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Metallochromic merocyanines of 8-hydroxyquinoline series

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Abstract

A number of merocyanines based on the 5- and 7-substituted 8-hydroxyquinoline nucleus have been synthesized, and the metallochromic and some metallofluorochromic properties of the prepared dyes have been studied. The most pronounced metallochromic effects are observed for the dyes containing low-basicity end nuclei. Maximum metallofluorochromic effects were demonstrated by the 7-substituted derivatives of 8-hydroxyquinoline upon interaction with Zn^{2+}, Cd^{2+}, and Hg^{2+} cations. A possible mechanism of metal binding is discussed.

Keywords: Merocyanines; Metallochromism; Metallofluorochromism; Metallocomplexes; 8-Hydroxyquinoline

1. Introduction

In recent years, Kubo et al. have published a number of papers on metallochromic near-IR dyes of the indoaniline type containing a metal-binding fragment, 5-substituted 8-hydroxyquinoline residue [1–4]. Interaction of these dyes with metal salts resulted in high bathochromic shifts of their absorption maxima, along with a significant increase in absorption intensities, an obvious advantage over the other types of ionophores [5–9].

The idea of binding the polymethine chromophore to the 8-hydroxyquinoline nucleus is not entirely new. Phillips et al. prepared some samples of this group of compounds much earlier. A number of merocyanines based on 5- and 7-substituted 8-hydroxyquinoline were synthesized and studied as analytical reagents [10–14]. However, a knowledge of their spectral and metallochromic properties and the effect of metal ions on the dye colour is inadequate. Ionofluorophoric properties of the above-mentioned dyes were not studied at all, except for the investigation on the ionofluorochromism of spiropyranes containing the 8-hydroxyquinoline core [15].

Since the chromophore structure of indoaniline dyes is close to that of cyanines, we have studied, in detail, the merocyanine dyes based on 5- and 7-substituted 8-hydroxyquinoline; the dye series under study was somewhat extended and their structure was modified as compared to Refs [10–14]. Spectroscopic investigation of their interaction with transition metal salts has been performed. Our main attention has been paid to the investigation of the effect of metal ions on the absorption spectra of these dyes.

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2. Experimental

Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer, and fluorescence spectra on a Hitachi-850 fluorescent spectrophotometer. Proton NMR spectra were obtained with a Varian VXR-300 instrument at 300 ÌHz using tetramethylsilane as internal standard. The purity of metal salts used for the spectral experiments was >99%. 5-Formyl-8-hydroxyquinoline **1** and 7-formyl-5-chloro-8-hydroxyquinoline **3** were prepared according to the published procedures [16,17]. The yields, melting points, and elemental analysis data of the synthesized dyes are summarized in Table 1.

*2.1. 5-[2-(1,3,3-Trimethyl-1,3-dihydro-indol-2-ylidene)-ethylidene]-5H-quinolin-8-one (**2a**)*

0.5 g (2.86 mmol) of aldehyde **1** and 0.5 g (2.86 mmol) of the Fischer base (1,3,3-trimethyl-2-methyleneindoline) were boiled with reflux in 15 ml of ethanol for 6 h. After cooling, the solution was filtered and evaporated under reduced pressure, and the residue was crystallized from the mixture toluene–hexane (3:1) to give red-brown crystals.

^{1}H NMR ($CDCl_3$): δ 1.76 (*s*, 6H, $C(CH_3)_2$); 3.47 (*s*, 3H, N-CH_3); 6.3 (*d*, 1H, $J = 13$ Hz, CH=); 6.78 (*d*, 1H, $J = 9.5$ Hz, CH_{Ar}); 6.94 (*d*, 1H, $J = 7.8$ Hz, CH_{Ar}); 7.1–7.33 (*m*, 3H); 7.52 (*m*, 1H, CH_{Ar}); 8.08 (*d*, 1H, $J = 9.5$ Hz, CH_{Ar}); 8.2 (*m*, 2H); 8.8 (*m*, 1H, CH_{Ar}).

*2.1.1. 5-[2-(3-Methyl-3H-benzothiazol-2-ylidene)-ethylidene]-5H-quinolin-8-one (**2b**)*

0.26 g (1.5 mmol) of aldehyde **1** and 0.5 g (1.5 mmol) of 2,3-dimethylbenzothiazolium *p*-toluenesulfonate in 15 ml of ethanol were refluxed for 6 h. On cooling, the oily crystalline precipitate was formed. Water (5 ml) was added and the reaction mixture was heated until the precipitate dissolved. After hot filtration, 3 ml of 25% aq. ammonia were added, and the dark-blue precipitate was filtered off and recrystallized from ethanol.

