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Polymethine dyes derived from 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratines with polymethylene bridge groups in the chromophore

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Abstract

Symmetric and unsymmetric carbocyanines derived from 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratines have been synthesized which contain the polymethylene bridge groups $(CH_2)_n$ ($n = 1, 2, 3$) in the chromophore. As shown, these groups acting as electron-donor substituents deepen the dye colour according to the Foerster–Dewar–Knott rule. The enhanced steric hindrances caused by them give rise to the broken planarity of the dye molecules. The ^{1}H NMR chemical shifts for the protons at the *meso*-position of the chromophore have been correlated with the π-charges on the corresponding carbon atoms calculated by the Pariser–Parr–Pople method.

Keywords: 2,2-Difluoro-3,1,2-(2*H*)-oxaoxoniaboratine; Polymethine dyes; Absorption; Fluorescence; Bathochromic shift; The Pariser–Parr–Pople method; NMR

1. Introduction

Polymethine dyes (PDs) derived from 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratines have captured manifold interest in recent years [1–4] which are attributed to their frequently manifested intensive fluorescence [1,3], spectral-sensitizing action on electrophotographic materials [1], and nonlinear optical properties [3]. At the same time, dyes of this kind with polymethylene bridge groups incorporated into their chromophore have been studied scantily [2,3]. The polymethylene five- and six-membered cyclic bridges in the PD chromophore are known to exert a significant effect on the dye spectral luminescent behaviour. The literature provides a considerable body of information on the carbocyanines with the bridge groups binding the α- and γ-positions of the polymethine chain (PC) [5–10]; a number of PDs are also described in which the bridge groups bind the α-atom of the PC with the nitrogen or carbon atom of the heterocyclic ring (see, e.g., Refs. [11–13]). The spectral effects of the bridge group incorporation into the dye chromophore were treated by quantum chemical methods [9–14]. In this connection, it was challenging to introduce the polymethylene bridges into the molecules of the 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratine PDs and to study the peculiarities of their light absorption and fluorescence. In this paper we report the spectral effects of the polymethylene bridge groups $(CH_2)_n$ ($n = 1, 2, 3$) introduced into the molecules of dye **1** [1] and compare absorption and fluorescence characteristics for **1** and resulting PDs **2** and **3** (see Fig. 1).

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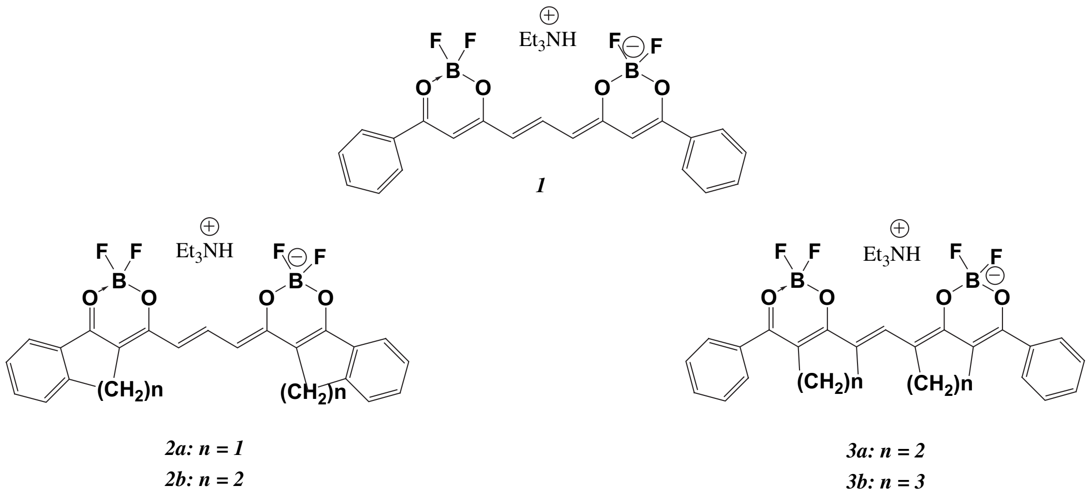


Fig. 1. Symmetric dyes **1**–**3** derived from 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratines with the polymethylene bridge groups $(CH_2)n$.

