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Series of polymethine dyes derived from 2,2-difluoro-1,3,2-(2*H*)-dioxaborine of 3-acetyl-7-diethylamino-4-hydroxycoumarin

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Abstract

A series of symmetrical and unsymmetrical dyes with different polymethine chain lengths based on the 2,2-difluoro-1,3,2-(2*H*)-dioxaborine of 3-aceto-4-hydroxy-7-diethylaminocoumarin were obtained. It was shown that anionic symmetrical dyes are deeply coloured and highly intense dyes with good fluorescence properties and photostability.

Spectral characteristics of the unsymmetrical dyes can be modified in a wide range by changing the electron-donating properties of the second terminal nucleus.

Keywords: Polymethine dyes; 2,2-Difluoro-1,3,2-(2*H*)-dioxaborine; UV/vis spectroscopy; Fluorescence spectroscopy; 4-Hydroxycoumarin

1. Introduction

The polymethine dyes based on boron fluoride complexes of β-diketones were first described in 1984 [1] (type A, Fig. 1). Although it was already clear from that report that the obtained compounds were deeply coloured and highly intense dyes with good fluorescence properties, only recently an increasing interest has been attracted by these complexes, due to the discovery of their non-linear optical (NLO) properties [2–7]. Such properties are typical for organic chromophores of general structure D–π–A, where D and A are electron donor and acceptor, respectively, and π is a conjugated pathway (phenyl, polyene, stilbene, etc.) with large dipole moment and first optical hyperpolarizability [8]. These compounds may be suitable in construction of non-linear optical devices, such as optoelectronic switches [9–11] and photorefractive polymers [12–16].

For dyes of types C and D [17–20] carbonyl group at C-5 position of 1,3,2-(2*H*)-dioxaborine cycle rigidify these molecules, which resulted in increase of absorption intensity and quantum yield of the fluorescence.

However, the general disadvantage of this class of dyes is their low stability, especially hydrolytic. It can be increased by the introduction of electron-donating substituent conjugated with dioxaborine cycle (type B, R = OCH_3) [21], which leads to the delocalization of the positive charge.

One could expect the introduction of dialkylamino group into the coumarin fragment of the molecule to cause considerable spectral effects (compounds of type E, Fig. 2). Dialkylamino group conjugated with chromophore system increases its branching. On the other hand, the resonance stabilization of positive charge by the contribution of mesomeric structures of types E2 and E3 should result in the increase of hydrolytic stability. Moreover, dialkylamino group as a polarizing substituent significantly extends the possibility of regulating the dipole moments of corresponding donor–acceptor systems.

The aim of this work was thus to prepare symmetrical dyes and systematic series of unsymmetrical dyes based on the dioxaborine complex of 3-aceto-7-diethylamino-4-hydroxycoumarin containing the terminal groups of different basicities and to investigate some of their physico-chemical properties. Necessary for the comparison dyes based on 7-unsubstituted

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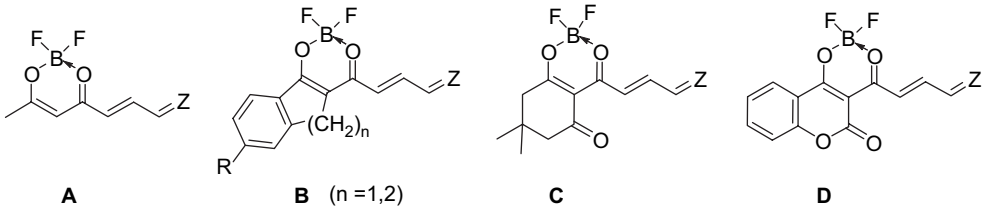
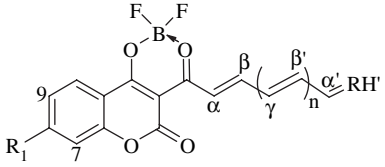


Fig. 1.

coumarin core were synthesised by modified protocol [19] or obtained for the first time.

2. Experimental

Electronic absorption spectra were recorded on Shimadzu UV-3100 spectrophotometer in acetonitrile and chloroform. Proton NMR spectra were obtained with Varian VXR-300 instrument (300 MHz) at 25 °C using tetramethylsilane as an internal standard. Fluorescent spectra were recorded on Varian Cary Eclipse fluorescent spectrophotometer and are not corrected. The relative quantum yields of fluorescence (φ) were determined using Rhodamine 6G ($\varphi = 0.95$, EtOH) [22] and indodicarbocyanine iodide ($\varphi = 0.25$, EtOH) [23] as the references.



2.1. 3-Acetyl-7-(diethylamino)-4-hydroxy-(2H)-chromen-2-one (3)

A mixture of coumarin **2** [24] (23.3 g, 0.1 mol), acetic anhydride (18.9 ml, 0.2 mol) and pyridine (40 ml) was refluxed for 2 h. The solution was cooled and water (40 ml) was added. The product was filtered off and washed with *i*-PrOH. Yield 22.3 g (81%). M.p. 142 °C. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J_{H,H} = 6.9$ Hz, 6H, CH_3), 2.75 (s, 3H, CH_3), 3.48 (q, $^3J_{H,H} = 6.9$ Hz, 4H, NCH_2), 6.43 (d, $^4J_{H,H} = 2.4$ Hz, 1H, 8-H), 6.65 (dd, $^3J_{H,H} = 9.0$ Hz, $^4J_{H,H} = 2.4$ Hz, 1H, 6-H), 7.84 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 5-H). Anal. calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.40; H, 6.16; N, 5.06.

2.2. 2,2-Difluoro-4-methyl-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (4)

A mixture of coumarin **1** (8.1 g, 0.05 mol), BF_3-etherate (7.9 g, 0.056 mol) and acetic anhydride (15 ml) was refluxed for 4–5 min. The mixture was cooled and allowed to stand for 4 h to crystallize. The precipitate was filtered off and washed with Et_2O. The obtained complex was used without further purification. Yield 10 g (80%). M.p. 198–200 °C (lit. 199–200°C [20]). ^{1}H NMR ($CDCl_3$): δ 3.00 (s, 3H, CH_3), 7.39 (d, $^3J_{H,H} = 8.0$ Hz, 1H, 7-H), 7.46 (t, $^3J_{H,H} = 8.0$ Hz, 1H, 9-H), 7.88 (t, $^3J_{H,H} = 8.0$ Hz, 1H, 8-H), 8.24 (d, $^3J_{H,H} = 8.0$ Hz, 1H, 10-H). λ_{max} 342 nm (MeCN). Anal. calcd. for $C_{11}H_7BF_2O_4$: C, 52.43; H, 2.80. Found: C, 52.40; H, 2.78.

2.3. 8-(Diethylamino)-2,2-difluoro-4-methyl-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (5)

Compound **3** (8 g, 29 mmol) was dissolved with heating in acetic anhydride (5.9 g, 58 mmol) and minimal quantity of dry acetonitrile. To the obtained solution BF_3-etherate (4.96 g, 35 mmol) was added and refluxed for 5 min. The mixture was cooled and allowed to stand for 12 h. The precipitate was filtered off and washed with acetonitrile. Yield 8.89 g (94%). M.p. 209 °C. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, $^3J_{H,H} = 7.2$ Hz, 6H, CH_3), 2.84 (s, 3H, CH_3), 3.50 (q, $^3J_{H,H} = 7.2$ Hz, 4H, NCH_2), 6.37 (d, $^4J_{H,H} = 2.4$ Hz, 1H, 8-H), 6.65 (dd, $^3J_{H,H} = 9.3$ Hz, $^4J_{H,H} = 2.4$ Hz, 1H, 9-H), 7.93 (d, $^3J_{H,H} = 9.3$ Hz, 1H, 10-H). λ_{max} 427 nm (MeCN). Anal. calcd. for $C_{15}H_{16}BF_2NO_4$: C, 55.76; H, 4.99; N, 4.34. Found: C, 55.78; H, 5.03; N, 4.33.

