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Metallochromic merocyanines of 8-hydroxyquinoline series. II. Dyes with end nuclei of low basicity

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Abstract

Based on 5-substituted 8-hydroxyquinoline, a number of complexing merocyanines with the end nuclei of low basicity have been synthesized. Dyes of this kind exhibit the most pronounced metallochromic effects manifested by drastic bathochromic and hyperchromic shifts on complexation with the salts of heavy and transition metals as well as lanthanide salts. The spectral effects observed are of a complicated character and arise from the interaction of the dye, metal, and solvent.

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1. Introduction

In recent years Kubo et al. have reported a number of studies on metallochromic near-IR dyes of the indoaniline type which contain the residue of 5-substituted 8-hydroxyquinoline as a complexing moiety [1–4]. Interaction of such dyes with metal salts gives rise to a drastic bathochromic shift and a significant enhancement of dye absorption bands. In this respect, the compounds concerned excel other types of ionochromogens which have received considerable recent attention [5–9].

It was just for this reason that our previous work was focused on the compounds structurally close to the above-mentioned indoanilines, namely, on the cyanine dyes derived from the 5- or 7-substituted 8-hydroxyquinoline nucleus [10]. When treated with heavy and transition metal salts, the merocyanines containing the residue of 7-substituted 8-hydroxyquinoline, were found to manifest hypsochromic shifts thus resembling the effect caused by acids. Similar results were obtained for the derivatives of 5-substituted 8-hydroxyquinoline which contained a heterocyclic end group of high or medium basicity. Also, a dye of this kind was synthesized, with its end group represented by a low-basicity heterocyclic residue (the 1,3,3-trimethylindoline nucleus). Interestingly, the ionochromic effects proved to be radically different in this case: addition of metal salts caused significant bathochromic rather than hypsochromic shifts, which was reminiscent of the behaviour typical of the indoaniline series [1–4].

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The present work has been aimed at a thorough study of this phenomenon, i.e. finding approaches to chemically modified basic structures of merocyanines of quinoline series which manifest drastic spectral changes under the action of metal salts. To this end, we have synthesized and spectroscopically investigated merocyanines based on the 5-substituted 8-hydroxyquinoline and containing varied heterocyclic nuclei of low basicity.

2. Experimental

Electronic absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100. ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz. The purity of metal salts used for the spectral measurements was over 99%. Aldehyde 1 was synthesized by the literature procedure [11]. The yields, melting points, and elemental analysis data of the synthesized dyes are summarized in Table 1.

*2.1. 5-[2-(2,6-Di(tert-butyl)pyran-4-ylidene) ethylidene]-5H-quinolin-8-one (**2a**)*

Aldehyde **1** (0.5 g, 2.86 mmol) and 2,6-di(*tert*-butyl)-4-methylpyrylium perchlorate (0.86 g, 2.86 mmol) were boiled in ethanol (20 ml) for 7 h. After cooling, triethylamine (0.5 ml) was added to the solution, and the mixture was poured into water (100 ml), extracted with methylene chloride, dried with magnesium sulphate, and evaporated. The residue was crystallized from ethanol.

Table 1
Characterization data for merocyanines 2

Dye	Mp (°C)	Yield (%)	Empirical formula	Elemental analysis (%)			
					C%	H%	N%
2a	231–232	27	$C_{24}H_{27}NO_2$	Calcd	79.8	7.5	3.9
				Found	79.6	7.4	3.8
2b	237–239	72	$C_{28}H_{19}NO_2$	Calcd	83.8	4.7	3.5
				Found	84.0	4.9	3.6
2c	256–257	40	$C_{28}H_{19}NOS$	Calcd	80.6	4.6	3.4
				Found	80.6	4.5	3.5
2d	187–189	41	$C_{26}H_{22}N_2O$	Calcd	82.5	5.9	7.4
				Found	82.4	6.0	7.3
2e	>300	22	$C_{22}H_{19}N_3O_2$	Calcd	70.8	5.1	11.3
				Found	70.7	5.1	11.3