2. Results and discussion

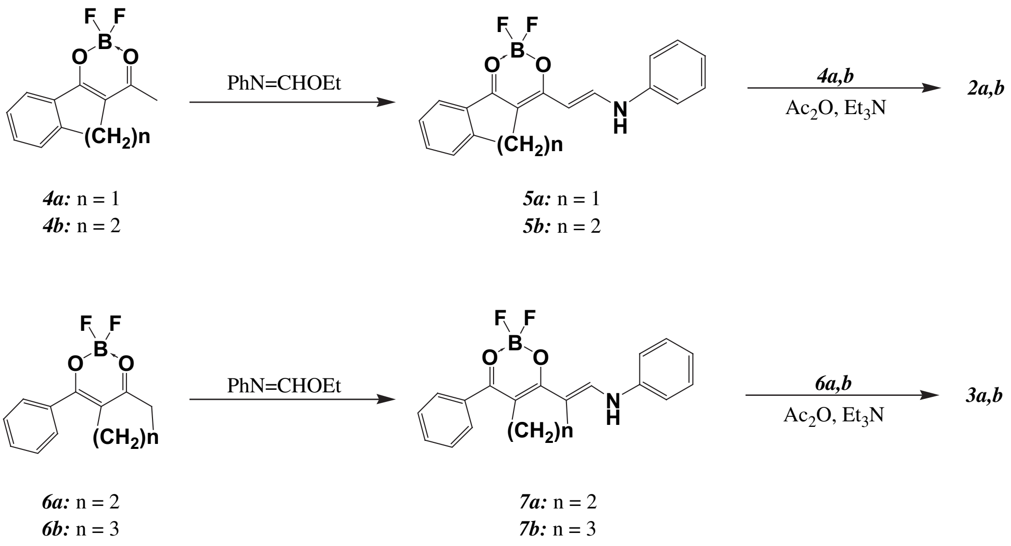
Symmetric PDs **2** and **3** were synthesized starting from boron complexes **4** and **6** as shown in Scheme 1.

Unsymmetrical dyes **8** were obtained likewise (see Fig. 2 and Scheme 2).

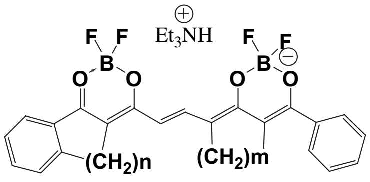
Table 1 gives the spectral parameters of dyes **1**–**3**, and **8** including absorption maxima (λ_{max}), molar extinction coefficients (ε), bridge-induced absorption maximum shifts relative to dye **1** ($\Delta\lambda_{max}$), fluorescence maxima (λ^{Φ}_{max}), Stokes shifts (S), and fluorescence quantum yields (Φ), all the data referring to dye solutions in methylene chloride.

Spectral luminescent properties of the PDs concerned are governed by their electronic structure, electronic effects of the bridge groups acting as substituents in the chromophore, and also by the molecular planarity breaking that may be induced by the substituents. To estimate the scope of the above-mentioned factors, we carried out quantum chemical calculations for some molecules of the dye family. The geometry optimization performed by the semiempirical AM1 method for dye **1** suggests that this molecule is practically planar, with the phenyl rings twisted less than 1°.

Rigidization of various chromophore portions in molecule **1** with polymethylene bridge groups results in modified spectral luminescent characterisitics, as is the case with dyes **2**, **3**, and **8**. Thus, molecular geometry optimization by the AM1 method for the compounds under study has revealed that the five-membered or six-membered ring closure between the phenyl and boratine ring leads the phenyl group to twist through an angle of 1.4° (for **2a**) or 14° (for **2b**) out of the chromophore plane; as a result, the initial molar extinction coefficient



Scheme 1.



8a: *n* = *1*, *m* = *2*
8b: *n* = *2*, *m* = *3*

Fig. 2. Unsymmetric dyes **8a** and **8b** derived from 2,2-difluoro-3,1,2-(2*H*)-oxaoxoniaboratines with the polymethylene bridge groups $(CH_2)n$.

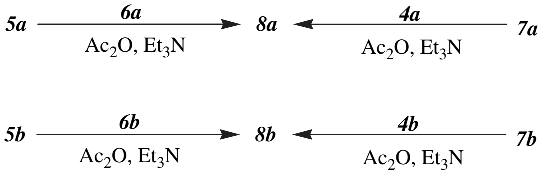
of 138,000 raises to 180,650 in the former case and reduces to 103,550 in the latter case. Moreover, fastening the phenyl rings in the molecular plane gives rise to an enhanced fluorescence quantum yield for compounds **2a** and **2b** (0.5 and 0.3, respectively) (see Figs. 3 and 4).