^{1}H NMR (DMSO-d_6): δ 3.89 (*s*, 3H, N-CH_3); 6.63 (*d*, 1H, $J = 9.3$ Hz, CH_{Ar}); 7.05 (*d*, 1H, $J = 13$ Hz, CH=); 7.36–7.68 (*m*, 4H); 7.95 (*d*, 1H, $J = 7$ Hz, CH_{Ar}); 8.11 (*d*, 1H, $J = 13$ Hz, CH=); 8.37 (*d*, 1H, $J = 9.3$ Hz, CH_{Ar}); 8.69 (*m*, 2H, CH_{Ar}).

Table 1
Characteristic substance data for merocyanines **2**, **4**

Dye	Mp (°C)	Yield (%)	Molecular formula	Elemental analysis (%)			
					C	H	N
2a	231–233	48	$C_{22}H_{20}N_2O$	Calcd	80.5	6.1	8.5
				Found	80.1	6.1	8.3
2b	233–236	28	$C_{18}H_{14}N_2OS$	Calcd	71.7	4.4	8.8
				Found	71.4	4.7	8.5
2c	235–238	28	$C_{21}H_{16}N_2O$	Calcd	80.8	5.1	8.9
				Found	80.6	5.0	8.6
4a	155–158	41	$C_{17}H_{13}ClN_2O \cdot 1.5H_2O$	Calcd	63.1	4.9	8.7
				Found	63.2	4.9	9.3
4b	173–175	56	$C_{17}H_{13}ClN_2O \cdot 1.5H_2O$	Calcd	63.1	4.9	8.7
				Found	63.4	5.1	8.7
4c	137–141	57	$C_{22}H_{19}ClN_2O$	Calcd	72.8	5.2	7.7
				Found	72.7	5.2	7.7
4d	237–240	63	$C_{26}H_{20}ClN_2O_4S_2$	Calcd	59.5	4.0	5.3
				Found	59.3	4.1	5.3
4f	282–285	75	$C_{19}H_{13}ClN_2OS$	Calcd	64.7	3.6	7.9
				Found	64.3	3.9	7.8
4e	198–201	70	$C_{22}H_{21}Cl_2N_2O \cdot HCl \cdot 3H_2O$	Calcd	54.0	5.5	5.7
				Found	53.7	5.4	5.7

*2.1.2. 5-[2-(1-Methyl-1H-quinolin-2-ylidene)-ethylidene]-5H-quinolin-8-one (**2c**)*

0.5 g (2.86 mmol) of aldehyde **1**, 0.81 g (2.86 mmol) of 1,2-dimethylquinolinium iodide, and 0.24 g (2.86 mmol) of piperidine were refluxed in 10 ml of pyridine for 6 h. The solvent was evaporated under reduced pressure, the residue was suspended in 25 ml of ethanol, and 3 ml of 25% aq. ammonia was added. The dark-blue precipitate was collected and recrystallized from the mixture methanol–water (2:1).

^{1}H NMR (DMSO-d_6): δ 3.97 (*s*, 3H, N-CH_3); 7.4–7.97 (*m*, 6H); 6.55 (*d*, 1H, *J* = 9 Hz, CH_{Ar}); 6.9 (*d*, 1H, *J* = 14 Hz, CH =); 8.34–8.42 (*m*, 2H); 8.63 (*m*, 2H); 8.95 (*d*, 1H, *J* = 7.8 Hz, CH_{Ar}).

*2.1.3. 5-Chloro-7-[2-(1-Methyl-1H-pyridin-2-ylidene)-ethylidene]-7H-quinolin-8-one (**4a**)*

0.5 g (2.4 mmol) of aldehyde **3**, 0.67 g (2.4 mmol) of 1,2-dimethylpyridinium *p*-toluenesulfonate, and 0.24 g (2.4 mmol) of piperidine in 5 ml of pyridine were refluxed for 6 h. The reaction mixture was concentrated under reduced pressure, the residue was dissolved in ethanol (5 ml) with heating, and then 3 ml of 25% aq. ammonia and 20 ml of water were added. On cooling, the green precipitate was filtered off and recrystallized from the mixture ethanol–water (2:1).

^{1}H NMR (DMSO-d_6): δ 4.06 (*s*, 3H, N-CH_3); 7.21 (*m*, 1H, CH_{Ar}); 7.5–7.72 (*m*, 3H); 7.9–8.18 (*m*, 4H); 8.39 (*m*, 1H); 8.61 (*m*, 1H, CH_{Ar}).

*2.1.4. 5-Chloro-7-[2-(1-Methyl-1H-pyridin-4-ylidene)-ethylidene]-7H-quinolin-8-one (**4b**)*

Synthesized as described for **4a**. Dark green crystals.

^{1}H NMR (DMSO-d_6): δ 3.99 (*s*, 3H, N-CH_3); 7.45–7.51 (*m*, 3H); 7,67 (*d*, 2H, *J* = 6.3 Hz, CH_{Ar}); 8.1 (*m*, 2H); 8.27 (*d*, 2H, *J* = 6.3 Hz, CH_{Ar}); 8.59 (*m*, 1H, CH_{Ar}).