^{1}H NMR ($CDCl_3$/TMS), δ: 1.4 (*s*, 18H, *t*-Bu); 6.32 (*d* + *broad s*, 3H, $J = 13$ Hz, CH = + β,β^1-H of the pyrylium ring); 6.73 (*d*, 1H, $J = 10$ Hz, C^7-H); 7.46 (*m*, 1H, β-H of the quinoline ring); 7.98 (*m*, 2H, CH_{Ar}); 8.36 (*d*, 1H, $J = 8$ Hz, γ-H of the quinoline ring); 8.79 (*m*, 1H, α-H of the quinoline ring).

*2.2. 5-[2-(2,6-Diphenylpyran-4-ylidene) ethylidene]-5H-quinolin-8-one (**2b**)*

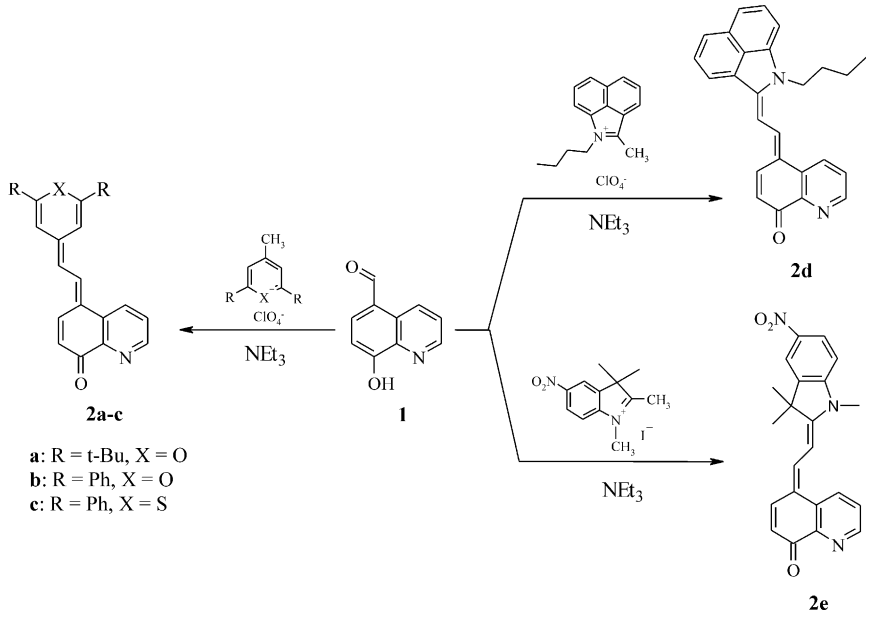
Aldehyde **1** (0.2 g, 1.14 mmol) and 2,6-diphenyl-4-methylpyrylium perchlorate (0.4 g, 1.14 mmol) were boiled in the mixture ethanol–acetonitrile (3:1, 20 ml) for 7 h. After cooling, the solution was evaporated to dryness and the residue was suspended in the mixture ethanol–acetonitrile (2:1). This was followed by adding triethylamine (0.3 ml), heating the solution to boiling and filtering it hot. The precipitate formed on cooling was filtered off and dried.

^{1}H NMR (DMSO-d_6/TMS), δ: 6.63 (*d*, 1H, $J = 10$ Hz, C^7-H); 6.92 (*d*, 1H, $J = 13.5$ Hz, CH =); 7.59 (*m*, 7H, 6C-H_{Ph} + β-H of the pyrylium ring); 7.77 (*m*, 1H, β-H of the quinoline ring), 8.06 (*m*, 4H, 4C-H_{Ph}); 8.21 (*d*, 1H, $J = 10$ Hz, C^6-H); 8.56 (*d*, 1H, $J = 13.5$ Hz, CH=); 8.75 (m, 1H, γ-H of the quinoline ring); 8.9 (*br. s*, 1H, β′-H of the pyrylium ring); 9.07 (*d*, 1H, $J = 8$ Hz, α-H of the quinoline ring).

