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ScienceDirect

Dyes and Pigments 77 (2008) 369–373

DYES and PIGMENTS

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Substituted xanthylocyanines, Part IV: Trinuclear dyes with a pyronine nucleus

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Received 18 January 2007; received in revised form 14 June 2007; accepted 15 June 2007

Abstract

Trinuclear, dicationic and cation–anionic dyes carrying a pyronine nucleus were synthesized. Whilst their absorption spectra displayed two bands corresponding to the absorption of the cyanine and pyronine chromophores, none of the dyes fluoresced, in contrast to the parent compounds. The spectral evidence suggests a significant, though not perpendicular, twist around the bond between the cyanine and pyronine moieties.

Keywords: Biscyanine dyes; Xanthylium dyes; Chromophore interaction, UV–vis spectra

1. Introduction

Bichromophoric organic dyes have received much attention in diverse application fields related to light energy conversion [1]. The main regularities of their light absorption [2] and luminescence [3] have been established to date in the studies of polymethine (cyanine) dyes with two identical chromophores (biscyanines) [2,3]. Synthetic strategies and research on the energy transfer for the compounds containing two structurally different non-cyanine chromophores (as a rule, typical luminophores) were described in a monograph nearly two decades ago [4]. The fluoro(chromo)phores in these systems were separated by non-conjugated bridge groups. To gain a deeper insight into radiationless processes and generally into the colour theory, it is informative to incorporate two luminophores of different constitutions into a combined dye system. Of special interest is the case when one of the luminophores is represented by a cyanine moiety, a unique light energy converter which affords purposeful and manifold transformations of light depending on dye structure [1]. The present work addresses the synthesis and spectral investigation of luminescent systems of this kind.

2. Results and discussion

The boiling of dialdehyde **1** [5] with 1,2,3,3-tetramethylindolinium and 2,6-diphenyl-4-methylpyrylium salts in acetic anhydride for several hours furnished the trinuclear dyes **2** and **5**. Compounds **3** and **4** were isolated in moderate yield as a result of the short-term heating of dialdehyde **1** with 2-methylbenzothiazolium and 2-methylquinolinium salts; longer heating resulted in decomposition of **3** and **4**. Condensation of compound **1** with appropriate methylene components in acetic anhydride yielded the cation–anionic dyes **6** and **7**, whose cation and anion were coloured (Scheme 1).

The wavelengths of absorption maxima ($\lambda_{\max}$) and the molar extinction coefficients (ε) of the dyes obtained are listed in Table 1. The characteristics of unsubstituted parent dyes, pyronine and the corresponding cyanines are also given for comparison.

The absorption spectra of dyes **2–6** displayed two electronic transitions, one being localized along the polymethine chain and the other occurring in the xanthene moiety