*2.1.5. Spiro(1′,3′,3′-trimethylindolino-2,2′-[2H]-pyrano-(5-chloro[3,2-h]quinoline)) (**4c**)*

0.2 g (0.96 mmol) of aldehyde **3** and 0.18g (0.96 mmol) of the Fischer base were boiled with reflux in 10 ml of pyridine for 5 h. The solvent was evaporated under reduced pressure; the residue was treated with 10 ml of boiling ethanol, filtered off, washed twice with hot EtOH, and dried. White crystals.

^{1}H NMR (DMSO-d_6): δ 1.14 (*s*, 3H, CH_3); 1.27 (*s*, 3H, CH_3); 2.7 (*s*, 3H, N-CH_3); 5.95 (*d*, 1H, *J* = 10 Hz, CH_{Ar}); 6.62–6.69 (*m*, 2H, CH_{Ar}); 6.82 (*t*, 1H, *J* = 7.5 Hz, CH_{Ar}); 7.05–7.17 (*m*, 2H, CH_{Ar}); 7.58 (*m*, 1H, CH_{Ar}); 7.68 (*s*, 1H, CH_{Ar}); 8.42 (*d*, 1H, *J* = 7.5 Hz, CH_{Ar}); 8.8 (*m*, 1H, CH_{Ar}).

2.1.6. 2-[2-(5-Chloro-8-hydroxy-quinolin-7-yl)-vinyl]-3-methylbenzothiazol-3-ium p-*toluenesulfonate (**4d**)*

0.5 g (2.4 mmol) of aldehyde **3** and 0.8 g (2.4 mmol) of 2,3-dimethylbenzothiazolium *p*-toluenesulfonate were boiled with reflux in 15 ml of ethanol for 5 h. The yellow-green precipitate formed upon cooling the reaction mixture was collected and recrystallized from the mixture isopropanol–water (3:1).

^{1}H NMR (DMSO-d_6): δ 2.27 (*s*, 3H, CH_3); 4.36 (*s*, 3H, N-CH_3); 7.1 (*d*, 2H, *J* = 5.4 Hz, *p*-CH_{Ar}); 7.48 (*d*, 2H, *J* = 5.4 Hz, *p*-CH_{Ar}); 7.76–7.84 (*m*, 3H); 8.12–8.21 (*m*, 2H); 8.36–8.51 (*m*, 4H); 9.02 (*m*, 1H, CH_{Ar}).

*2.1.7. 2-[2-(5-Chloro-8-hydroxy-quinolin-7-yl)-vinyl]-1,3,3-trimethyl-3H-indolium chloride hydrochloride trihydrate (**4e**)*

0.1 g (0.48 mmol) of aldehyde **3** and 0.087 g (0.48 mmol) of 1,3,3-trimethylindolinium chloride were refluxed in 5 ml of ethanol for 5 h. The solvent was evaporated under reduced pressure and the residue was crystallized from the mixture isopropanol–water (2:1) containing few drops of conc. HCl to give orange crystals.

^{1}H NMR (DMSO-d_6): δ 1.82 [*s*, 6H, $C(CH_3)_2$]; 4.19 (*s*, 3H, N-CH_3); 5.7 (*br. s.*, 11H); 7.65 (*m*, 3H); 7.94 (*m*, 3H); 8.64 (*m*, 3H); 9.09 (*m*, 1H, CH_{Ar}).

*2.1.8. 5-Cloro-7[2-(3-methyl-3H-benzothiazol-2-ylidene)-ethylidene]-7H-quinolin-8-one (**4f**)*

0.9 g (1.7 mmol) of compound **4d** was dissolved upon heating in 25 ml of the mixture ethanol–water (3:1), and 5 ml of 25% aq. ammonia was added. The dark-green precipitate formed on cooling was filtered off and recrystallized from the mixture methanol–water (2:1).

^{1}H NMR (CF_3CO_2D): δ 4.52 (*s*, 3H, N-CH_3); 7.99–8.66 (*m*, 10H); 9.28 (*m*, 1H, CH_{Ar}); 9.52 (*m*, 1H, CH_{Ar}).

3. Results and discussion

The merocyanine dyes used in this study were prepared starting from 5- and 7-formyl derivatives of 8-hydroxyquinoline **1** and **3**.

The synthesis of merocyanines from 5-formyl-8-hydroxyquinoline **1** was performed via the condensation of aldehyde **1** with the Fischer base or 2,3-dimethylbenzothiazolium *p*-toluenesulfonate in ethanol (**2a** and **2b**, respectively), whereas **2c** was obtained from 1,2-dimethylquinolinuim iodide in pyridine in the presence of the equimolar amount of piperidine (Scheme 1).