*2.3. 5-[2-(2,6-Diphenylthiopyran-4-ylidene) ethylidene]-5H-quinolin-8-one (**2c**)*

Aldehyde **1** (0.35 g, 2 mmol) and 2,6-diphenyl-4-methylthiopyrylium perchlorate (0.73 g, 2 mmol) were boiled in ethanol (15 ml) for 6 h. The solid precipitating on cooling was filtered off, suspended in acetonitrile (10 ml), and heated to boiling. After adding triethylamine (0.7 ml), the solution was filtered hot. The precipitate formed on cooling was filtered off.

^{1}H NMR (DMSO-d_6/TMC), δ: 6.61 (*d*, 1H, $J = 10$ Hz, C^7-H); 7.19 (*d*, 1H, $J = 14$ Hz, CH=); 7.54 (*m*, 8H, 6C-H_{Ph} + β,β^1-H of the thiopyrylium ring); 7.6 (*m*, 1H, β-H of the quinoline ring); 7.79



Scheme 1.

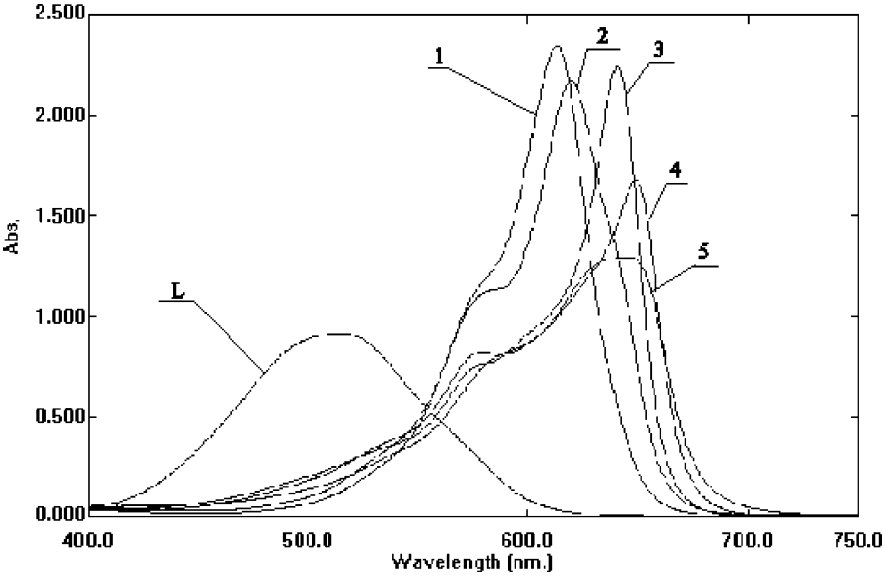


Fig. 1. Absorption spectra of merocyanine **2a** (L) on addition of metal salts in tetrahydrofuran ($C = 2 \cdot 10^{-5}$) at the ligand–metal molar ratio 1:1: (1) **2a** + $Hg(ClO_4)_2$; (2) **2a** + $Cd(ClO_4)_2$; (3) **2a** + $Zn(ClO_4)_2$; (4) **2a** + $Ni(ClO_4)_2$; (5) **2a** + $Co(ClO_4)_2$.

(*m*, 4H, 4C-H_{Ph}); 8.27 (*d*, 1H, *J* = 10 Hz, C^6-H); 8.52 (*d*, 1H, *J* = 14 Hz, CH=); 8.72 (*m*, 1H, γ-H of the quinoline ring); 9.01 (*d*, 1H, *J* = 8 Hz, α-H of the quinoline ring).