According to the computed geometrical data for dyes **3a** and **3b**, binding of the boratine ring to the PC by the di- and trimethylene bridge groups breaks the dye planarity significantly, so that the phenyl groups in both the compounds are twisted about 46° out of the chromophore plane. In the case of dye **3b**, the planarity of the PC is also broken (see Fig. 5), which leads to the reduced molar extinction coefficient and hence the minimum fluorescence intensity.

The changes observed in the absorption spectra are mainly due to the electronic effects of the polymethylene bridge groups, as evidenced by our calculations using the Pariser–Parr–Pople (PPP) method (with the same parameter set as in Ref. [15]). Since the PPP method is based on the π-electronic approximation, the electron-donor influence of the hydrocarbon substituents was modelled by the decreased ionization potentials I_c of the carbon atoms bearing such substituents. The electron-donor effect arising from superconjugation is known to be weaker for a trimethylene than for dimethylene group [10] and a methylene group bound to an aromatic ring (as in dye **2a**) should be the least efficient as a donor. We therefore suggested the following ranking of electron-donor abilities in the calculations:

$$CH_2\text{–}(Ar) < (CH_2)_3 < (CH_2)_2$$

The ionization potentials of the carbon atoms bound to these bridges were, respectively, decreased by 0.20, 0.25, and 0.58 eV. Computational results obtained for dyes **1–3** using these parameters are listed in Table 2.



Scheme 2.

Table 1
Spectral luminescent properties of dyes **1–3**, and **8**

Dye	λ_{max} (nm)	$\varepsilon \times 10^{-5}$	$\Delta\lambda_{max}$ (nm)	λ^{Φ}_{max} (nm)	S (cm^{-1})	Φ
1	600	1.3800				
2a	613	1.8065	13	621	210	0.50
2b	625	1.0355	25	636	277	0.30
3a	671	1.0895	71	691	431	0.08
3b	625	0.9720	25	655	733	0.01
8a	638	1.5210	38	648	242	0.21
8b	622	1.3195	22	644	549	0.10

The table presents calculated absorption maximum positions (λ^{calc}_{max}), their bridge-induced shifts ($\Delta\lambda_{max}$), oscillator strengths (f), and the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. The ground-state atomic π-charges for dye **1** are indicated in the molecular diagram shown below (Fig. 6).

As seen from the diagram, π-electron density is increased on the α- and γ-atoms and decreased on the β-atoms of the PC, which is typical of PDs. According to the Foerster–Dewar–Knott rule [16,17], electron-donor substituents at odd positions of the chromophore, i.e., on the α- and γ-atoms of the PC, should deepen the colour, as is the case with dyes **3a** and **3b**.

The calculated positions of absorption maxima somewhat deviate from those observed experimentally, but the agreement between the predicted and measured shifts caused by the bridge groups is much better (cf. the data in Tables 1 and 2).

Both the calculations and measurements provide the smallest value of bathochromic shift (9.8 and 13 nm, respectively) for dye **2a**, more pronounced effects are demonstrated for **2b** (28.4 and 25 nm) and **3b** (27.3 and 25 nm), and the absorption is red-shifted for most of the molecules of **3a** (62.1 and 71 nm) in which the chromophore is bound to the dimethylene bridge through positions 3, 5 and 7, 9. These effects are mainly attributed to the electron-donor action of the bridge hydrocarbon substituents and the magnitude of bathochromic shift is known to depend upon the HOMO coefficients on the substituent-bearing atoms [10]. The HOMO coefficients on atoms 15 (25), 3 (9), and 5 (7) appear as 0.161, 0.324, and 0.406, respectively, and the sensitivity to substituent effects increases in the same order. At the same time, the LUMO coefficients of the atoms bound to the bridge groups are found to be negligible. Colour deepening induced by a donor bridge would thus be expected from a change in the energy levels. Indeed, the LUMO energy of about −8.257 eV is practically the same for the unbridged and bridged dyes, whereas the HOMO raises from −12.136 eV for **1** to −12.088, −11.992, −11.868, and −12.018 eV for **2a**, **2b**, **3a**, and **3b**, respectively (see Table 2). Thus, it is clear that the bridge-induced bathochromic effect, $\Delta\lambda_{max}$, should be the smallest for **2a** and the largest for **3a**.