Merocyanines were also synthesized from 7-formyl-5-chloro-8-hydroxyquinoline **3** by condensing it with quaternary salts of appropriate heterocycles containing an active methyl group. Reaction in pyridine in the presence of 1 equiv of piperidine yielded dyes **4a–b**. Merocyanine salts **4d–e** were obtained in ethanol (Scheme 2).

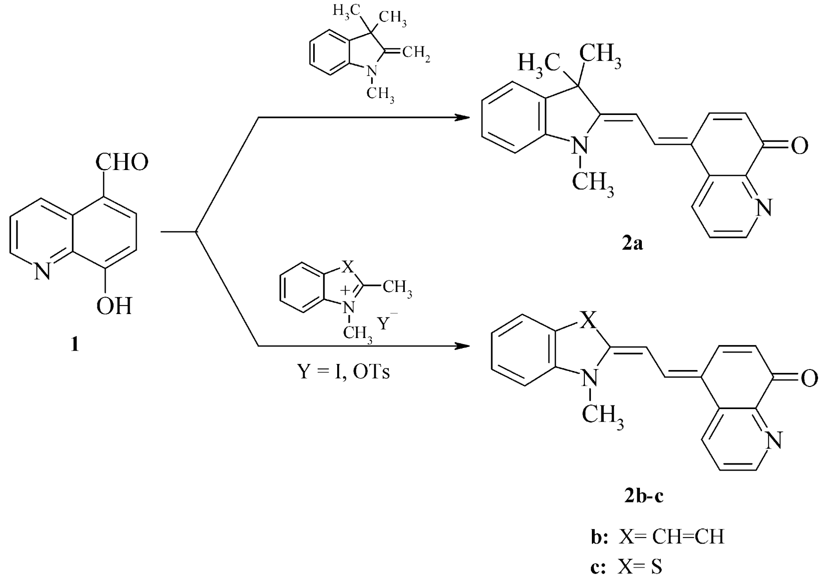
It was found that in pyridine only the traces of **4d** were formed, and the reaction of the starting aldehyde with the Fischer base in pyridine or ethanol led to the formation of spiropyrane **4c**.

Compound **4f** was prepared in a good yield by the treatment of its salt **4d** with aqueous ammonia (Scheme 3).

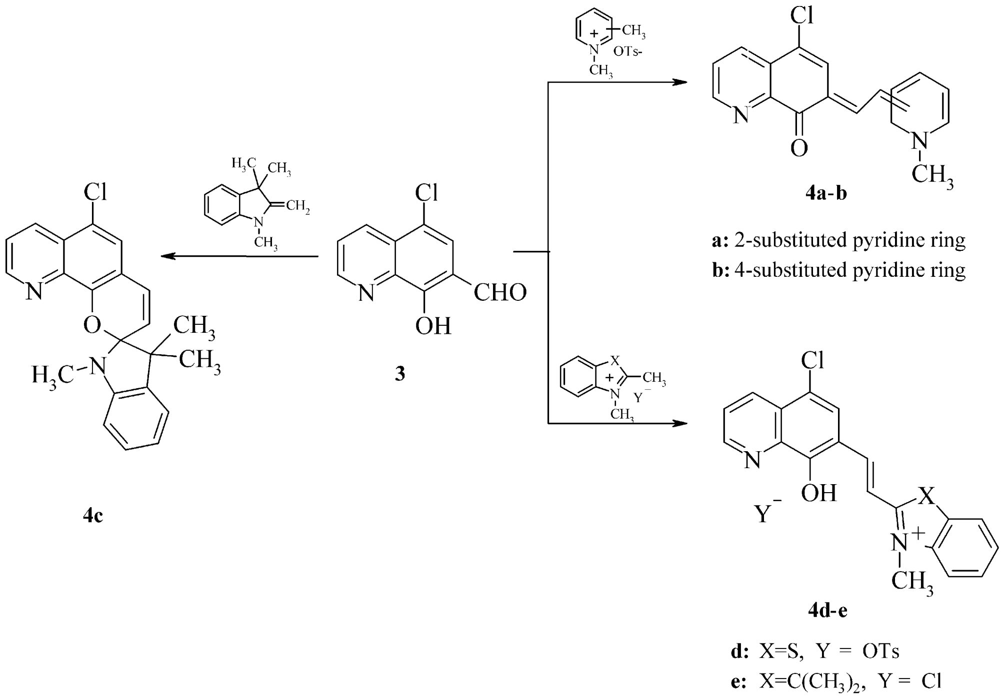
The study of the compounds isolated as salts (**4d–e**) demonstrated that they easily lost the acid residue HY in diluted solutions of polar organic solvents, which resulted in the sharp deepening of their colour (i.e. they exist predominantly in the merocyanine form). The same changes were also characteristic of the salts obtained from the compounds of the 5-formyl-8-hydroxyquinoline series. This important feature allowed the study of metallochromism of investigated compounds in the form of salts, without isolation of the corresponding merocyanines.