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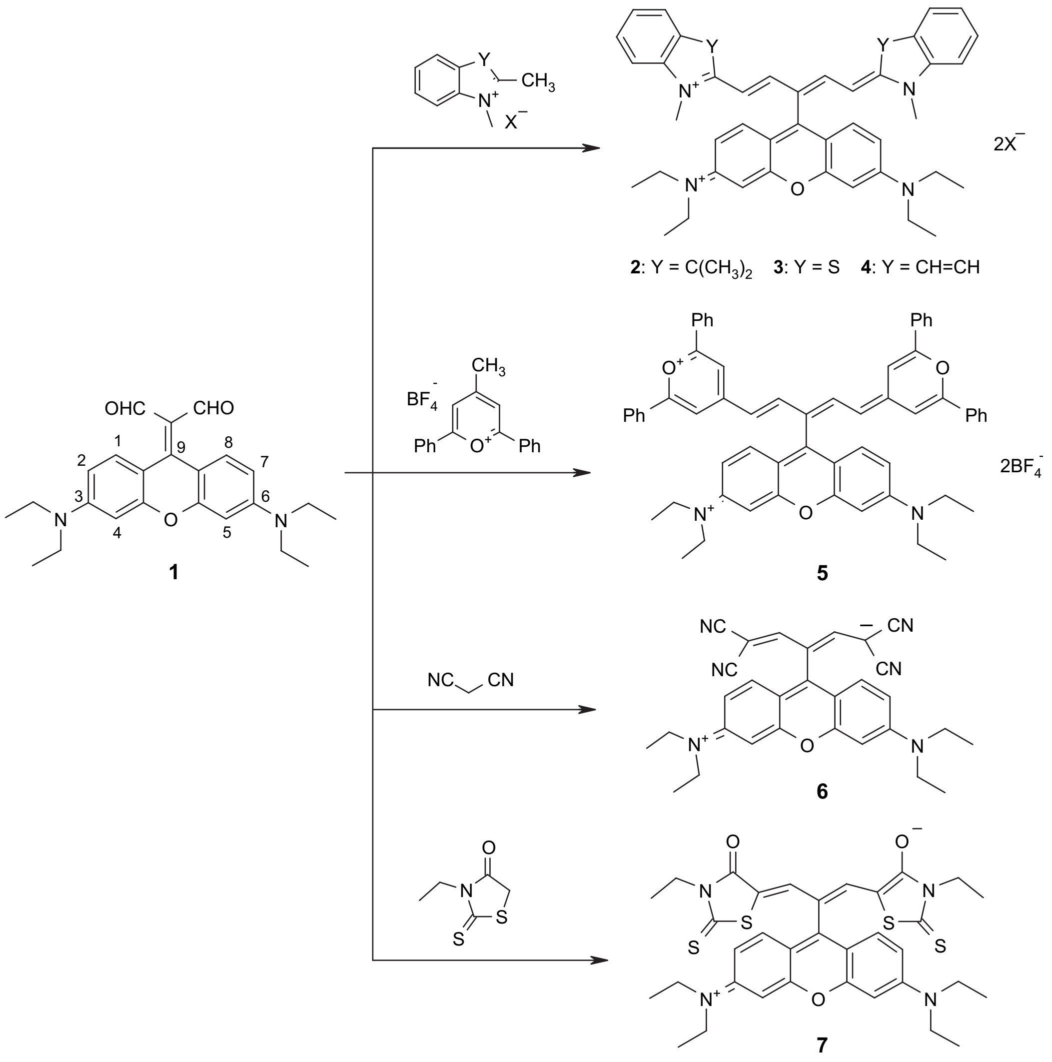
doi:10.1016/j.dyepig.2007.06.007



Scheme 1.

(see Table 1 and Figs. 1 and 2). The cyanine bands were shifted hypsochromically relative to the corresponding absorption of the parent dyes, whereas the pyronine bands demonstrated a bathochromic shift compared to the pyronine B. The two absorption bands of dye **5** were the most separated (Table 1) and their molar extinction coefficients were comparable to those of the parent dyes. In contrast, **2–4** showed pronounced overlapping of these bands, with their intensities

Table 1
Spectral characteristics of dyes **2–7** and the corresponding unsubstituted parent dyes in acetonitrile

Trinuclear dye	λ_{max}, nm ($\varepsilon \times 10^{-4}$ l/(mol cm))	Parent dyes λ_{max}, нм ($\varepsilon \times 10^{-4}$ l/(mol cm))
2	564 (16.3)	550 (10.6)
	627 (18.5)	638 (21.1) [6]
3	561 (16.1)	550 (10.6)
	631 (17.3)	658 (24.9), EtOH [6]
4	561 (13.5)	550 (10.6)
	676 (18.3)	704 (20.5)
5	566 (11.4)	550 (10.6)
	776 (23.5)	792 (22.4)
6	430 (9.4)	441 (9.7), EtOH
	570 (12.3)	550 (10.6)
7	592 (17.0)	613 (11.0), EtOH [7]
		550 (10.6)