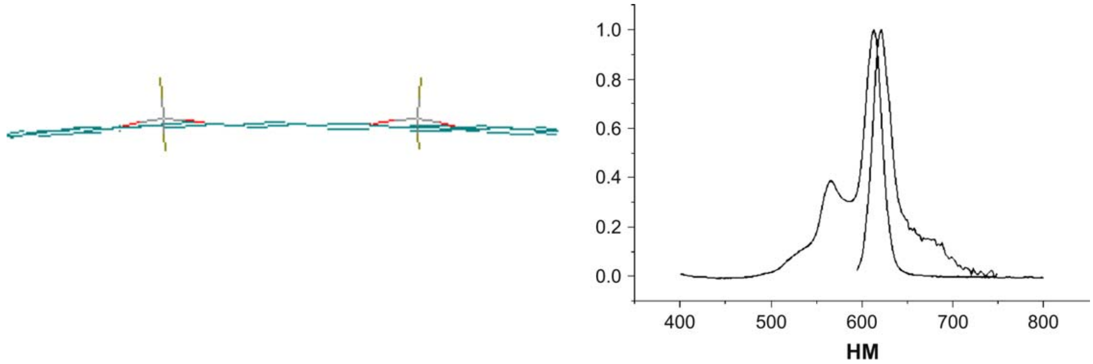


Fig. 3. Optimized molecular geometry and the absorption and fluorescence spectra of dye **2a**.

Like most PDs, the dyes studied manifest a correlation between the ^{1}H NMR chemical shifts, δH, of PC protons and the π-charges on the carbon atoms, q, bound to them. Table 3 lists the chemical shifts of the protons at the PC *meso*-position (β-protons) for dyes **2a** and **3a** as well as for symmetric dye **9** (Fig. 7) derived from the boron complex of 2-acetyldimedone [15], thiacarbo [18], and indocarbocyanine [19], along with the calculated π-charges on the corresponding carbon atoms.

The least-squares method provides the correlation dependence:

$$\delta H_\beta = 6.569 + 10.662 q_\beta,$$

with the correlation coefficient $R = 0.972$.

Spectral luminescent properties of dyes **8a** and **8b** demonstrate the additive effects of the polymethylene bridges introduced at positions 3, 5 (7, 9) and 3, 15 (9, 25). The additivity is attested by the extremely small deviation values (4 nm for **8a** and 3 nm for **8b**) and by the fluorescence quantum yields close to the arithmetical means of those for the corresponding parent dyes (see Table 1).

3. Experimental

Electronic absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100, and fluorescence spectra were taken on a Cary Eclipse fluorescent spectrophotometer and not corrected. ^{1}H NMR spectra were obtained with a Varian VXR-300 instrument at 300 MHz using TMS as internal reference. The fluorescence quantum yields (Φ) of the synthesized dyes were determined by known method [21] relatively to the Nile Blue, the absolute fluorescence yield of which being 0.27 [20]. Boron complexes **4** and **6** were obtained by the literature procedures [22] and [2], respectively. The yields, melting points, and elemental analysis data of the synthesized dyes are summarized in Table 4.

*3.1. 4-[2-Anilinoethenyl]-2,2-difluoro-5H-indeno-[2,1-e]-3,1,2-oxaoxoniaboratine (**5a**)*

A mixture of a boron complex **4a** (0.1 mol) and *N*-ethoxymethylideneaniline (0.12 mol) was heated at 120 °C for 1 h and then cooled to a room temperature. The resulting solid was suspended in acetone (50 ml), the precipitate was filtered off, washed with acetone (2 × 25 ml), and crystallized from acetic acid; ^{1}H NMR

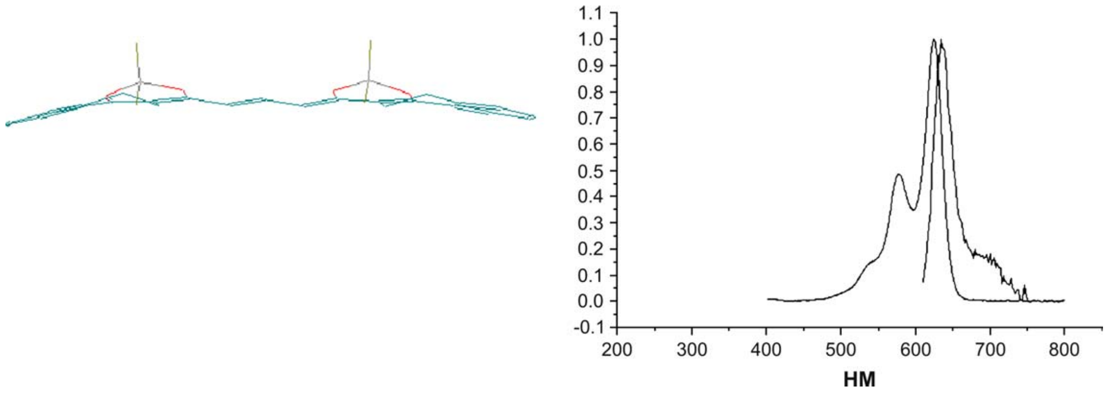


Fig. 4. Optimized molecular geometry and the absorption and fluorescence spectra of dye **2b**.