2.4. 5-[2-(1-(n-Butyl)-1H-benz[c,d]indol-2-ylidene)ethylidene]-5H-quinolin-8-one (**2d**)

Aldehyde **1** (0.28 g, 1.62 mmol) and 1-(n-butyl)-2-methylbenz[c,d]indolium perchlorate (0.5 g, 1.55 mmol) were boiled in ethanol (15 ml) for 6 h. The solid precipitating on cooling was filtered off and dissolved in boiling ethanol (10 ml). After adding triethylamine (0.7 ml), the solution was filtered hot. The precipitate formed on cooling was filtered off.

^{1}H NMR (DMSO-d_6/TMS), δ: 0.93 (*m*, 3H, $\underline{CH_3}CH_2CH_2CH_2N$); 1.41 (*m*, 2H, $CH_3\underline{CH_2}CH_2$-CH_2N); 1.75 (*m*, 2H, $CH_3CH_2\underline{CH_2}CH_2N$); 4.17 (*m*, 2H, $CH_3CH_2CH_2\underline{CH_2}N$); 6.62 (*d*, 1H, *J* = 10 Hz, C^7-H); 7.01 (*d*, 1H, *J* = 13 Hz, CH=); 7.09 (m, 1H, CH_{Ar}); 7.47 (*m*, 2H, CH_{Ar}); 7.62 (*m*, 1H, CH_{Ar}); 7.78 (*t*, 1H, *J* = 8 Hz, C^4-H of the benz[c,d]indolium ring); 7.98 (*d*, 1H, *J* = 8 Hz, C^3-H of the benz[c,d]indolium ring); 8.46 (*m*, 2H, CH_{Ar}); 8.67 (*d*, 1H, *J* = 13 Hz, CH=); 8.7 (*m*, 2H, CH_{Ar}).

2.5. 5-[2-(1,3,3-Trimethyl-5-nitro-1,3-dihydroindol-2-ylidene)ethylidene]-5H-quinolin-8-one (**2e**)

Aldehyde 1 (0.22 g, 1.3 mmol) and 5-nitro-1,2,3,3-tetramethylindolium iodide (0.45 g, 1.3 mmol) were boiled in ethanol (15 ml) for 6 h. Then triethylamine (0.3 ml) was added to the reaction mixture and it was boiled for another 5 min. The solid formed was filtered off and recrystallized from the mixture acetonitrile–DMF (3:1).

^{1}H NMR (DMSO-d_6/TMS), δ: 1.77 (*s*, 6H, $C(CH_3)_2$); 3.58 (*s*, 3H, N–CH_3); 6.59 (*d*, 1H, *J* = 10 Hz, C^7-H); 6.69 (*d*, 1H, *J* = 13 Hz, CH =); 7.3 (*d*, 1H, *J* = 9 Hz, C^7-H of the indolium ring); 7.68 (*m*, 1H, CH_{Ar}); 8.27 (*m*, 2H, CH_{Ar}); 8.41-8.46 (*m*, 2H, CH_{Ar}); 8.72 (*m*, 2H, CH_{Ar}).

3. Results and discussion

As a starting substance, 5-formyl-8-hydroxyquinoline 1 was used and as dye end groups, we

Table 2
UV/VIS spectral data for merocyanines **2** on addition of metal salts in tetrahydrofuran[a]