The behaviour of compound **4e** in solution is particularly interesting. Addition of bases to its acetonitrile solution results in the immediate colour deepening (associated with the merocyanine form of the compound) which however disappears in a few seconds (due to the formation of a more stable spiropyrane structure).

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



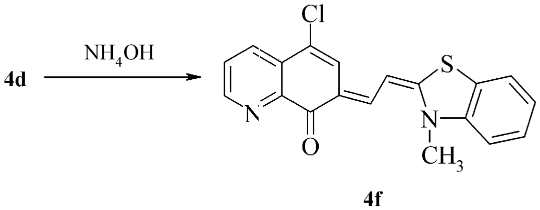
Scheme 1.



a: 2-substituted pyridine ring
b: 4-substituted pyridine ring

d: X=S, Y = OTs
e: X=C(CH_3)$_2$, Y = Cl

Scheme 2.



Scheme 3.

All the prepared dyes demonstrate metallochromic properties upon the interaction with divalent transition metal ions and the maximum effects are achieved at the ligand–metal molar ratio 1:1.

Metallochromic effects of 5-substituted derivatives **2a–c** depend on the basicity of the heterocycle conjugated to the 8-hydroxyquinoline residue (Fig. 1, Table 2). A substantial bathochromic shift and a strong increase in absorption intensity of metallocomplexes are observed upon addition of metal salts to merocyanine **2a** containing the low-basicity indoline ring. In the case of compound **2c** with the medium-basicity end nuclei, complexation with Ni^{2+}, Co^{2+}, Cd^{2+}, and Hg^{2+} cations causes a slight bathochromic shift, whereas a hypsochromic shift is characteristic of the complexes with Cu^{2+} and Zn^{2+} cations. This points to the intermediate nature of the metallocomplexes of this compound. For dye **2b** containing a highly basic quinoline ring, addition of metal salts generally results in a hypsochromic shift (shown as $\Delta\lambda$ with a negative value in Table 2) and a decrease in absorption intensity (Fig. 2, Table 2). It is probable that for compounds with more basic end nuclei, a higher contribution of form B of the merocyanine is observed, while for low-basic 1,3,3-trimethylindoline residue, form A should contribute more to the equilibrium (Scheme 4). Upon complex formation, the electronic density redistribution takes place shifting the equilibrium to form B and resulting in the colour deepening.

It is noteworthy that in some cases addition of divalent copper salts leads to the destruction of the dyes resulting in almost complete decolouration of their solutions.

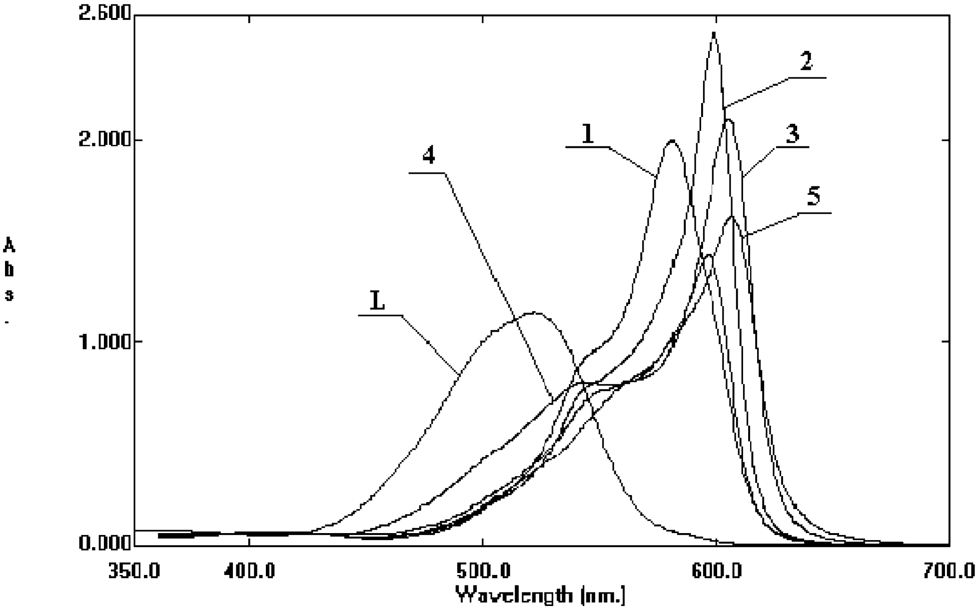


Fig. 1. Absorption spectra of merocyanine **2a** (L) on addition of metal salts in tetrahydrofuran (2 10^{-5} M): (1) **2a** + $Cd(ClO)_4$; (2) **2a** + $Zn(ClO_4)_2$; (3) **2a** + $Ni(ClO_4)_2$; (4) **2a** + $Hg(ClO_4)_2$; (5) **2a** + $Co(ClO_4)_2$.