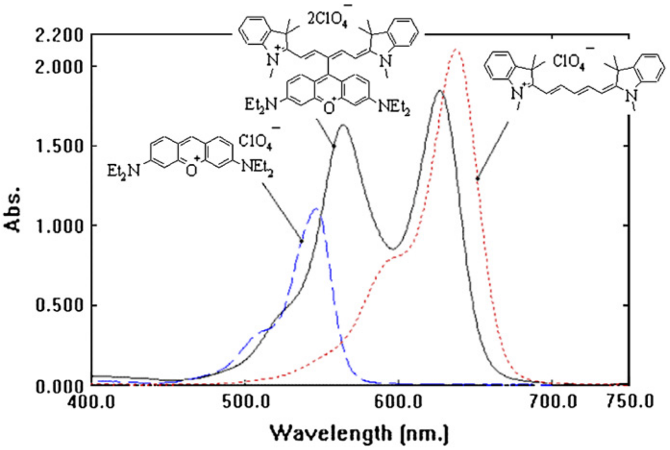


Fig. 1. Absorption spectra of compound **2**, pyronine B, and indodicarbocyanine perchlorate (CH$_3$CN, 1×10^{-5} M).

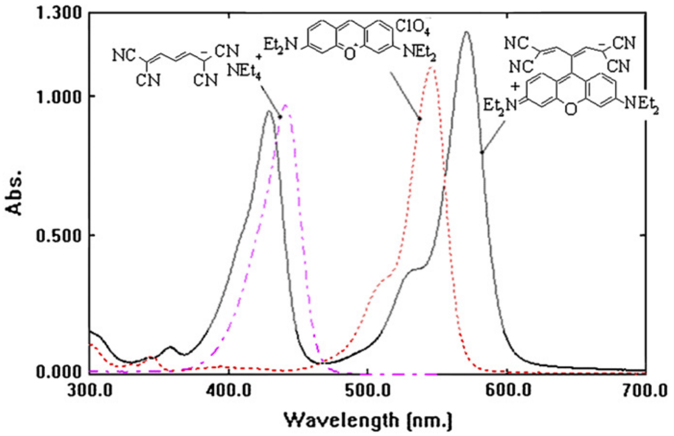
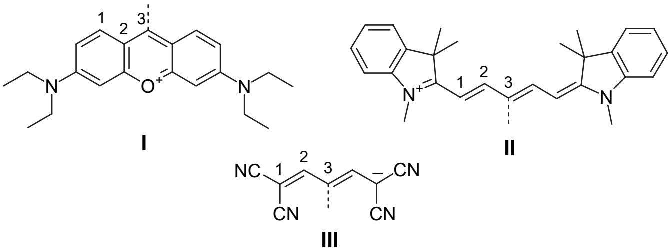


Fig. 2. Absorption spectra of compound **6**, pyronine B, and tetraethylammonium tetracyanopentadien-2,4-ide (CH_3CN, 1×10^{-5} M).

Table 2
Charge distribution in the ground and first excited states of the pyronine and cyanine chromophores



		C_1	C_2	C_3
I	S_0	−0.002	−0.222	0.120
	S_1	−0.115	0.040	−0.216
II	S_0	−0.329	0.101	−0.303
	S_1	−0.070	−0.213	0.019
III	S_0	−0.214	0.090	−0.374
	S_1	−0.022	−0.256	0.019

redistributed in such a way that the polymethine bands are weakened and the pyronine bands markedly enhanced in comparison with the corresponding parent dyes. The absorption bands for dye **7** are superposed, which makes them more intense than the parent dyes.

Although **2** and **3** bear the pyronine, indodicarbocyanine and thiadicarbocyanine moieties, which are known fluorescent systems [6], almost no fluorescence was detectable on excitation within either absorption band. The other dyes synthesized also proved to be non-fluorescent. One can, therefore, conclude that although steric hindrances cause the pyronine and cyanine chromophores to be located in different planes, the twisting angle does not amount to 90°. Were the planes mutually perpendicular thus completely ruling out a π-conjugation between the chromophores, the dyes would be expected to fluoresce.

Quantum chemical calculations of the charge distribution in the chromophores under study were calculated using the semi-empirical AM1 method with a standard parameter set [8] to the restricted Hartree–Fock approximation. The calculations took into account the interactions of the excited configurations, which were provided by all possible electronic transitions from five LUMO to five HOMO. The molecular geometry was optimized by the Polak–Ribiere algorithm until the root mean square energy gradient was 0.001 kcal/(Å mol).