Dye	L	Ni^{2+}		Co^{2+}		Zn^{2+}		Cd^{2+}		Hg^{2+}		Sm^{3+}	
	λ_{max} (ε)	λ_{max}	Δλ	λ_{max} (ε)	Δλ	λ_{max} (ε)	Δλ	λ_{max} (ε)	Δλ	λ_{max} (ε)	Δλ	λ_{max} (ε)	Δλ
2a	520 (48,000)	644 (92,000)	124	650 (60,000)	130	640 (106,000)	120	619 (109,000)	99	613 (117,000)	93	622 (80,000)	102
2b	532 (27,000)	701 (42,000)	169	700 (23,000)	168	666 (26,000)	134	671 (34,000)	139	–		673 (25,000)	141
		642 (27,000)	110	631 (20,800)	99	615 (29,000)	83	617 (29,000)	85			621 (23,000)	89
2c	544 (48,000)	713 (42,000)	169	721 (36,000)	177	731 (31,000)	187	711 (53,000)	167	703 (34,000)	179	715 (45,000)	171
		675 (40,000)	131	658 (34,000)	114	644 (55,000)	100	658 (48,000)	114	639 (47,000)	95	657 (42,000)	113
2d	597 (32,000)	732 (54,000)	135	712 (38,000)	115	725 (51,000)	128	703 (46,300)	106	697 (21,000)	100	709 (46,000)	112
				659 (28,000)	62					620 (31,000)	23		
2e	508 (45,000)	612 (54,000)	104	612 (35,000)	104	609 (81,000)	101	585 (70,400)	77	589 (35,000)	81	591 (57,000)	83
		555 (27,000)	47	557 (24,000)	49					548 (23,000)	40		

[a] λ_{max}, absorption maximum, nm; $\Delta\lambda = \lambda_{max}$ (metal complex or protonated form) $-\lambda_{max}$ (free ligand); ε, extinction coefficient ($mol^{-1}\ cm^{-1}$), all data were obtained at the metal–ligand molar ratio 1:1.

chose heterocycles of the lowest possible basicity, i.e. those characterized by sufficiently small values of electron-donor ability estimated after Il′chenko [12] (parenthesized): 1-(*n*-butyl)-1,2-dihydrobenz[c,d]indol-2-ylidene (1.05), 2,6-di(*tert*-butyl)-4H-pyran-4-ylidene (0.97), 2,6-diphenyl-4H-pyran-4-ylidene (0.66), 2,6-diphenyl-4H-thiopyran-4-ylidene (0.66), and 2,3-dihydro-5-nitro-1,3,3-trimethyl-1H-indol-2-ylidene (0.53). This parameter is regarded as an approximate empirical estimate; it is calculated from the deviations [13,14] of the styryl dyes containing the residues of the relevant heterocycles. One should take into account that the deviations themselves are calculable exactly only with the proviso that the corresponding symmetric parent dyes absorb in much the same spectral region [15] and their absorption bands are similar in shape to each other and to those of the unsymmetric dyes concerned [16]. This is not always the case in our study, and that is why the values of electron-donor ability coincide for the oxygen- and sulfur-containing heterocyclic residues which enter into dyes **2b** and **2c**. In view of the absorption band shapes for the unsymmetric carbocyanines constituted by the 2,6-diphenylpyrylium and 2,6-diphenylthiopyrylium residues, it has been inferred that the sulfur-containing heterocyclic nucleus is less electron-donor than its oxygen-containing analogue [16].

Merocyanines **2a–e** were synthesized by the condensation of the starting aldehyde **1** with the salts of 1-(*n*-butyl)-2-methylbenz[c,d]indolium, 2,6-di(*tert*-butyl)-4-methylpyrylium, 2,6-diphenyl-4-methylpyrylium, 2,6-diphenyl-4-methylthiopyrylium, and 5-nitro-1,2,3,3 tetramethylindolium in ethanol or, for sparingly soluble substances, in the mixture of ethanol and acetonitrile (Scheme 1).

The styryls with a hydroxyl group in the quinoline ring which form in the reaction were immediately converted into merocyanines by the treatment with triethylamine. Interestingly, the dyes based on 2,6-diphenylpyran (thiopyran) and 5-nitro-1,3,3-trimethylindole, i.e. on the lowest-basicity heterocyclic nuclei of the series involved, give rise to a mixture of the styryl and merocyanine forms of the target compound already in the reaction mixture before adding triethylamine. In general, heterocyclic moieties of rather low basicity incorporated by all the dyes obtained make the corresponding hydroxy-substituted styryls unstable so that they eliminate an acid molecule in polar solvents much easier than their analogues with more basic end groups [10].

