 2). The PDs with $n = 0$ (**3a**–**c**) display the first absorption band maximum in the region 581–620 nm and the second one in the region 460–496 nm. With the lengthening of the polymethine chain to $n = 1$ (**4a**–**c**),

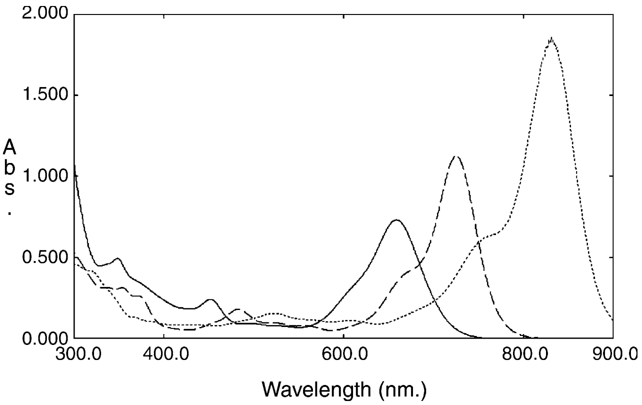


Fig. 1. Absorption spectra of dyes **2a** (solid line), **2b** (broken line, long dashes) and **2c** (broken line, short dashes) in MeCN.

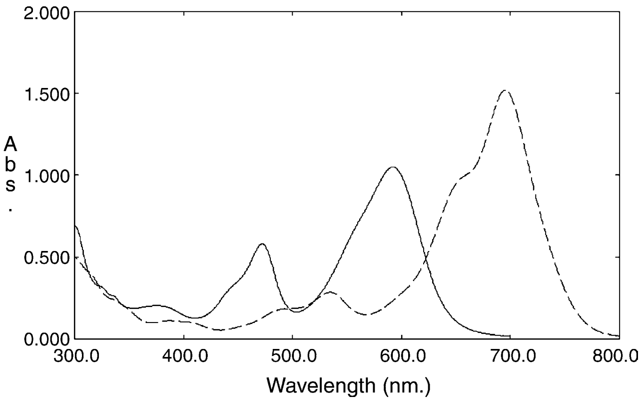


Fig. 2. Absorption spectra of slightly asymmetric dyes **3b**, $n = 0$ (solid line) and **4b**, $n = 1$ (broken line) in MeCN. Spectra of this kind are typical of the dyes with small effective length of the second heterocyclic nucleus.

different values of the vinylene shift are observed for the two bands, namely, about 100 nm for the long-wavelength absorption maximum and only 50–60 nm for the short-wavelength one. The nitrogen-containing pseudoazulene PDs thus demonstrate much larger vinylene shifts of the long-wavelength band than their oxa-analogues, whereas the short-wavelength band is shifted likewise in both PD vinylogous series [3]. This effect points to a higher electronic symmetry of PDs containing the aza-heterocyclic end nuclei. It is the increased electronic symmetry that gives rise to a deeper absorption of unsymmetric PDs **3a**–**c** and **4a**–**c** as against the analogous oxygen-containing PDs, in contrast to the symmetric PDs **2a**,**b**. As the value *n* increases from 0 (**3a**–**c**) to 1 (**4a**–**c**), the intensity ratio between the second and the first absorption bands reduces drastically. Such a change in the intensities is pronounced more for the nitrogen-containing than for the oxygen-containing PDs [3], which is indicative of the fact that the contribution of the aza-heterocyclic end residues to the long-wavelength polymethine electronic transition increases to a greater degree with the lengthening of the polymethine chain.

Unsymmetric PDs **3d**,**e** and **4d**,**e** characterized by the large effective length *L* and the low-electron-donor ability Φ_0 of the second heterocyclic residue (**d**,**e**) show the only intensive absorption band in the vision region which is broadened for the residue **e** and manifests fine structure for **3e** (see Table 1 and Fig. 3). The broadening is likely to arise from the enhanced vibronic interaction caused, in turn, by the largely differing electron-donor abilities of the heterocyclic end residues which give rise to strong bond order alternation and distinct localization of the electronic density on the flavilium moiety. The absorption maxima of PDs **3d**,**e** and **4d**,**e** are shifted to shorter wavelengths relative to their oxa-analogues by 30 and 71 nm ($n = 0$), and 6 and 136 nm ($n = 1$), respectively. The hypsochromic shift is apparently due to much stronger electronic asymmetry of the nitrogen-containing PDs.