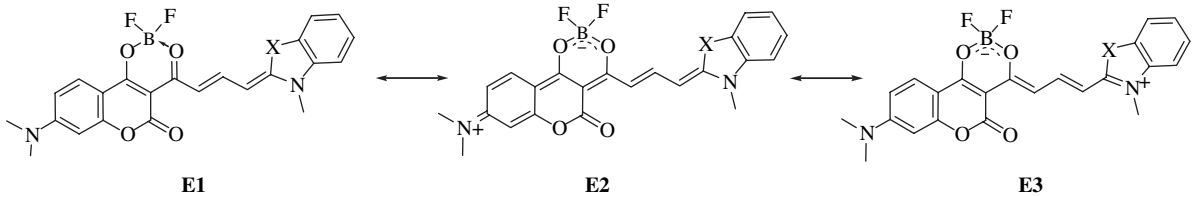


Fig. 2.

*2.4. 2,2-Difluoro-5-oxo-4-(2-(phenylamino)vinyl)-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**6**)*

A mixture of **4** (2.5 g, 10 mmol) and ethylisoformanilide (3 g, 20 mmol) was fused at 120 °C for 2 h. The melt was cooled and triturated with chloroform. The resulting solid was collected by filtration and washed with chloroform. Yield 3.1 g (88%). M.p. 284–286 °C. ^{1}H NMR (DMSO-d_6): δ 7.32 (m, 1H, 7-H), 7.50 (m, 7H, 9-H, PhH, α-H), 7.86 (t, $^3J_{H,H} = 8.1$ Hz, 1H, 8-H), 8.05 (d, $^3J_{H,H} = 8.1$ Hz, 1H, 10-H), 8.98 (t, $^3J_{H,H} = 12.3$ Hz, 1H, β-H), 12.55 (d, $^3J_{H,H} = 12.3$ Hz, 1H, NH). λ_{max} 416 nm (MeCN). Anal. calcd. for $C_{18}H_{12}BF_2NO_4$: C, 60.88; H, 3.41; N, 3.94. Found: C, 60.75; H, 3.36; N, 3.98.

*2.5. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-(2-(phenylamino)vinyl)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**7**)*

Compound **7** was prepared from **5** as described above for **6**. Yield 98%. M.p. 263–265 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 1.14 (t, $^3J_{H,H} = 5.6$ Hz, 6H, CH_3), 3.48 (q, $^3J_{H,H} = 5.6$ Hz, 4H, NCH_2), 6.5 (s, 1H, 7-H), 6.81 (d, $^3J_{H,H} = 7.6$ Hz, 1H, 9-H), 7.23 (m, 1H, PhH), 7.33 (d, $^3J_{H,H} = 9.2$ Hz, 1H, α-H), 7.43 (m, 4H, PhH), 7.73 (d, $^3J_{H,H} = 7.6$ Hz, 1H, 10-H), 8.77 (dd, $^3J_{H,H} = 9.2$, 11.2 Hz, 1H, β-H), 12.00 (d, $^3J_{H,H} = 11.2$ Hz, 1H, NH). λ_{max} 480 nm (MeCN). Anal. calcd. for $C_{24}H_{21}BF_2N_2O_4$: C, 61.99; H, 4.97; N, 6.57. Found: C, 61.89; H, 4.91; N, 6.64.

*2.6. 2,2-Difluoro-5-oxo-(5H)-4-(4-(N-phenylacetamido)-1,3-butadienyl)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**8**)*

A mixture of **4** (2.5 g, 10 mmol) and malonaldehyde dianil hydrochloride (2.59 g, 10 mmol) in acetic anhydride (8–10 ml) was refluxed for 5–10 min. The mixture was cooled and allowed to crystallize for 12 h. The precipitate was filtered off, washed with glacial acetic acid and diethyl ether. Yield 2.78 g (66%). M.p. 274–275 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 2.03 (s, 3H, CH_3), 5.49 (t, $^3J_{H,H} = 12.4$ Hz, 1H, β′-H), 7.26 (d, $^3J_{H,H} = 8.2$ Hz, 1H, 7-H), 7.48 (d, $^3J_{H,H} = 13.2$ Hz, 1H, α-H), 7.54 (m, 3H, PhH, 9-H), 7.68 (m, 3H, PhH), 7.89 (t, $^3J_{H,H} = 8.2$ Hz, 1H, 8-H), 8.08 (d, $^3J_{H,H} = 8.2$ Hz, 1H, 10-H) 8.63 (t, $^3J_{H,H} = 12.0$ Hz, 1H, β-H), 8.85 (d, $^3J_{H,H} = 13.4$ Hz, 1H, α′-H). λ_{max} 477 nm (MeCN). Anal. calcd. for $C_{22}H_{16}BF_2NO_5$: C, 62.44; H, 3.81; N, 3.31. Found: C, 62.37; H, 3.74; N, 3.37.

*2.7. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-(4-(N-phenylacetamido)-1,3-butadienyl)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**9**)*

Prepared from **5** by the procedure described for **8**. Yield 78%. M.p. 295–297 °C. ^{1}H NMR (DMSO-d_6): δ 1.17 (t, 6H, CH_3), 2.09 (s, 3H, CH_3), 3.54 (q, 4H, NCH_2), 5.35 (t, $^3J_{H,H} = 12$ Hz, 1H, β′-H), 6.56 (s, 1H, 7-H), 6.86 (d, $^3J_{H,H} = 9.6$ Hz, 1H, 9-H), 7.4 (m, 3H, PhH, α-H), 7.61 (m, 3H, PhH), 7.79 (d, $^3J_{H,H} = 9.3$ Hz, 1H, 10-H), 8.23 (dd, $^3J_{H,H} = 12.3$, 13.2 Hz, 1H, β-H), 8.6 (d, $^3J_{H,H} = 13.5$ Hz, 1H, α′-H). λ_{max} 519 nm (MeCN). Anal. calcd. for $C_{26}H_{25}BF_2N_2O_5$: C, 63.18; H, 5.10; N, 5.67. Found: C, 63.15; H, 5.06; N, 5.69.

*2.8. Dyes **10–13***

A mixture of **4** or **5** (1 mmol), the corresponding hemicyanine **6–9** (1 mmol) and the corresponding tertiary amine (2.2 mmol) in acetic anhydride (5–8 ml) was stirred at room temperature for 12 h. The product was filtered off, washed with glacial acetic acid and diethyl ether.

*2.8.1. Triethylammonium 2,2-difluoro-4-[3-(2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1-propenyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**10**)*

Yield 71%. M.p. 280–282 °C (MeCN; lit. 285–286 °C [19]). ^{1}H NMR (DMSO-d_6): δ 1.18 (t, $^3J_{H,H} = 7.3$ Hz, 9H, CH_3), 3.11 (m, 6H, NCH_2), 7.76 (m, 6H, 7-H, 9-H, α-H), 7.84 (t, $^3J_{H,H} = 7.9$ Hz, 2H, 8-H), 8.04 (d, $^3J_{H,H} = 8.1$ Hz, 2H, 10-H), 8.86 (t, $^3J_{H,H} = 13.4$ Hz, 1H, β-H). Anal. calcd. for $C_{29}H_{27}B_2F_4NO_8$: C, 56.62; H, 4.42; N, 2.28. Found: C, 56.49; H, 4.36; N, 2.40.