For all the compounds of the 7-substituted 8-hydroxyquinoline series, addition of metal salts leads to a hypsochromic shift of the dye absorption maximum in the electronic spectrum, mainly accompanied with a decrease in absorption band intensity. Sometimes Cd^{2+}, Hg^{2+} or Cu^{2+} salts cause destruction (or protonation) of the corresponding merocyanines (Fig. 3, Table 3). These

Table 2
UV/VIS spectral data for merocyanines **2** (L), their protonated forms (H^+), and on addition of metal salts

Dye	Solvent	L	H^+		Ni^{2+}		Co^{2+}		Zn^{2+}		Cd^{2+}		Cu^{2+}		Hg^{2+}		Nd^{3+}	
		λ_{max}[a] (ε[b])	λ_{max} (ε)	$\Delta\lambda$[c]	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	CH_3CN	543	446	−97	599	56	602	59	572	29	589	46	571	28	570	28	575	32
		(57,850)	(24,200)		(80,900)		(32,950)		(79,250)		(69,850)		(56,500)		(46,000)		(54,850)	
	THF	521			605		84	601	80	599	78	581	55	D[d]	596	75	584	63
		(57,150)			(10,5100)		(59,050)		(12,5800)		(99,600)				(71,100)		(48,400)	
2b	CH_3CN	570	428	−142	596	26	598	28	563	−7	581	11	541	−29	585	15	571	1
		(61,500)	(20,100)		(62,450)		(58,300)		(48,950)		(55,350)		(37,950)		(60,800)		(38,950)	
	THF	550			605	55	555	5	600	10	586	36	540	−10	589	−39	554	4
		(47,900)			(30,900)		(31,300)		(61,600)		(99,600)		(19,300)		(29,750)		(27,950)	
2c	CH_3CN	611	409	−202	602	−9	576	−35	558	−53	576	−35	537	−74	590	−21	548	−63
		(35,950)	(12,700)		(36,400)		(24,300)		(30,700)		(33,000)		(26,250)		(33,550)		(24,450)	
	THF	576			586	10	587	11	588	12	588	12	D		551	−25	561	−15
		(24,500)			(16,250)		(14,500)		(22,300)		(20,700)				(15,400)		(16,950)	

[a] λ_{max}, absorption maximum, nm.
[b] ε, extinction coefficient (mol^{-1} cm^{-1}).
[c] $\Delta\lambda = \lambda_{max}$ (metal complex or protonated form) $-\lambda_{max}$ (free ligand).
[d] D= dye destruction.

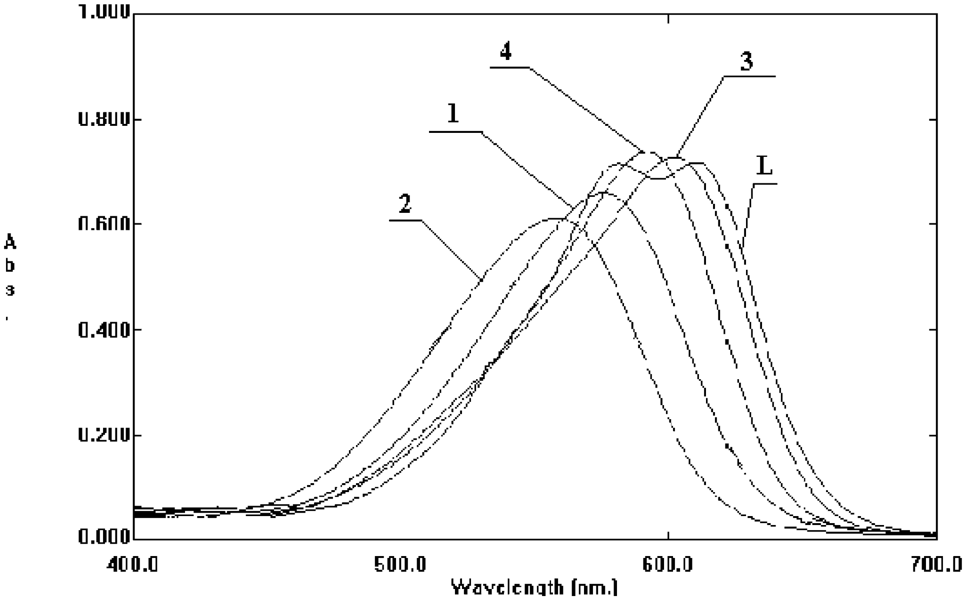
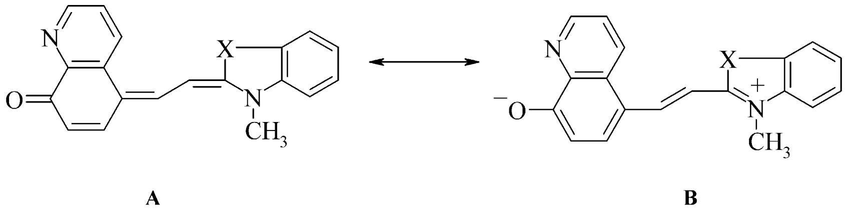


Fig. 2. Absorption spectra of merocyanine **2c** (L) on addition of metal salts in acetonitrile ($2\cdot10^{-5}$ M): (1) **2c** + $Cd(ClO)_4$; (2) **2c** + $Zn(ClO_4)_2$; (3) **2c** + $Ni(ClO_4)_2$; (4) **2c** + $Hg(ClO_4)_2$.