Starting from the calculated ground-state and excited-state atomic charges in the parent dye ions (see Table 2), the mutual electronic influence of the chromophores in the resulting dyes was analyzed. First, we compared the partial charges on the atoms through which the chromophores bind to each other in dyes **2**–**7**. As seen from Table 2, the pyronine chromophore carries a considerable positive charge at position 9 (on the C_3 atom) in the ground state (S_0). On the contrary, a negative charge is localized at the *meso* position of the cyanine chromophore in the ground state of both cationic (**2**–**5**) and anionic (**6** and **7**) dyes. On electronic excitation, the electron density of pyronine is transferred to a large extent to position 9 from neighbouring atoms, which results in the negatively charged C_3 atom in the first singlet excited state (S_1). The *meso* position of the cyanine chromophores is also involved in the excitation-induced charge redistribution: it acquires a positive charge both in cations and anions (see Table 2).

The spectral behaviour of dyes **2**–**7** was treated in terms of the Foerster–Dewar–Knott rule [9–11]. Thus, the pyronine moiety that binds to the cyanine chromophore through the positively charged C_3 atom appears as an electron-acceptor residue; it should, therefore, hypsochromically shift the cyanine bands of dyes **2**–**7** relative to those of parent dyes, which is really the case. On the other hand, if this shift was attributable to the electronic effect of the pyronine substituent, one might expect, in accordance with the same rule, that the pyronine band position would in turn be influenced by the cyanine substituent. Carrying the negative charge at the *meso* position, the cyanine moieties (especially anionic ones) introduced at position 9 of the pyronine chromophore act as electron-donor substituents and hence should cause the hypsochromic shift of the pyronine band. However, this assumption is at variance with the experimental data listed in Table 1 and we have to infer that the approach of absorption bands of parent chromophores (as with compounds **2**–**5** and **7**) or their moving apart (as with compound **6**) is not dictated by the electronic effects of substituents. It is more likely that the resulting spectral peculiarities are accounted for by the interaction between the pyronine and cyanine chromophores because it can dominate over substituent effects. If the chromophores are not strictly perpendicular to each other, as is the case in the molecules concerned, the interaction can occur both through space (by the inductive resonance mechanism) and through the system of conjugated bonds (by the exchange resonance mechanism) [12].

The chromophore interaction is additionally evidenced by the fact that none of the dyes displayed the strong fluorescence that is typical of pyronine. The quenching of the pyronine fluorescence cannot be explained merely by intramolecular energy transfer from one moiety to another because it was observed not only for dyes **2**–**5** and **7**, with their cyanine chromophores absorbing light at longer wavelengths than the pyronine chromophore, but also for dye **6**, which contains interchanged positions of the absorption bands (cf. Figs. 1 and 2). Moreover, the quenching of the fluorescent cyanine chromophores [6] in dyes **2** and **3** is another indication of such chromophore interaction.

3. Experimental

Electronic absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100 in acetonitrile. ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz.

*3.1. 1,3,3-Trimethyl-2-[3-(3,6-bis(diethylamino)-xanthylium-9-yl)-5-(1,3,3-trimethyl-1,2-dihydro-3*H*-indol-2-ylidene)-1,3-pentadienyl]-3*H*-indolium ditetrafluoroborate (**2**)*

Dialdehyde **1** (0.196 g, 0.5 mmol) and 1,2,3,3-tetramethylindolium tetrafluoroborate (0.3 g, 1.2 mmol) in acetic anhydride (3 ml) were boiled for 2 h. On cooling, the reaction mixture was diluted with water (20 ml) containing ammonium tetrafluoroborate (0.5 g) and left to stand at room temperature for several hours. The product was filtered off and recrystallized from isopropanol. Yield: 0.15 g (34%); m.p.: 265 °C.