*2.8.2. Tributylammonium 2,2-difluoro-4-[3-(8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1-propenyl]-5-oxo-(5H)-8-diethylamino)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**11**)*

Yield 79%. M.p. 276–278 °C. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, $^3J_{H,H} = 7.3$ Hz, 9H, CH_3), 1.21 (m, 12H, CH_3), 1.44 (m, 6H, CH_2), 1.8 (m, 6H, CH_2), 3.29 (m, 6H, NCH_2), 3.4 (m, 8H, NCH_2), 6.35 (s, 2H, 7-H), 6.55 (d, $^3J_{H,H} = 9$ Hz, 2H, 9-H), 7.5 (d, $^3J_{H,H} = 13.2$ Hz, 2H, α-H), 7.83 (d, $^3J_{H,H} = 9$ Hz, 2H, 10-H), 8.90 (t, $^3J_{H,H} = 13.8$ Hz, 1H, β-H). Anal. calcd. for $C_{43}H_{57}B_2F_4N_3O_8$: C, 61.37; H, 6.83; N, 4.99. Found: C, 61.29; H, 6.80; N, 5.11.

*2.8.3. Triethylammonium 2,2-difluoro-4-[5-(2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1,3-pentadienyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**12**)*

Yield 47%. M.p. 284–286 °C (MeCN). ^{1}H NMR (DMSO-d_6): δ 1.16 (t, $^3J_{H,H} = 7.3$ Hz, 9H, CH_3), 3.08 (m, 6H, NCH_2), 6.71 (m, 1H, γ-H), 7.42 (m, 6H, 7-H, 9-H, α-H), 7.79 (t, $^3J_{H,H} = 6.0$ Hz, 2H, 8-H), 8.00 (d, $^3J_{H,H} = 6.4$ Hz, 2H, 10-H), 8.23 (m, 2H, β-H). Anal. calcd. for $C_{31}H_{29}B_2F_4NO_8$: C, 58.07; H, 4.56; N, 2.18. Found: C, 58.03; H, 4.47; N, 2.31.

*2.8.4. Triethylammonium 2,2-difluoro-4-[5-(8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1,3-pentadienyl]-8-(diethylamino)-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**13**)*

Yield 65%. M.p. 260–263 °C. ^{1}H NMR (DMSO-d_6): δ 1.2 (m, 21H, CH_3), 3.12 (m, 6H, NCH_2), 3.51 (m, 8H, NCH_2), 6.55 (m, 3H, 7-H, γ-H), 6.82 (d, $^3J_{H,H} = 9$ Hz, 2H, 9-H),

7.29 (d, $^3J_{H,H}$ = 13.2 Hz, 2H, α-H), 7.75 (d, $^3J_{H,H}$ = 9 Hz, 2H, 10-H), 8.03 (t, $^3J_{H,H}$ = 12.9 Hz, 2H, β-H), 8.88 (br s, 1H, N^+H). Anal. calcd. for $C_{39}H_{47}B_2F_4N_3O_8$: C, 59.79; H, 6.05; N, 5.36. Found: C, 59.71; H, 5.99; N, 5.47.

*2.8.5. Triethylammonium 2,2-difluoro-4-(7-(2,2-difluoro-5-oxo-(5H)-8-(diethylamino)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborin-4-ylidene)-1,3,5-heptatrienyl]-5-oxo-(5H)-8-(diethylamino)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborinate (**14**)*

A mixture of **5** (646 mg, 2 mmol), glutaconic aldehyde dianil hydrochloride (286 mg, 1 mmol) and triethylamine (252 mg, 5 mmol) in acetic anhydride (7–9 ml) was stirred at room temperature for 24 h. The precipitate was filtered off and crystallized from acetic anhydride. Yield 60 mg (7%). M.p. 211–213 °C. ^{1}H NMR (DMSO-d_6): δ 1.17 (m, 21H, CH_3), 3.12 (m, 6H, NCH_2), 3.48 (m, 8H, NCH_2), 6.52 (m, 4H, 7-H, γ-H), 6.78 (d, $^3J_{H,H}$ = 9.6 Hz, 2H, 9-H), 7.23 (d, $^3J_{H,H}$ = 12.9 Hz, 2H, α-H), 7.57 (d, $^3J_{H,H}$ = 13.2 Hz, 1H, δ-H), 7.70 (d, $^3J_{H,H}$ = 9.6 Hz, 2H, 10-H), 7.82 (t, $^3J_{H,H}$ = 13.8 Hz, 2H, β-H), 8.81 (br s, 1H, N^+H). Anal. calcd. for $C_{41}H_{49}B_2F_4N_3O_8$: C, 60.84; H, 6.10; N, 5.19. Found: C, 60.65; H, 6.01; N, 5.27.

*2.9. Dyes **15–17***

A mixture of **4** or **5** (1 mmol) and the corresponding aldehyde (1.2 mmol) in acetic anhydride (3–5 ml) was refluxed for 3 min, cooled and allowed to crystallize for 12 h. The precipitate was filtered off, washed with glacial acetic acid and diethyl ether.

*2.9.1. 4-(4-(Diethylamino)styryl)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**15**)*

Yield 80%. M.p. 256–258 °C. ^{1}H NMR (DMSO-d_6): δ 1.20 (m, 6H, CH_3), 3.62 (m, 4H, NCH_2), 6.97 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, 3′-H, 5′-H), 7.50 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, 2′-H, 6′-H), 7.87 (m, 3H, 7-H, 8-H, 9-H), 8.10 (m, 2H, 10-H, α-H), 8.46 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, β-H). Anal. calcd. for $C_{22}H_{20}BF_2NO_4$: C, 64.26; H, 4.90; N, 3.41. Found: C, 64.24; H, 4.87; N, 3.51.

*2.9.2. 8-(Diethylamino)-4-(4-(diethylamino)styryl)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**16**)*

Yield 79%. M.p. 229–231 °C (AcOH). ^{1}H NMR ($CDCl_3$): δ 1.18 (m, 12H, CH_3), 3.53 (m, 8H, NCH_2), 6.58 (s, 1H, 7-H), 6.86 (m, 3H, 9-H, 3′-H, 5′-H), 7.73 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, 2′-H, 6′-H), 7.8 (d, $^3J_{H,H}$ = 9.2 Hz, 1H, 10-H), 8.07 (d, $^3J_{H,H}$ = 14.7 Hz, 1H, α-H), 8.24 (d, $^3J_{H,H}$ = 14.7 Hz, 1H, β-H). Anal. calcd. for $C_{26}H_{29}BF_2N_2O_4$: C, 64.74; H, 6.06; N, 5.81. Found: C, 64.71; H, 5.98; N, 5.88.

*2.9.3. 8-(Diethylamino)-4-[4-(4-(dimethylamino) phenyl)-1,3-butadienyl]-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**17**)*

Yield 75%. M.p. 290–292 °C. ^{1}H NMR (DMSO-d_6): δ 1.16 (m, 6H, CH_3), 3.04 (s, 6H, NCH_3), 3.54 (m, 4H, NCH_2), 6.57 (s, 1H, 7-H), 6.76 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, 3′-H, 5′-H), 6.85 (d, $^3J_{H,H}$ = 9.5 Hz, 1H, 9-H), 7.26 (m, 1H, β′-H), 7.53 (d, $^3J_{H,H}$ = 14.0 Hz, 1H, α-H), 7.60 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, 2′-H, 6′-H), 7.70 (d, $^3J_{H,H}$ = 14.0 Hz, 1H, α′-H), 7.80 (d, $^3J_{H,H}$ = 9.5 Hz, 1H, 10-H), 8.07 (m, 1H, β′-H). Anal. calcd. for $C_{26}H_{27}BF_2N_2O_4$: C, 65.02; H, 5.67; N, 5.83. Found: C, 64.91; H, 5.64; N, 5.89.

*2.10. Dyes **18–23**, **25**, **27**, **29** and **31***

A mixture of the corresponding quaternary salt (1.2 mmol), hemicyanine **6–9** (1 mmol) and diisopropylethylamine (1.5 mmol) in acetic anhydride (3–5 ml) was refluxed for 3 min, cooled and allowed to stand for 12 h. The precipitate was filtered off, washed with glacial acetic acid and diethyl ether.