Scheme 4.

changes may be explained by the electronic structure arising in metallocomplexes which is intermediate between the structures of merocyanine and its cationic (protonated) form, and results in the appearance of the intermediately located absorption band. Such a mechanism of the coordination of the dye ligand with a metal cation is in fact similar to the protonation of the oxygen atom of the merocyanine. Addition of metal salts to the colourless spiropyrane **4c** results in the ring-opening to afford the corresponding metallocomplex. It is evidenced by the appearance of the long-wavelength absorption band, which was previously reported also for the analogues of **4c** [15].

Studying the metallochromism of the synthesized compounds, we have found that in less polar solvents, e.g. tetrahydrofuran, metallochromic effects and absorption intensity increase, so we have used this solvent for the experiments on metallofluorochromic effects.

In the case of 5-substituted 8-hydroxyquinolines, addition of Zn^{2+}, Cd^{2+}, and Hg^{2+} salts to their solutions resulted only in slight Stokes shifts and increased emission intensities, and Co^{2+}, Ni^{2+}, Cu^{2+}, and Nd^{3+} cations completely quenched the fluorescence.

For merocyanines based on 7-substituted 8-hydroxyquinoline, addition of Co^{2+}, Ni^{2+}, Cu^{2+}, and Nd^{3+} salts also led to the quenched or slightly

Table 3
UV/VIS spectral data for merocyanines **4** (L), their protonated forms (H^+), and on addition of metal salts

Dye	Solvent	L	H^+		Ni^{2+}		Co^{2+}		Zn^{2+}		Cd^{2+}		Cu^{2+}		Hg^{2+}		Nd^{3+}	
		$^a\lambda_{max}$ (ε^b)	λ_{max} (ε)	$\Delta\lambda^c$	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)	$\Delta\lambda$
4a	CH_3CN	567	330	−237	496	−71	487	−80	480	−87	490	−77	479	−88	489	−87	485	−82
		(52,250)	(33,300)		(20,450)		(18,150)		(20,600)		(12,000)		(17,650)		(19,650)		(17,350)	
	THF	592	453	−139	517	−75	511	−81	510	−82	514	−78	496	−96	505	−87	499	−93
		(33,650)	(14,150)		(18,500)		(15,300)		(18,600)		(21,100)		(11,550)		(18,250)		(16,350)	
4b	CH_3CN	593	334	−259	506	−87	487	−106	492	−101	H^{+d}		492	−101	502	−91	485	−108
		(10,050)	(32,950)		(20,600)		(20,700)		(20,350)				(18,450)		(18,400)		(13,550)	
	THF	623	470	−153	517	−106	501	−122	504	−119	509	−114	486	−125	493	−130	499	−124
		(11,600)	(8800)		(8100)		(6700)		(7350)		(8050)		(14,500)		(7800)		(7100)	
4c	CH_3CN	275	446		561		562		550		D^e		H^+		559		549	
		(36,200)	(20,300)		(29,500)		(25,250)		(24,500)						(30,060)		(26,800)	
4d	CH_3CN	604	425	−179	543	−61	532	−72	526	−78	H^+		527	−77	H^+		527	−77
		(40,900)	(15,400)		(30,000)		(26,900)		(21,750)				(27,900)				(29,700)	
			336	−268														
			(12,150)															
	THF	611	363	−248	566	−45	567	−46	561	−50	566	−45	513	−91	555	−56	547	−64
		(26,700)	(30,200)		(14,250)		(13,450)		(16,200)		(17,250)		(8850)		(14,500)		(13,550)	
			319	−292														
			(33,750)															
4e	CH_3CN	446			576	−121	552	−106	543	−97	H^+		544	−98	D		549	−103
		(24,750)			(36,750)		(23,700)		(23,400)				(27,200)				(23,350)	

[a] λ_{max}, absorption maximum, nm.
[b] ε, extinction coefficient (mol^{-1} cm^{-1}).
[c] $\Delta\lambda = \lambda_{max}$ (metal complex or protonated form) $-\lambda_{max}$ (free ligand).
[d] $H^+ =$ appearance of the absorption band assigned to the protonated form of the corresponding dye.
[e] D = dye destruction.