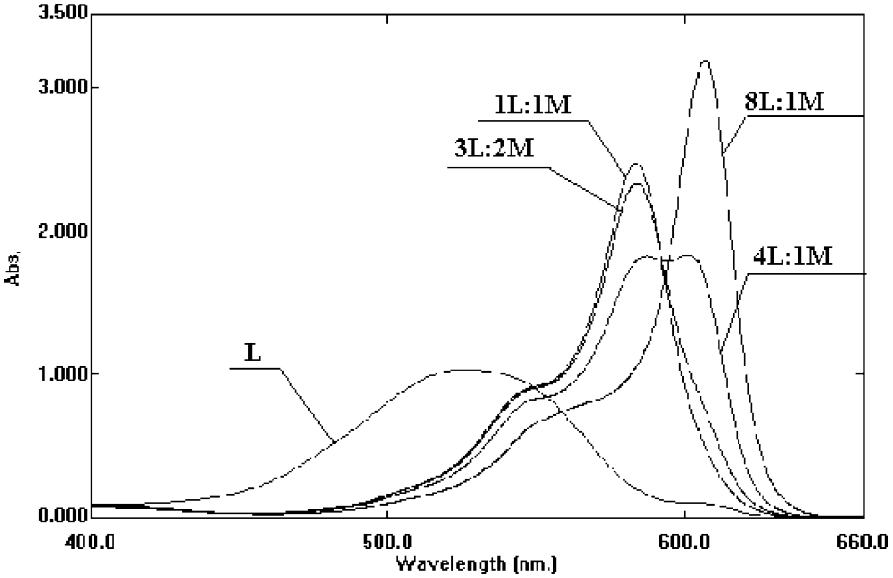


Fig. 2. Absorption spectra of merocyanine **2e** (L) on addition of $Zn(ClO_4)_2$ in acetonitrile ($C = 2\cdot10^{-5}$) at different ligand–metal molar ratios, L:M.

The structures of the synthesized compounds have been confirmed by elemental analysis (Table 1) and ^{1}H NMR spectroscopy.

Merocyanines **2a**–**e** show broad bands of low (as against most of cyanines) intensity in absorption spectra. Adding metal salts always causes batho- and predominantly hyperchromic effects, which are manifested, however, differently in different solvents. As metal salts are added gradually to the dye solutions in tetrahydrofuran, the absorption maxima regularly shift toward longer wavelengths, with the deepest absorption reached at the salt-dye molar ratio 1:1 (Fig. 1 and Table 2). Such spectral behaviour typical of dye-metal complexes was observed by us in a plenty of instances [9,10]. In contrast, titration of the dyes in acetonitrile solutions with metal salts causes the maximum spectral changes already at the salt–dye molar ratio 1:8 (Fig. 2 and Table 3). A further increase in the salt concentration results in lesser bathochromic shifts and complicated band shapes which are seen to comprise several extrema. The effect saturation sets in at the salt–dye molar ratio 1:1 (from this point on, the titration produces no changes in absorption spectra).

It is clear that the dye–metal interaction which comes about on adding metal salts to the merocyanines concerned polarizes the electronic structure of the dye chromophore, so that it switches from essentially polyenic to essentially polymethinic [17,18] (i.e., the enhanced charge alternation and the weakened bond-order alternation in the conjugation chain result, and the absorption maximum shifts bathochromically). For such a switch to occur, the interaction between the metal ion and the binding sites, viz. the oxygen and nitrogen atoms, should cause a sufficient but not excessive polarization, so as to bring the chromophore structure possibly close to the cyanine limit [19] but not beyond it. If the polyenic-type chromophore with the initially predominant merocyanine form (as is the case with the dyes containing the end groups of low basicity) is "overpolarized" by complexing with a metal ion, another polyenic chromophore arises, with the styryl form prevailing (as in dyes with highly basic end nuclei), whereas the cyanine limit corresponding to the equal contributions from the two limiting forms is passed by.