*2.10.1. 2,2-Difluoro-5-oxo-(5H)-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**18**)*

Yield 73%. M.p. >300 °C (lit. 328–330 °C [19]). ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 6H, $C(CH_3)_2$), 3.59 (s, 3H, NCH_3), 6.40 (d, $^3J_{H,H}$ = 12.5 Hz, 1H, α-H), 7.11 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, 7-H), 7.26–7.7.31 (m, 2H, 9-H, 4′-H), 7.35 (m, 1H, 6′-H), 7.39 (m, 2H, 5′-H, 7′-H), 7.60 (d, $^3J_{H,H}$ = 12.5 Hz, 1H, α′-H), 7.67 (m, 1H, 8-H), 8.19 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, 10-H), 8.85 (m, 1H, β-H). Anal. calcd. for $C_{24}H_{20}BF_2NO_4$: C, 66.23; H, 4.63; N, 3.22. Found: C, 66.25; H, 4.64; N, 3.25.

*2.10.2. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-[3-(1,3,3-trimethylindolin-2-ylidene)-1-propenyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**19**)*

Yield 76%. M.p. 280–282 °C. ^{1}H NMR ($CDCl_3$): δ 1.26 (m, 6H, CH_3), 1.70 (s, 6H, $C(CH_3)_2$), 3.48 (m, 7H, NCH_3, NCH_2), 6.07 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, α-H), 6.43 (s, 1H, 7-H), 6.67 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 9-H), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, 4′-H), 7.20 (m, 1H, 6′-H), 7.34 (m, 2H, 5′-H, 7′-H), 7.59 (d, $^3J_{H,H}$ = 13.2 Hz, 1H, α′-H), 7.94 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 10-H), 8.75 (t, $^3J_{H,H}$ = 13.5 Hz, 1H, β-H). Anal. calcd. for $C_{28}H_{29}BF_2N_2O_4$: C, 66.42; H, 5.77; N, 5.53. Found: C, 66.40; H, 5.73; N, 5.55.

*2.10.3. 2,2-Difluoro-5-oxo-(5H)-4-[5-(1,3,3-trimethylindolin-2-ylidene)-1,3-pentadienyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**20**)*

Yield 51%. M.p. >300 °C (Ac_2O). ^{1}H NMR (DMSO-d_6): δ 1.67 (s, 6H, $C(CH_3)_2$), 3.75 (s, 3H, NCH_3), 6.64 (m, 2H, α-H, γ-H), 7.14 (d, $^3J_{H,H}$ = 12.8 Hz, 1H, α′-H), 7.35–7.44 (m, 3H, 7-H, 5′-H, 6′-H), 7.49 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, 9-H), 7.56 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, 4′-H), 7.68 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, 7′-H), 7.74 (m, 1H, 8-H), 7.95 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, 10-H), 8.24 (t, $^3J_{H,H}$ = 13.2 Hz, 1H, β-H), 8.35 (t, $^3J_{H,H}$ = 14.4 Hz, 1H, β′-H). Anal. calcd. for $C_{26}H_{22}BF_2NO_4$: C, 67.70; H, 4.81; N, 3.04. Found: C, 67.55; H, 4.88; N, 3.12.

*2.10.4. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-[5-(1,3,3-trimethylindolin-2-ylidene)-1,3-pentadienyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**21**)*

Yield 74%. M.p. 282–283 °C. ^{1}H NMR (DMSO-d_6): δ 1.18 (m, 6H, $C(CH_3)_2$), 1.68 (s, 6H, CH_3), 3.5 (m, 4H, NCH_2), 3.63 (s, 3H, NCH_3), 6.33 (d, $^3J_{H,H}$ = 14.3 Hz, 1H, α-H), 6.53–6.59

(m, 2H, 7-H, γ-H), 6.81 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 9-H), 7.20–7.28 (m, 2H, 6′-H, α′-H), 7.41 (m, 2H, 4′-H, 5′-H), 7.62 (d, $^3J_{H,H}$ = 7.4 Hz, 1H, 7′-H), 7.75 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 10-H), 8.19–8.32 (m, 2H, β-H, β′-H). Anal. calcd. for $C_{30}H_{31}BF_2N_2O_4$: C, 67.68; H, 5.87; N, 5.26. Found: C, 67.63; H, 5.88; N, 5.30.

*2.10.5. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-[3-(3-ethylbenzothiazol-2(3H)-ylidene)-1-propenyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**22**)*

Yield 81%. M.p. >300 °C. ^{1}H NMR (DMSO-d_6): δ 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 3.51 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, NCH_2), 4.55 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, NCH_2), 6.51 (s, 1H, 7-H), 6.80 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 9-H), 6.89 (d, $^3J_{H,H}$ = 13.5 Hz, 1H, α-H), 7.32 (d, $^3J_{H,H}$ = 12.6 Hz, 1H, α′-H), 7.51 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, 6′-H), 7.64 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, 5′-H), 7.73 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 10-H), 7.88 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, 4′-H), 8.07 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, 7′-H), 8.29 (t, $^3J_{H,H}$ = 12.9 Hz, 1H, β-H). Anal. calcd. for $C_{26}H_{25}BF_2N_2O_4S$: C, 61.19; H, 4.94; N, 5.49. Found: C, 61.09; H, 4.98; N, 5.47.

*2.10.6. 8-(Diethylamino)-2,2-difluoro-5-oxo-(5H)-4-[5-(3-ethylbenzothiazol-2(3H)-ylidene)-1,3-pentadienyl]-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**23**)*

Yield 76%. M.p. >300 °C. ^{1}H NMR (DMSO-d_6): δ 1.15 (t, $^3J_{H,H}$ = 7.92 Hz, 6H, CH_3), 1.36 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 3.47 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, NCH_2), 4.51 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, NCH_2), 6.50–6.58 (m, 2H, 7-H, γ-H), 6.77–6.86 (m, 2H, 9-H, α-H), 7.06 (d, $^3J_{H,H}$ = 12 Hz, 1H, α′-H), 7.50 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, 5′-H), 7.63–7.72 (m, 2H, 10-H, 6′-H), 7.92 (m, 3H, 7′-H, β-H, β′-H), 8.11 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, 4′-H). Anal. calcd. for $C_{28}H_{27}BF_2N_2O_4S$: C, 62.70; H, 5.07; N, 5.22. Found: C, 62.53; H, 4.89; N, 5.34.

*2.10.7. 4-[5-(1-Butylquinolin-2(1H)-ylidene)-1,3-pentadienyl]-8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**25**)*

Yield 74%. M.p. >300 °C. ^{1}H NMR (DMSO-d_6): δ 1.01 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 1.15 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3), 1.59 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 3.47 (m, 4H, NCH_2), 4.62 (m, 2H, NCH_2), 6.45 (s, 1H, 7-H), 6.64 (t, $^3J_{H,H}$ = 11.6 Hz, 1H, γ-H), 6.74 (m, 2H, 9-H, α-H), 7.00 (d, $^3J_{H,H}$ = 12 Hz, 1H, α′-H), 7.64–7.68 (m, 2H, 10-H, 6′-H), 7.83–7.92 (m, 2H, 7′-H, β-H), 8.03 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, 8′-H), 8.12 (d, $^3J_{H,H}$ = 9.2 Hz, 1H, 5′-H), 8.29–8.33 (m, 2H, 3′-H, β′-H), 8.40 (d, $^3J_{H,H}$ = 9.2 Hz, 1H, 4′-H). Anal. calcd. for $C_{32}H_{33}BF_2N_2O_4$: C, 68.83; H, 5.96; N, 5.02. Found: C, 69.01; H, 6.11; N, 5.04.