^{1}H NMR ($CDCl_3$/TMS) δ: 1.34 (12H, t, CH_3), 1.77 (12H, s, $C(CH_3)_2$), 3.35 (6H, s, NCH_3), 3.62 (8H, q, NCH_2), 5.28 (2H, d, $J = 14.4$ Hz, α-CH), 6.94 (4H, br s, $H^4 + H^5 + 2$ArH), 7.1 (2H, d, $J = 7.5$ Hz, ArH), 7.2–7.4 (6H, m, $H^2 + H^7 + 4$ArH), 7.55 (2H, d, $J = 9.9$ Hz, $H^1 + H^8$), 8.59 (2H, d, $J = 14.4$ Hz, β-CH). Anal. Calcd ($C_{48}H_{56}B_2F_8N_4O$): C, 65.6; H, 6.4; N, 6.4; found: C, 65.5; H, 6.4; N, 6.5.

*3.2. 3-Methyl-2-[3-(3,6-bis(diethylamino)xanthylium-9-yl)-5-(3-methylbenzothiazol-2-ylidene)-1,3-pentadienyl]benzothiazolium diperchlorate (**3**)*

Dialdehyde **1** (0.392 g, 1 mmol) and 2,3-dimethylbenzothiazolium perchlorate (0.738 g, 3 mmol) in acetic anhydride (3 ml) were boiled for a short time. The reaction mixture was left for a night. The resulting crystals were filtered off and washed with acetic anhydride. Yield: 0.09 g (11%); m.p.: 272–273 °C.

^{1}H NMR (DMF-d_7/TMS) δ: 1.34 (12H, t, $4CH_3$), 3.69 (6H, s, $2NCH_3$), 3.82 (8H, q, $4NCH_2$), 6.16 (2H, d, $J = 13.8$ Hz, 2α-CH), 7.07 (2H, s, $H^4 + H^5$), 7.29 (2H, d, $J = 9.6$ Hz, $H^2 + H^7$), 7.52 (2H, t, $J = 7.5$ Hz, $2H^{55'}$), 7.63 (2H, t, $J = 7.5$ Hz, $2H^{65'}$), 7.72–7.76 (4H, m, $H^1 + H^8 + 2H^{75'}$), 8.13 (2H, d, $J = 8.1$ Hz, $2H^{45'}$), 8.51 (2H, d, $J = 14.4$ Hz, β-CH). Anal. Calcd ($C_{42}H_{44}Cl_2N_4O_9S_2$): C, 57.1; H, 5.0; N, 6.3; Cl, 8.0; found: C, 57.0; H, 5.1; N, 6.3; Cl, 8.1.

*3.3. 1-Methyl-2-[3-(3,6-bis(diethylamino)xanthylium-9-yl)-5-(1-methyl-1H-quinolin-2-ylidene)-1,3-pentadienyl]quinolinium diperchlorate (**4**)*

Dialdehyde **1** (0.392 g, 1 mmol) and 1,2-dimethylquinolinium perchlorate (0.774 g, 3 mmol) in acetic anhydride (5 ml) were heated for 16 min (the bath temperature is 165 °C). The reaction mixture was left for a night. The resulting crystals were filtered off and washed with acetic acid. Yield: 0.11 g (13%); m.p.: 266–267 °C.

^{1}H NMR (DMSO-d_6/TMS) δ: 1.25 (12H, t, $4CH_3$), 3.60 (6H, s, $2NCH_3$), 3.70 (8H, q, $4NCH_2$), 5.65 (2H, d, $J = 15.3$ Hz, 2 α-CH), 7.02 (2H, s, $H^4 + H^5$), 7.16 (2H, d, $J = 9.3$ Hz, $H^2 + H^7$), 7.50–7.60 (4H, m, $H^1 + H^8 + 2H^{65'}$), 7.78 (2H, t, $J = 8.1$ Hz, $2H^{75'}$), 7.85–7.93 (4H, m, $2H^{55'} + 2H^{85'}$), 8.08 (2H, d, $J = 9.3$ Hz, $2H^{35'}$), 8.24 (2H, d, $J = 9.3$ Hz, $2H^{45'}$), 8.58 (2H, d, $J = 14.1$ Hz, β-CH). Anal. Calcd ($C_{46}H_{48}Cl_2N_4O_9$): C, 63.4; H, 5.6; N, 6.4; Cl, 8.1; found: C, 63.5; H, 5.5; N, 6.3; Cl, 8.0.