Table 3
UV/VIS spectral data for merocyanines **2**, their protonated forms, and on addition of metal salts in acetonitrile[a]

Dye	L	H$^+$			Ni^{2+}			Co^{2+}			Zn^{2+}			Cd^{2+}			Hg^{2+}			Sm^{3+}		
	λ_{max} (ϵ)	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$	λ_{max}	(ϵ)	$\Delta\lambda$
2a	540 (44,000)	435	(22,000)	−105	639	(135,000)	99	640	(106,000)	100	625	(112,000)	85	635	(120,000)	85	626	(86,000)	86	612	(58,000)	72
2b	545 (41,000)	458	(36,000)	−87	686	(123,000)	141	689	(109,000)	144	677	(110,000)	132	680	(86,000)	135	673	(94,000)	128	–		
2c	564 (39,000)	492	(29,400)	−72	740	(106,000)	176	743	(103,000)	179	729	(99,000)	165	729	(72,000)	165	724	(68,000)	160	706	(53,000)	142
2d	615 (30,000)	511	(17,600)	−104	720	(69,400)	105	695	(43,000)	80	712	(64,000)	97	693	(43,000)	78	689	(49,000)	74	685	(39,000)	70
2e	526 (52,000)	451	(27,000)	−75	613	(165,000)	87	617	(128,000)	91	606	(159,000)	80	606	(107,000)	80	604	(111,000)	78	588	(108,000)	62

[a] λ_{max}, absorption maximum, nm; $\Delta\lambda = \lambda_{max}$ (metal complex or protonated form)-λ_{max} (free ligand); ϵ, extinction coefficient (mol^{-1} cm^{-1}) all data were obtained at the metal–ligand molar ratio 1:8.

To exemplify, compare the ionochromic behaviour of the dyes **2a–e** in low-polarity (tetrahydrofuran) and high-polarity (acetonitrile) solvents. The compounds under study, like other 8-hydroxyquinoline derivatives, are able of forming metallocomplexes of various constitution (with the metal to ligand ratios 1:1, 1:2, and 1:3) which are at equilibrium with the free dye. As shown, the largest bathochromic shifts suggesting the essentially polymethinic chromophore result for the complexes forming at the metal to ligand molar ratio 1:1 in tetrahydrofuran and 1:8 in acetonitrile. Thus, a much milder polarizing action of the metal ion is necessary in the latter case in order to provide the appropriately increased contribution of the styryl form, which is due to the additional stabilization of this form by the polar solvent. Accordingly, further enhancement of the metal-induced polarization already brings the chromophore structure beyond the cyanine limit, as evidenced by the fact that the bathochromic shifts observed for the metallocomplexes in acetonitrile solutions decrease, as the metal to ligand molar ratio becomes larger than 1:8.

Although dyes **2a–e** have sufficiently varied chemical structure, they generally demonstrate a qualitatively similar spectral response to the action of metal salts. In all cases, the most pronounced effects are evoked by transition metal ions: they give rise to bathochromic shifts of 100–170 nm with rather low selectivity. The ions of heavy metals and samarium^{3+} influence the dye spectra to a much lesser degree. The deepest-coloured metallocomplexes are produced by the merocyanine with the end residue derived from 2,6-diphenylthiopyrane.

4. Conclusion

A number of novel merocyanines have been synthesized which contain the 8-hydroxyquinoline nucleus, with the polymethine chromophore incorporated at position 5, and a heterocyclic end group of low basicity. The metallochromic behaviour of the compounds obtained appears as appreciable bathochromic shifts and distinctly increased intensities of dye absorption bands in the presence of the transition metal ions. These spectral effects result from the complicated interaction of the dye, metal ion, and solvent, and can be understood in terms of polyene–polymethine relationships. The largest bathochromic shifts associated with the closeness to the cyanine limit are observed for the metal to ligand molar ratio of 1:1 in tetrahydrofuran and 1:8 in acetonitrile.

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