*2.10.8. 8-(Diethylamino)-2,2-difluoro-4-[5-(1-methylpyridin-4(1H)-ylidene)-1,3-pentadienyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**27**)*

Yield 55%. M.p. >300 °C (AcOH). ^{1}H NMR (DMSO-d_6): δ 1.12 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3), 3.44 (q, $^3J_{H,H}$ = 7.2 Hz, 4H, NCH_2), 4.06 (s, 3H, NCH_3), 6.28 (t, $^3J_{H,H}$ = 14.4 Hz, 1H, γ-H), 6.43 (m, 2H, 7-H, α-H), 6.69–6.76 (m, 2H, 9-H, α′-H), 7.50 (t, $^3J_{H,H}$ = 12.8 Hz, 1H, β-H), 7.61 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, 10-H), 7.83 (m, 3H, 3′-H, 5′-H, β′-H), 8.48 (d, $^3J_{H,H}$ = 6.2 Hz, 2H, 2′-H, 6′-H). Anal. calcd. for $C_{25}H_{25}BF_2N_2O_4$: C, 64.40; H, 5.40; N, 6.01. Found: C, 64.29; H, 5.43; N, 6.08.

*2.10.9. 4-[5-(1-Butylquinolin-4(1H)-ylidene)-1,3-pentadienyl]-8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**29**)*

Yield 82%. M.p. >300 °C. ^{1}H NMR (DMSO-d_6): δ 0.91 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 1.13 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3), 1.36 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 3.45 (m, 4H, NCH_2), 4.68 (m, 2H, NCH_2), 6.45 (s, 1H, 7-H), 6.54 (t, $^3J_{H,H}$ = 12.0 Hz, 1H, γ-H), 6.72 (d, $^3J_{H,H}$ = 9.5 Hz, 1H, 9-H), 6.92 (d, $^3J_{H,H}$ = 12.0 Hz, 1H, α-H), 7.31 (d, $^3J_{H,H}$ = 14.5 Hz, 1H, α′-H), 7.64 (d, $^3J_{H,H}$ = 9.5 Hz, 1H, 10-H), 7.77 (t, $^3J_{H,H}$ = 13.0 Hz, 1H, β-H), 7.81 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, 6′-H), 8.05 (m, 2H, 3′-H, 7′-H), 8.22 (m, 2H, 8′-H, β′-H), 8.63 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, 5′-H), 8.78 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, 2′-H). Anal. calcd. for $C_{32}H_{33}BF_2N_2O_4$: C, 68.83; H, 5.96; N, 5.02. Found: C, 68.75; H, 5.98; N, 5.06.

*2.10.10. 8-(Diethylamino)-2,2-difluoro-4-[5-(1-methylpyridin-2(1H)-ylidene)-1,3-pentadienyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**31**)*

Yield 64%. M.p. >300 °C (AcOH). ^{1}H NMR (DMSO-d_6): δ 1.14 (t, $^3J_{H,H}$ = 6.7 Hz, 6H, CH_3), 3.44 (q, $^3J_{H,H}$ = 6.7 Hz, 4H, NCH_2), 4.12 (s, 3H, NCH_3), 6.37–6.47 (m, 2H, 7-H, γ-H), 6.57 (d, $^3J_{H,H}$ = 14.4 Hz, 1H, α-H), 6.73 (d, $^3J_{H,H}$ = 9.4 Hz, 1H, 9-H), 6.77 (d, $^3J_{H,H}$ = 11.8 Hz, 1H, α′-H), 7.47 (m, 1H, 5′-H), 7.57–7.68 (m, 2H, 10-H, β-H), 7.94 (m, 1H, β′-H), 8.15 (m, 1H, 4′-H), 8.33 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, 3′-H), 8.56 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, 6′-H). Anal. calcd. for $C_{25}H_{25}BF_2N_2O_4$: C, 64.40; H, 5.40; N, 6.01. Found: C, 64.31; H, 5.42; N, 6.05.

*2.11. Dyes **24**, **26**, **28** and **30***

A mixture of the corresponding quaternary salt (1.2 mmol), hemicyanine **7** (1 mmol) and diisopropylethylamine (1.5 mmol) in acetic anhydride (5–10 ml) was stirred at room temperature for 12 h. The precipitate was filtered off, washed with glacial acetic acid and diethyl ether.

*2.11.1. 4-[3-(1-Butylquinolin-2(1H)-ylidene)-1-propenyl]-8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**24**)*

Yield 56%. M.p. >300 °C (DMF). ^{1}H NMR (DMSO-d_6): δ 1.00 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 1.16 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3), 1.59 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 3.48 (m, 4H, NCH_2), 4.64 (m, 2H, NCH_2), 6.50 (s, 1H, 7-H), 6.73–6.80 (m, 2H, 9-H, α-H), 7.29 (d, $^3J_{H,H}$ = 12 Hz, 1H, α′-H), 7.62 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, 6′-H), 7.69 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, 10-H), 7.90 (m, 1H, 7′-H), 8.04–8.12 (m, 2H, 5′H, 8′-H), 8.19 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 3′-H), 8.33 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, 4′-H), 8.53 (t, $^3J_{H,H}$ = 13.2 Hz, 1H, β-H). Anal. calcd. for

$C_{30}H_{31}BF_2N_2O_4$: C, 67.68; H, 5.87; N, 5.26. Found: C, 67.79; H, 6.01; N, 5.28.

*2.11.2. 8-(Diethylamino)-2,2-difluoro-4-[3-(1-methylpyridin-4(1H)-ylidene)-1-propenyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**26**)*

Yield 51%. M.p. >300 °C (AcOH). ^{1}H NMR (DMSO-d_6): δ 1.14 (t, $^3J_{H,H} = 7.2$ Hz, 6H, CH_3), 3.45 (q, $^3J_{H,H} = 7.2$ Hz, 4H, NCH_2), 4.05 (s, 3H, NCH_3), 6.36 (d, $^3J_{H,H} = 15.3$ Hz, 1H, α-H), 6.47 (s, 1H, 7-H), 6.73 (d, $^3J_{H,H} = 9.3$ Hz, 1H, 9-H), 6.91 (d, $^3J_{H,H} = 11.7$ Hz, 1H, α′-H), 7.65 (d, $^3J_{H,H} = 9.3$ Hz, 1H, 10-H), 7.73 (d, $^3J_{H,H} = 6.6$ Hz, 2H, 3′-H, 5′-H), 8.10 (dd, $^3J_{H,H} = 15.3$, 12.0 Hz, 1H, β-H), 8.37 (d, $^3J_{H,H} = 6.6$ Hz, 2H, 2′-H, 6′-H). Anal. calcd. for $C_{23}H_{23}BF_2N_2O_4$: C, 62.75; H, 5.27; N, 6.36. Found: C, 62.70; H, 5.20; N, 6.38.

*2.11.3. 4-[3-(1-Butylquinolin-4(1H)-ylidene)-1-propenyl]-8-(diethylamino)-2,2-difluoro-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**28**)*

Yield 83%. M.p. >300 °C. ^{1}H NMR (DMSO-d_6): δ 0.91 (t, $^3J_{H,H} = 7.2$ Hz, 3H, CH_3), 1.14 (t, $^3J_{H,H} = 7.2$ Hz, 6H, CH_3), 1.38 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 3.47 (m, 4H, NCH_2), 4.66 (m, 2H, NCH_2), 6.48 (s, 1H, 7-H), 6.74 (d, $^3J_{H,H} = 9.2$ Hz, 1H, 9-H), 7.28 (m, 2H, α-H, α′-H), 7.66 (d, $^3J_{H,H} = 9.2$ Hz, 1H, 10-H), 7.75 (t, $^3J_{H,H} = 7.8$ Hz, 1H, 6′-H), 7.88 (d, $^3J_{H,H} = 7.0$ Hz, 1H, 3′-H), 8.02 (m, 1H, 7′-H), 8.18 (d, $^3J_{H,H} = 8.8$ Hz, 1H, 8′-H), 8.47 (m, 1H, β-H), 8.60 (d, $^3J_{H,H} = 7.0$ Hz, 1H, 2′-H), 8.72 (d, $^3J_{H,H} = 8.3$ Hz, 1H, 5′-H). Anal. calcd. for $C_{30}H_{31}BF_2N_2O_4$: C, 67.68; H, 5.87; N, 5.26. Found: C, 67.65; H, 5.86; N, 5.28.