enhanced fluorescence. However, Zn^{2+}, Cd^{2+}, and Hg^{2+} strongly increased the emission of metallocomplexes as compared to free ligands and moreover gave rise to the relatively large Stokes shifts (Table 4). For example, the fluorescence intensities of the dyes **4a** and **4b** increased ca. 17 and 16 times with Zn^{2+} cations, ca. 19 and 17 times with Hg^{2+}, and ca. 42 and 24 times with Cd^{2+}, respec-

Table 4
Fluorescent properties of merocyanines **4** on addition of metal salts in tetrahydrofurane[a]

Dye	L		Zn^{2+}				Cd^{2+}				Hg^{2+}			
	$\lambda_{em}{}^b$	ΔS^c	λ_{em}	ΔS	$\Delta\lambda_{em}{}^d$	$I/I_0{}^e$	λ_{em}	ΔS	$\Delta\lambda_{em}$	I/I_0	λ_{em}	ΔS	$\Delta\lambda_{em}$	I/I_0
4a	650	59	602	92	48	17.2	611	96	39	42.4	602	97	48	19.3
4b	682	59	626	122	56	16.0	626	117	59	24.5	619	126	63	16.5
4d	643	32	623	62	20	6.1	630	64	13	15.6	626	71	17	5.3

[a] In all cases excitation wavelengths correspond to the maxima in the absorption spectra.
[b] λ_{em}, emission maximum, nm.
[c] ΔS, Stokes shift, nm.
[d] $\Delta\lambda_{em} = \lambda_{em}$ (free ligand) $-\lambda_{em}$ (metal complex).
[e] I and $I_0 =$ relative fluorescence intensities of the metal complex and the free ligand, respectively (I and I_0 were measured at the maximum emission wavelength).

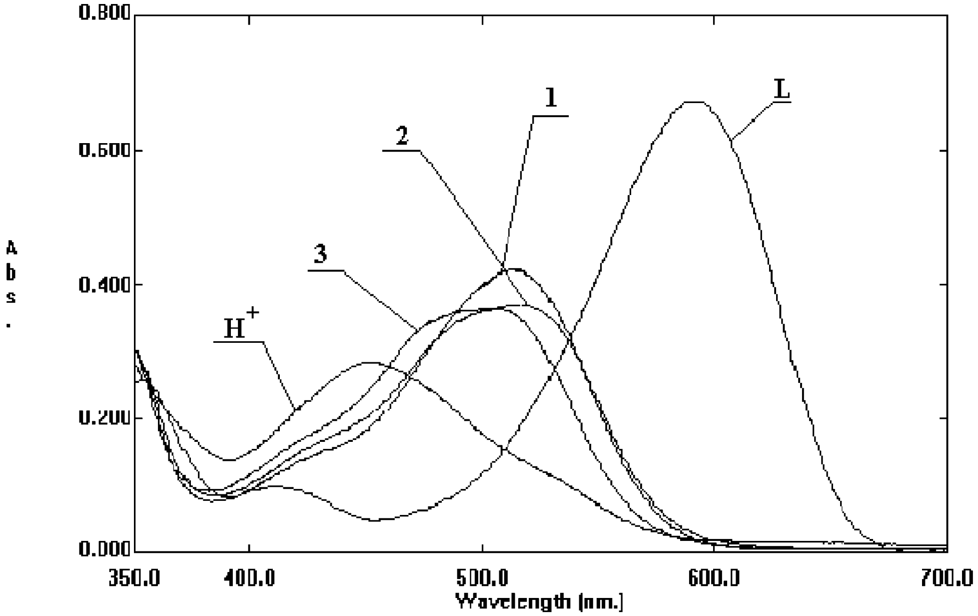


Fig. 3. Absorption spectra of merocyanine **4a** (L), its protonated form (H$^+$), and on addition of metal salts in tetrahydrofuran (2 10^{-5} M): (1) **4a** + Cd(ClO)$_4$; (2) **4a** + Ni(ClO$_4$)$_2$; (3) **4a** + Hg(ClO$_4$)$_2$.

tively. At the same time, the values of ionofluorochromic shift ($\Delta\lambda_{em}$) correlated with those of hypsochromic shift for the corresponding dyes.

The experimental results obtained for spiropyrane **4e** were in accordance with the previously published data [15].

4. Conclusion

Thus, the merocyanine dyes containing the fragment of 8-hydroxyquinoline have been found to display significant metallochromic properties and can be used as indicators for the presence of transition metal cations. However, bathochromic effects are observed only for the derivatives substituted at the C-5 position and containing end nuclei of low basicity. This is in agreement with the results obtained for the structurally analogous compounds of the indoaniline type [1–4]. Remarkable metallofluorochromic effects have been observed upon interaction of Zn^{2+}, Cd^{2+}, and Hg^{2+} cations with the dyes based on 7-substituted 8-hydroxyquinoline.

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