Table 1
Characteristics of absorption spectra for PDs **2**–**5** in MeCN

Dye	λ, nm (log ε)
2a	659 (4.56)
2b	726 (4.75)
2c	831 (5.27)
3a	620 (4.83), 496 (4.35)
3b	592 (4.72), 472 (4.46)
3c	581 (4.78), 460 (4.46)
3d	653 (4.81)
3e	636 (4.64), 601 (4.66)
4a	721 (4.85), 554 (3.97)
4b	696 (4.88), 535 (4.15)
4c	683 (5.09), 522 (4.25)
4d	754 (4.70)
4e	666 (4.66)
5a	552 (4.22), 434 (4.33)
5b	621 (4.73), 492 (4.56)

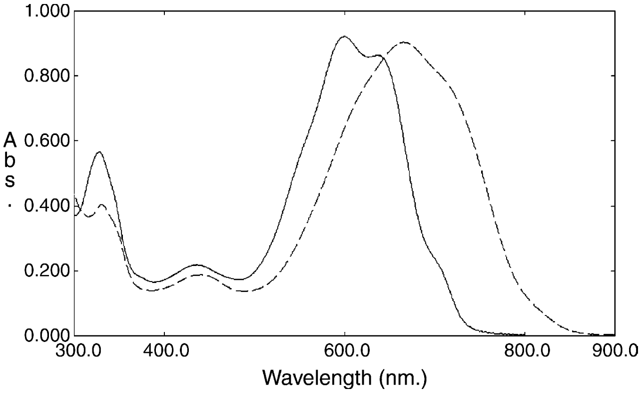


Fig. 3. Absorption spectra of strongly asymmetric dyes **3e**, $n = 0$ (solid line) and **4e**, $n = 1$ (broken line) in MeCN. Spectra of this kind are typical of the dyes with large effective length of the second heterocyclic nucleus.

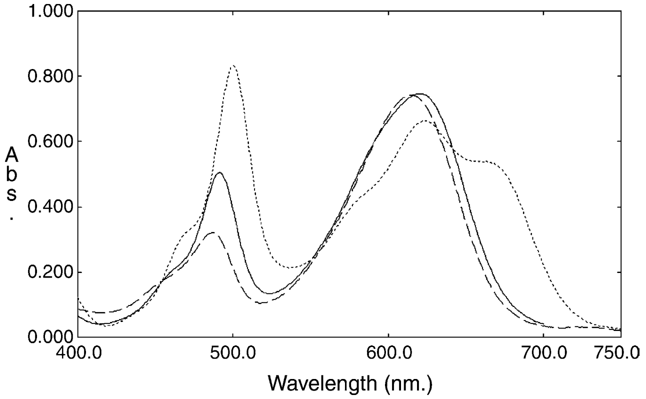


Fig. 4. Absorption spectra of merocyanine **5b** in MeCN (solid line), MeOH (broken line, long dashes) and PhMe (broken line, short dashes).

Merocyanine dyes **5** dissolved in acetonitrile, much like their oxa-analogues [5], exhibit two absorption bands in the visible region (see Table 1). In passing from **5a** to **5b**, the first and the second vinylene shifts, respectively, amount to 69 and 58 nm, which implies the strongly coupled S_0–S_1 and S_0–S_2 transitions in the dye molecules. Whereas the second band is more intensive than the first one for dye **5a**, the intensities interchange for dye **5b**. The solvatochromic study of merocyanines **5** reveals that both band maxima shift hypsochromically in going from acetonitrile to methanol and bathochromically in going from acetonitrile to toluene (see Fig. 4). The band shapes and intensity ratio change substantially with the solvent polarity. Both for **5a** and **5b**, the intensity ratio between the second and the first absorption bands tends to rise as the polarity decreases in the series MeOH–MeCN–PhMe (see Table 2). Merocyanines **5** absorb at longer wavelengths than their analogues containing the indeno[2,1-*b*]chromene nucleus, with the first and the second bands bathochromically shifted by 19 and 54 nm for **5a**, and by 24 and 37 nm for **5b** [5] (Table 3).

In conclusion, the specific spectral features of PDs derived from pseudoazulene heterocycles are mostly retained on substituting the nitrogen for the oxygen atom in the heterocyclic nuclei. Certain distinctions such as the absorption maxima shifted hypsochromically for symmetric or strongly asymmetric (containing the low-electron-donor second end residue) dyes and bathochromically for slightly asymmetric (containing the

Table 2
Characteristics of absorption spectra for merocyanines **5a**,**b** in different solvents

Dye	$\lambda_{1,2}$, nm ($\varepsilon_2/\varepsilon_1$) in MeOH	$\lambda_{1,2}$, nm ($\varepsilon_2/\varepsilon_1$) in MeCN	$\lambda_{1,2}$, nm ($\varepsilon_2/\varepsilon_1$) in PhMe
5a	545, 422 (1.03)	552, 434 (1.30)	565, 441 (1.56)
5b	616, 487 (0.43)	621, 492 (0.68)	624, 500 (1.25)