*2.11.4. 8-(Diethylamino)-2,2-difluoro-4-[3-(1-methylpyridin-2(1H)-ylidene)-1-propenyl]-5-oxo-(5H)-chromeno[4,3-d]-1,3,2-(2H)-dioxaborine (**30**)*

Yield 48%. M.p. >300 °C (AcOH). ^{1}H NMR (DMSO-d_6): δ 1.14 (t, $^3J_{H,H} = 6.9$ Hz, 6H, CH_3), 3.45 (q, $^3J_{H,H} = 6.9$ Hz, 4H, NCH_2), 4.08 (s, 3H, NCH_3), 6.48 (m, 2H, 7-H, α-H), 6.74 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 9-H), 7.05 (d, $^3J_{H,H} = 11.6$ Hz, 1H, α′-H), 7.38 (t, $^3J_{H,H} = 6.0$ Hz, 1H, 5′-H), 7.66 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 10-H), 8.04 (t, $^3J_{H,H} = 7.7$ Hz, 1H, 4′-H), 8.18 (m, 2H, 3′-H, β-H), 8.48 (d, $^3J_{H,H} = 6.5$ Hz, 1H, 6′-H). Anal. calcd. for $C_{23}H_{23}BF_2N_2O_4$: C, 62.75; H, 5.27; N, 6.36. Found: C, 62.78; H, 5.33; N, 6.41.

*2.12. Alkaline hydrolysis of dye **19***

*2.12.1. 7-(Diethylamino)-4-hydroxy3-[4-(1,3,3-trimethylindolin-2-ylidene)-2-butenoyl]-(2H)-chromen-2-one (**32**)*

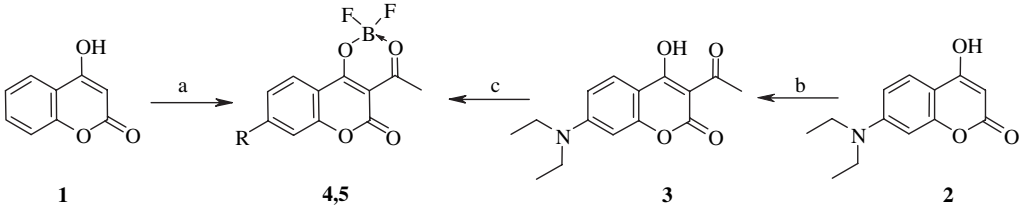
To a suspension of **19** (0.5 g, 1 mmol) in a mixture of acetonitrile and water (4:1, 4 ml) was added 25% methanolic solution of tetramethylammonium hydroxide (1 g, 3 mmol) and the mixture was refluxed for 5–10 min. The resultant solution was cooled, diluted with water (10 ml) and acidified with acetic acid. The precipitate was filtered off. Yield 0.35 g (76%). M.p. 245–247 °C (DMF). ^{1}H NMR (DMSO-d_6): δ 1.14 (m, 6H, CH_3), 1.60 (s, 6H, $C(CH_3)_2$), 3.28 (s, 3H, NCH_3), 3.41 (m, 4H, NCH_2), 5.97 (d, $^3J_{H,H} = 13.2$ Hz, 1H, α-H), 6.40 (s, 1H, 7-H), 6.69 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 9-H), 7.02 (m, 1H, 6′-H), 7.14 (m, $^3J_{H,H} = 7.8$ Hz,1H, 4′-H), 7.30 (m, 1H, 5′-H), 7.38–7.45 (m, 2H, 7′-H, α′-H), 7.71 (d, $^3J_{H,H} = 9.0$ Hz, 1H, 10-H), 8.38 (t, $^3J_{H,H} = 13.8$ Hz, 1H, β-H). Anal. calcd. for $C_{28}H_{30}N_2O_4$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.26; H, 6.50; N, 6.09.

3. Results and discussion

The starting dioxaborine derivatives of coumarines **4** and **5** were obtained using different synthetic approaches (Scheme 1). It was found that the heating of 4-hydroxycoumarin **1** in the mixture of acetic anhydride and boron trifluoride etherate provided the derivative **4** in a good yield. The reaction of dialkylamino substituted coumarin **2** [24] is not so unambiguous, so complex **5** was prepared by two-step synthesis.

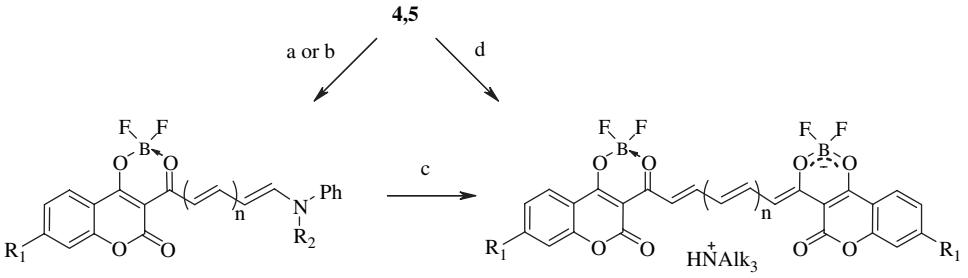
Compounds **4** and **5** easily react with ethylisoformanilide or malonaldehyde dianil hydrochloride forming the corresponding hemicyanines **6–9**, which react with the second molar equivalent of the boron complex forming the symmetrical anionic tri- and pentamethinecyanines **10–13** (Scheme 2). To increase the solubility of the dye **11** we used the tributylammonium counterion (instead of triethylammonium used in other cases). Symmetrical heptamethinecyanine **14** was prepared by the direct condensation of coumarin **5** with glutaconic aldehyde dianil hydrochloride. All the dyes **10–13** can be obtained by direct reaction as well, but in much lower yields.

As can be seen from Table 1 and Fig. 3, the synthesized dyes are intensely coloured. Upon elongation of polymethine chain in the case of the dyes with unsubstituted coumarin fragment **10** and **12** the vinylene shift is observed (ca. 100 nm), whereas the molar absorptivities remain almost unchanged.



1 **4,5** **3** **2**

Scheme 1. R = H (**4**), R = NEt_2 (**5**); (a) Ac_2O, BF_3–Et_2O; (b) Py, Ac_2O; (c) Ac_2O, BF_3–Et_2O, CH_3CN.



6 n = 0, R_1 = H, R_2 = H
7 n = 0, R_1 = NEt_2, R_2 = H
8 n = 1, R_1 = H, R_2= $COCH_3$
9 n = 1, R_1 = NEt_2, R_2= $COCH_3$

10 n = 0, R_1 = H, Alk = Et
11 n = 0, R_1 = NEt_2, Alk = Bu
12 n = 1, R_1 = H, Alk = Et
13 n = 1, R_1 = NEt_2, Alk = Et
14 n = 2, R_1 = NEt_2, Alk = Et

Scheme 2. (a) PhN=CH–OEt, 120 °C, 2 h (**6** and **7**); (b) PhN=CH–CH=CH–NHPh·HCl, Ac_2O (**8** and **9**); (c) Ac_2O, Alk_3N, **4** (for **10** and **12**) or **5** (for **11** and **13**); (d) PhN=CH–CH=CH–CH=CH–NHPh·HCl, Ac_2O, Et_3N (**14**).