*3.4. 2,6-Diphenyl-4-[3-(3,6-bis(diethylamino)-xanthylium-9-yl)-5-(2,6-diphenylpyran-4-ylidene)-1,3-pentadienyl]pyrylium ditetrafluoroborate (**5**)*

It was obtained similarly to compound **2** and recrystallized from acetic acid. Yield: 0.1 g (20%); m.p.: 270–271 °C.

^{1}H NMR (DMSO-d_6/TMS) δ: 1.24 (12H, t, CH_3), 3.69 (8H, q, NCH_2), 5.95 (2H, d, α-CH), 7.08 (2H, s, $H^4 + H^5$), 7.22 (2H, d, $H^2 + H^7$), 7.4–8.1 (26H, m), 8.72 (2H, d, β-CH). Anal. Calcd ($C_{60}H_{54}B_2F_8N_2O_3$): C, 70.3; H, 5.3; N, 2.7; found: C, 70.5; H, 5.3; N, 2.7.

*3.5. 1,1,5,5-Tetracyano-3-[3,6-bis(diethylamino)-xanthylio-9-yl]pentadien-2,4-ide (**6**)*

Dialdehyde **1** (0.196 g, 0.5 mmol) and malononitrile (0.1 g, 1.5 mmol) in acetic anhydride (3 ml) were boiled for 5 min. On cooling, the reaction mixture was diluted with water (20 ml) and left to stand for several hours. The product was filtered off and recrystallized from acetic acid. Yield: 0.1 g (41%); m.p.: >300 °C.

^{1}H NMR (DMSO-d_6/TMS) δ: 1.21 (12H, t, CH_3), 3.63 (8H, q, NCH_2), 6.91 (2H, s, $H^4 + H^5$), 7.17 (2H, d, $J = 9.6$ Hz, $H^2 + H^7$), 7.45 (2H, d, $J = 9.6$ Hz, $H^1 + H^8$), 7.74 (2H, s, CH). Anal. Calcd ($C_{30}H_{28}N_6O$): C, 73.8; H, 5.8; N, 17.2; found: C, 73.7; H, 5.8; N, 17.3.

3.6. 3-Ethyl-5-[2-(3,6-bis(diethylamino)xanthylio-9-yl)-3-(3-ethyl-2-thioxo-4-oxothiazolidin-5-ylidene)-propenyl]-2-thioxo-2,3-dihydrothiazol-4-olate (7)

A mixture of dialdehyde **1** (0.196 g, 0.5 mmol), *N*-ethylrhodanine (0.2 g, 1.25 mmol), acetic anhydride (3 ml), and triethylamine (1 drop) was boiled for 3 min. The product precipitating from the hot solution was filtered off and recrystallized from DMF. Yield: 0.18 g (53%); m.p.: >300 °C.

^{1}H NMR (DMSO-d_6/TMS) δ: 1.04 (6H, t, CH_3), 1.24 (12H, t, CH_3), 3.65 (8H, q, NCH_2), 3.91 (4H, q, NCH_2), 7.03 (2H, s, $H^4 + H^5$), 7.14 (2H, d, $J = 9.3$ Hz, $H^2 + H^7$), 7.45 (2H, d, $J = 9.3$ Hz, $H^1 + H^8$), 7.82 (2H, s, CH). Anal. Calcd ($C_{34}H_{38}N_4O_3S_4$): C, 60.2; H, 5.6; N, 8.3; found: C, 60.1; H, 5.6; N, 8.2.

4. Conclusions

The trinuclear, dicationic and cation–anionic dyes displayed two bands corresponding to absorption of the cyanine and pyronine chromophores. None of the dyes fluoresced, in contrast to the parent compounds; spectral evidence suggests a significant, though not perpendicular, twist around the bond between the cyanine and pyronine moieties.

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