Table 3
Characterization data for compounds **2a**–**c**, **3a**–**e**, **4a**–**e** and **5a**,**b**

Compound	Empirical formula	Calculated (%)	Found (%)	M.p. (°C)	Yield (%)
2a	$C_{47}H_{33}IN_2$	C − 75.00 H − 4.42 I − 16.86 N − 3.72	C − 74.83 H − 4.46 I − 16. 78 N − 3.83	257–258	76
2b	$C_{49}H_{35}IN_2$	C − 75.58 H − 4.53 I − 16.30 N − 3.60	C − 75.53 H − 4.42 I − 16.38 N − 3.61	>250	83
2c	$C_{51}H_{37}IN_2$	C − 76.12 H − 4.63 I − 15.77 N − 3.48	C − 75.98 H − 4.72 I − 15.82 N − 3.56	260–261	91
3a	$C_{35}H_{27}IN_2$	C − 69.77 H − 4.52 I − 21.06 N − 4.65	C − 69.83 H − 4.44 I − 20.83 N − 4.67	>250	87
3b	$C_{34}H_{27}IN_2S$	C − 65.60 H − 4.37 I − 20.38 N − 4.50 S − 5.15	C − 65.63 H − 4.43 I − 20.44 N − 4.40 S − 5.12	209–211	83
3c	$C_{36}H_{31}BF_4N_2$	C − 74.75 H − 5.40 F − 13.14 N − 4.84	C − 74.82 H − 5.44 F − 13.12 N − 4.81	262–263	84
3d	$C_{42}H_{30}BF_4NO$	C − 77.43 H − 4.64 F − 11.66 N − 2.15	C − 77.30 H − 4.61 F − 11.84 N − 2.13	>250	82
3e	$C_{40}H_{28}ClNO_5$	C − 75.29 H − 4.42 Cl − 5.56 N − 2.19	C − 75.23 H − 4.51 Cl − 5.68 N − 2.17	>250	91
4a	$C_{37}H_{29}IN_2$	C − 70.70 H − 4.65 I − 20.19 N − 4.46	C − 70.63 H − 4.72 I − 19.98 N − 4.49	>250	83
4b	$C_{36}H_{29}IN_2S$	C − 66.67 H − 4.51 I − 19.57 N − 4.32 S − 4.94	C − 66.75 H − 4.32 I − 19.53 N − 4.44 S − 5.03	>250	78
4c	$C_{38}H_{33}BF_4N_2$	C − 75.50 H − 5.50 F − 12.57 N − 4.63	C − 75.56 H − 5.57 F − 12.39 N − 4.67	226–228	75
4d	$C_{44}H_{32}BF_4NO$	C − 78.00 H − 4.76 F − 11.22 N − 2.07	C − 77.83 H − 4.83 F − 11.25 N − 2.01	263–264	84
4e	$C_{42}H_{30}ClNO_5$	C − 75.96 H − 4.55 Cl − 5.34 N − 2.11	C − 76.06 H − 4.67 Cl − 5.51 N − 2.09	>250	88
5a	$C_{30}H_{23}N_3O_3$	C − 76.09 H − 4.90 N − 8.87	C − 76.03 H − 4.95 N − 8.78	>250	89
5b	$C_{32}H_{25}N_3O_3$	C − 76.94 H − 5.04 N − 8.41	C − 77.05 H − 5.01 N − 8.47	254–255	91

high- or medium-electron-donor second end residue) dyes are evidently due to higher electron-donor ability of the 5*H*-indeno[2,1-*b*]quinoline nucleus with respect to the indeno[2,1-*b*]chromene nucleus.

1. Experimental

^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz. ^{1}H NMR spectral measurements failed for dyes **2–5** due to their extremely sparing solubility in available solvents. Absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100, with spectral grade acetonitrile used as a solvent.

*1.1. 5-Methyl-11-phenyl-6H-indeno [2,1-b]quinolinium iodide (**A**)*

A mixture of 11-phenyl-6*H*-indeno[2,1-*b*]quinoline (11.72 g, 40 mmol) and methyl iodide (100 ml) in benzene (400 ml) was boiled under reflux for 2 h. The product was filtered off and washed with diethyl ether. Yield 11.80 g (68%). ^{1}H NMR (CF_3COOD): 4.89 (s, 2H), 4.95 (s, 3H), 6.93 (d, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.66 (m, 3H), 7.87 (d, $J = 7.2$ Hz, 1H), 7.97 (m, 3H), 8.07 (t, $J = 7.2$ Hz, 1H), 8.21 (d, $J = 8.1$ Hz, 1H), 8.36 (t, $J = 7.2$ Hz, 1H), 8.60 (d, $J = 8.7$ Hz, 1H).