Introduction of diethylamino group into the coumarin structural fragment leads to the relatively small bathochromic shift (ca. 40 nm), but marked hyperchromic effect (increase in absorption intensity) is observed, which becomes especially noticeable with elongation of the polymethine chain. However, the biggest difference between the symmetrical dyes from both series is in their fluorescence properties (Table 1). Dialkylamino derivatives show much higher quantum yield of the fluorescence.

As was predicted, the introduction of dialkylamino group increases the hydrolytic stability of corresponding dyes. For example, the addition of organic bases (piperidine or triethylamine) to the aqueous acetonitrile solutions of the dyes **10** and **11** causes complete loss of colour of the first compound within several hours, whereas the second provides the first signs of hydrolysis under analogous conditions only in 24 h.

By changing the electron-donating properties of the second terminal group in donor–acceptor systems we can change

Table 1
Spectral characteristics of synthesized dyes in acetonitrile and chloroform

No.	Absorption		Fluorescence	
	$\lambda_{max\ (CHCl_3)}$, nm (ε*10^{-5} cm^2 mol^{-1})	$\lambda_{max\ (MeCN)}$, nm (ε*10^{-5} cm^2 mol^{-1})	$\lambda_{max\ (CHCl_3)}$, nm (φ)	$\lambda_{max\ (MeCN)}$, nm (φ)
10	581 (1.45),[a] 581 (2.11)	572 (2.15)	588 (0.185)	581 (0.04)
11	625 (2.36)	615 (2.52)	635 (0.845)	639 (0.4)
12	678 (2.13)	671 (2.29)	687	678 (0.155)
13	715 (3.03)	712 (3.00)	730	732 (0.76)
14	817	810 (2.86)	–	–
15	588 (1.18)	586 (1.02)	609 (0.015)	603 (<0.005)
16	583 (1.52)	590 (1.25)	610 (0.48)	642 (<0.005)
17	621 (0.93)	623 (0.94)	699	–
18	569 (0.98),[a] 569 (1.49)	568 (0.79)	590 (0.03)	590 (<0.005)
19	582 (2.31)	584 (1.95)	601 (0.74)	607 (0.105)
20	665 (2.57)	663 (1.38)	677 (0.26)	675 (0.005)
21	668 (2.33)	678 (2.31)	686 (0.515)	701 (0.37)
22	594[b]	590 (1.71)	606 (0.395)	608 (0.105)
23	687[b]	685 (2.24)	702 (0.67)	705 (0.38)
24	617 (2.48)	603 (1.55)	639 (0.02)	637 (<0.005)
25	721 (3.15)	700 (1.73)	729	–
26	611[b]	564 (0.66)	627 (0.30)	609 (0.065)
27	718[b]	590 (0.65)	731	705
28	669(2.71)	646 (1.26)	676	670 (0.05)
29	775 (3.31)	741 (1.13)	–	770
30	585 (1.69)	552 (0.66)	603 (0.095)	597 (0.01)
31	684[b]	577 (0.60)	–	681
32	–	531 (1.07)	–	566 (0.33)

[a] Data from Ref. [19].
[b] The ε value could not be determined due to low solubility.

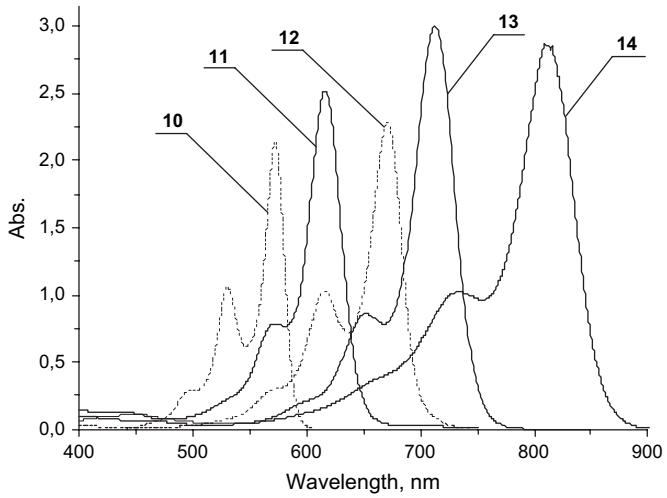


Fig. 3. Absorption spectra of **10**–**14** in acetonitrile (1×10^{-5} M).

their dipole moment. Therefore, it was interesting to prepare the series of unsymmetrical merocyanines based on the boron fluoride acetylcoumarin complexes.

The styryls **15** and **16** were synthesized by the reaction of compounds **4** and **5** with diethylaminobenzaldehyde in acetic anhydride, and the vinyl analog of the styryl **17** was prepared from dimethylaminocinnamic aldehyde under similar conditions (Scheme 3).

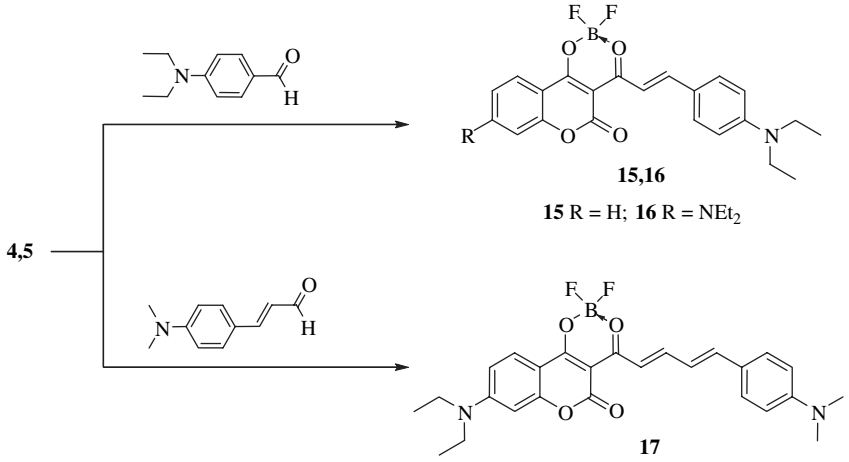
All the other merocyanines were prepared from corresponding hemicyanines **6**–**9** and quaternary salts of heterocycles (Scheme 4). Most of them were synthesized using reflux in acetic anhydride in the presence of diisopropylethylamine as a base. Ambiguous results were obtained in these reaction conditions for dyes **24**, **26**, **28**, and **30**; therefore they were prepared by stirring the reaction mixtures for 12 h at room temperature to achieve much cleaner reactions. The molar absorptivities for re-synthesized dyes **10** and **18** were found to be inconsistent with literature data [19], and previously reported values appeared to be underestimated (the absorption maxima coincide).

It can be seen from Table 1 that the introduction of diethylamino group at the C-7 position of coumarin somewhat deepens the colour of the dyes, with simultaneous increase of their molar absorptivities as compared to unsubstituted analogs.

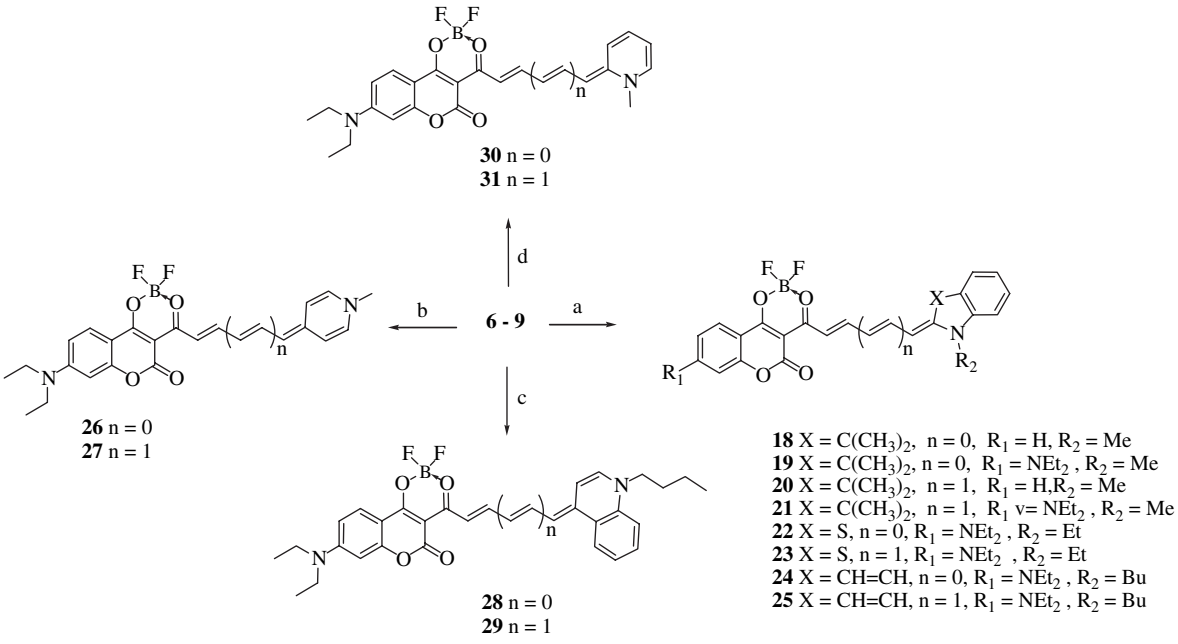
The derivatives of unsubstituted coumarin (dyes **15**, **18** and **20**) show the negative solvatochromic effect upon changing the solvent from chloroform to acetonitrile. The introduction of diethylamino group decreases the electron-accepting properties of dioxaborine fragment, causing small but already positive solvatochromism. The increase of the electron-donating properties of the second terminal nucleus is accompanied by the bathochromic shift of the absorption maxima of the dyes **19**, **22**, **24** and **28** in acetonitrile with broadening of the absorption bands and decrease of their intensity (Fig. 4). The reverse picture is observed in chloroform where the absorption intensity increases with the increase of electron-donating ability of the second nucleus (Table 1). The same regularities remain with the increase of the polymethine chain length. The dyes containing the most electron-donating pyridyl nuclei (**26**, **27**, **30** and **31**) show the largest negative solvatochromic effects (Table 1, Fig. 5). For instance, the difference between the absorption maxima in chloroform and acetonitrile reaches 128 nm for compound **27**.

Introduction of diethylamino group considerably influences the fluorescence intensity as well. The fluorescence quantum yields (φ) for unsubstituted and substituted analogs sometimes differ by more than one order of magnitude (Table 1, compare compounds **18**, **19**, **20** and **21**).

The diethylamino group shows significant effect on hydrolytic stability of the complexes. For example, styryl **15** (R = H) completely hydrolyzes in water–acetonitrile mixture in the presence of triethylamine to the corresponding 1,3-dicarbonyl derivative within several minutes. At the same time, styryl **16** ($R = NEt_2$) provides the first signs of hydrolysis under analogous conditions only in 24 h. The dyes with more electron-donating nuclei (compounds **19**, **21**–**31**) are generally stable to the organic bases. The hydrolysis of these compounds occurs only upon heating in alkaline medium. In



Scheme 3.



Scheme 4. (a) 1,2,3,3-Tetramethylindolinium tetrafluoroborate (**18**–**21**), 2,3-dimethylbenzothiazolium *p*-toluenesulfonate (**22**, **23**), 1-butyl-2-methylquinolinium *p*-toluenesulfonate (**24**, **25**); (b) 1,4-dimethylpyridinium *p*-toluenesulfonate (**26**, **27**); (c) 1-butyl-4-methylquinolinium *p*-toluenesulfonate (**28**, **29**); (d) 1,2-dimethylpyridinium *p*-toluenesulfonate (**30**, **31**).

this way we obtained 1,3-dicarbonyl derivative **32** from the dye **19** (Scheme 5).

Symmetrical dyes, styryls and unsymmetrical dyes containing indoline and benzothiazole nuclei of both series demonstrate high photostability (one month storage of the acetonitrile solutions of all mentioned dyes led to the decrease in molar absorptivities not exceeding 10%). At the same time, photostability of the unsymmetrical dyes containing more basic nuclei (quinoline, pyridine) is much lower, and complete decolourization occurs within 3–7 days. The increase of polymethine chain length also leads to the decrease of photostability.

4. Conclusions

The series of symmetrical and unsymmetrical dyes based on the boron fluoride complex of 3-aceto-4-hydroxy-7-diethylaminocoumarin have been efficiently prepared. The introduction of diethylamino group into the coumarin nucleus causes relatively small effect on the positions of absorption and fluorescence maxima of symmetrical dyes, but dramatically increases the intensity of absorption and emission. Some of the prepared symmetrical dyes belong to the group of efficient longwave emitting luminophores. The newly synthesized symmetrical

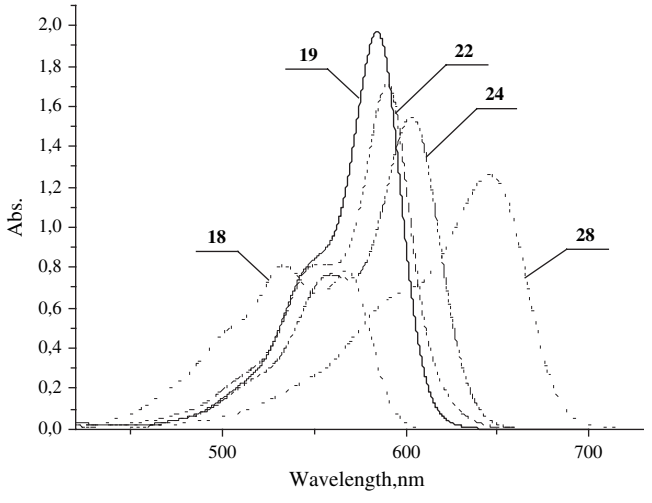


Fig. 4. Absorption spectra of **18**, **19**, **22**, **24**, **28** in acetonitrile (1×10^{-5} M).

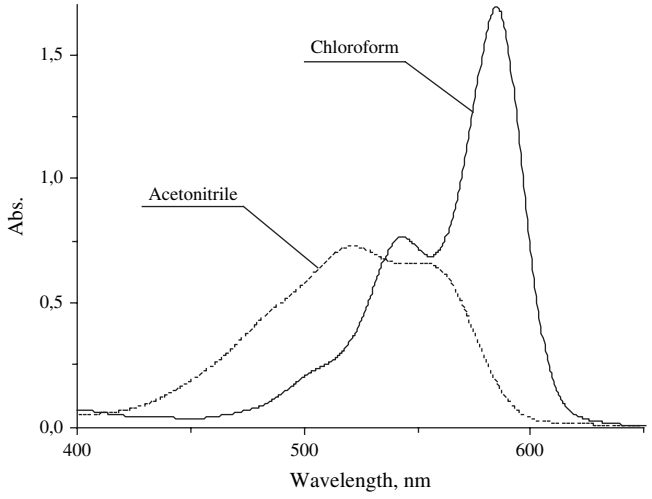
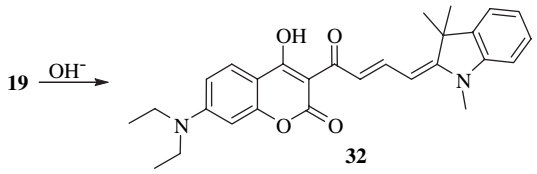


Fig. 5. Absorption spectra of **30** in acetonitrile (1×10^{-5} M) and chloroform (1×10^{-5} M).



Scheme 5.

dyes are probably the most stable dyes among known derivatives of boron fluoride complexes of β-diketonate type.

High reactivity of dioxaborine complex **5** and relatively high stability of the dyes based on this fragment allows the facile modification of physico-chemical properties of unsymmetrical merocyanines to cover a broad range of spectral-luminescence characteristics of the dyes.

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