*1.2. 5-Methyl-11-phenyl-5H-indeno [2,1-b]quinoline (**B**)*

A mixture of **A** (4.35 g, 10 mmol) and NaOAc (1.64 g, 20 mmol) in ethanol (40 ml) was heated to boiling. The colour changed to violet and a precipitate formed was filtered off and washed with water after cooling the reaction mixture. Yield 2.98 g (97%). ^{1}H NMR (DMSO-d_6): 3.97 (s, 3H), 6.22 (s, 1H), 6.52 (d, $J =$ 7.5 Hz, 1H), 6.71 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 7.2$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.43 (m, 3H), 7.67 (m, 4H), 7.78 (d, $J = 8.1$ Hz, 1H).

*1.3. 5-Methyl-11-phenyl-5H-indeno [2,1-b]quinoline-6-carbaldehyde (**1a**)*

To a stirred and cooled solution of **B** (0.307 g, 1 mmol) in DMF (10 ml), $POCl_3$ was added dropwise (0.306 g, 2 mmol). The reaction mixture became red. On stirring at room temperature for 0.5 h, the mixture was poured into a 10% aqueous solution of NaOH (50 ml). The precipitate formed was thoroughly washed with water and recrystallized from 2-propanol. Yield 0.32 g (95%). ^{1}H NMR (DMSO-d_6): 4.51 (s, 3H), 6.45 (d, $J = 7.5$ Hz, 1H), 6.88 (t, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.47 (m, 4H), 7.72 (m, 3H), 7.90 (m, 1H), 8.19 (d, $J = 8.7$ Hz, 1H), 8.52 (d, $J = 7.5$ Hz, 1H), 10.49 (s, 1H).

*1.4. 3-(5-Methyl-11-phenyl-5H-indeno [2,1-b]quinolin-6-yl)-2-propenal (**1b**)*

To a stirred and cooled solution of 3-dimethylamino-2-propenal (0.099 g, 1 mmol) in MeCN (10 ml), $POCl_3$ was added (0.153 g, 1 mmol). Ten minutes later, **B** (0.307 g, 1 mmol) was strewn to the mixture and it was stirred at room temperature for 0.5 h. Then triethylamine (0.404 g, 4 mmol) was added and the mixture was stirred for another 3 h. Then it was poured into a cooled 10% aqueous solution of NaOH (20 ml); the precipitate coagulated was thoroughly washed with hot water and recrystallized from MeCN. Yield 0.33 g (92%). ^{1}H NMR (DMSO-d_6): 4.45 (s, 3H), 6.49 (d, $J = 7.2$ Hz, 1H), 6.59 (dd, $^3J = 15.2$ Hz, $^3J = 8.1$ Hz, 1H), 6.90 (t, $J = 8.1$ Hz, 1H), 7.40 (m, 5H), 7.71 (m, 3H), 7.86 (m, 2H), 8.06 (d, $J = 8.7$ Hz, 1H), 8.42 (d, $J = 15.0$ Hz, 1H), 9.59 (d, $J = 7.8$ Hz, 1H).

*1.5. General procedure for preparation of symmetric dyes **2a**,**b***

A mixture of the corresponding aldehyde **1** (1 mmol) and salt **A** (0.435 g, 1 mmol) in acetanhydride (15 ml) was boiled under reflux for 10 min. On cooling, the precipitate was filtered off and recrystallized from 2-nitropropane. Analytical data are in Table 3.

*1.6. Preparation of symmetric dye **2c***

A mixture of salt **A** (0.435 g, 1 mmol) and *N*-(5-phenylimino-1,3-pentadienyl)aniline hydrochloride (0.143 g, 0.5 mmol) in acetanhydride (15 ml) was heated to boiling. On cooling and adding three drops of triethylamine, the mixture was again heated to boiling. The precipitate formed was filtered off, washed with water, and recrystallized from 2-nitropropane. Analytical data are in Table 3.

*1.7. General procedure for preparation of unsymmetric dyes **3** and **4***

A mixture of the corresponding aldehyde **1** (1 mmol) and the salt of heterocycle **a**–**e** (1 mmol) in acetanhydride (15 ml) was boiled under reflux for 10 min. On cooling, acetanhydride was decomposed with an excess of methanol and the reaction mixture was evaporated under vacuum. The residue was recrystallized from 2-nitropropane.

*1.8. General procedure for preparation of merocyanine dyes **5a**,**b***

A mixture of the corresponding aldehyde **1** (1 mmol) and 1,3-dimethylbarbituric acid (0.156 g, 1 mmol) in acetanhydride (15 ml) was boiled under reflux for 1 h.

The precipitate formed was filtered off and recrystallized from 2-nitropropane. Analytical data are in Table 3.

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