3a **3b**

Fig. 5. Optimized molecular geometry of dyes **3a** and **3b**.

(DMSO-d_6): δ 3.67 (s, CH_2), 5.72 (d, H_β, $J = 12.6$ Hz), 7.10–7.70 (m, 9HAr), 8.50 (d, H_α, $J = 12.8$ Hz,), 11.44 (s, NH); VIS (CH_2Cl_2): λ_{max} 451 nm, 72,400 (ε).

*3.2. 4-[2-Anilinoethenyl]-2,2-difluoro-5H,6H-naphtho-[2,1-e]-3,1,2-oxaoxoniaboratine (**5b**)*

A mixture of a boron complex **4b** (0.1 mol) and *N*-ethoxymethylideneaniline (0.12 mol) was heated at 60 °C for 2 h and then cooled to a room temperature. The resulting solid was suspended in isopropanol (50 ml), the precipitate was filtered off, washed with isopropanol (2 × 25 ml), and crystallized from acetic acid; ^{1}H NMR (DMSO-d_6): δ 2.53 (t, CH_2, $J = 8.1$ Hz), 2.87 (t, CH_2, $J = 7.5$ Hz), 5.87 (d, H_β, $J = 12.0$ Hz), 7.10–7.50 (m, 8HAr), 7.75 (d, 1HAr, $J = 7.5$ Hz), 8.55 (d, H_α, $J = 12.0$ Hz), 11.48 (s, NH); VIS (CH_2Cl_2): λ_{max} 463 nm, 56,250 (ε).

*3.3. 7-[Anilinomethylidene]-2,2-difluoro-4-phenyl-5H,6H,7H-cyclopenta[d]-3,1,2-oxaoxoniaboratine (**7a**)*

A mixture of a boron complex **6a** (0.1 mol) and *N*-ethoxymethylideneaniline (0.12 mol) was heated at 60 °C for 2 h and then cooled to a room temperature. The resulting solid was suspended in ether (50 ml), the precipitate was filtered off, washed with ether (2 × 25 ml), and crystallized from acetic anhydride; ^{1}H NMR (DMSO-d_6): δ 2.74 (m, CH_2), 3.01 (m, CH_2), 7.07–7.88 (m, 10HAr), 8.28 (m, H_α), 10.43 (m, NH); VIS (CH_2Cl_2): λ_{max} 462 nm, 52,330 (ε).

Table 2
Computational data obtained for the molecules of dyes **1**–**3** by the PPP method

Dye	λ_{max}^{calc} (nm)	f	$\Delta\lambda_{max}$ (nm)	HOMO energy (eV)	LUMO energy (eV)
1	656.0	1.243	0	−12.136	−8.257
2a	665.8	1.249	9.8	−12.088	−8.257
2b	684.0	1.262	28.4	−11.992	−8.255
3a	718.1	1.326	62.1	−11.868	−8.353
3b	683.3	1.276	27.3	−12.018	−8.298

*3.4. 8-[Anilinomethylidene]-2,2-difluoro-4-phenyl-5H,6H,7H,8H-cyclohexa[d]-3,1,2-oxaoxoniaboratine (**7b**)*

A mixture of a boron complex **6b** (0.1 mol) and *N*-ethoxymethylideneaniline (0.12 mol) was heated at 60 °C for 2 h and then cooled to a room temperature. The resulting solid was suspended in ether (50 ml), the precipitate was filtered off, washed with ether (2 × 25 ml), and crystallized from acetic anhydride; ^{1}H NMR (DMSO-d_6): δ 1.69 (q, $CH_2\mathit{CH_2}CH_2$, $J = 5.1$ Hz), 2.52–2.60 (m, $\mathit{CH_2}CH_2\mathit{CH_2}$), 7.20–7.67 (m, 10HAr), 8.53 (d, H_α, $J = 14.7$ Hz), 10.43 (d, NH, $J = 14.7$ Hz); VIS (CH_2Cl_2): λ_{max} 450 nm, 50,900 (ε).

*3.5. Triethylammonium-4-[3-(2,2-difluoro-5H-indeno-[1,2-d]-1,3,2-dioxaboratine-4-ylidene)-1-propenyl]-2,2-difluoro-5H-indeno-[2,1-e]-3,1,2-oxaoxoniaboratine (**2a**)*

To a mixture of boron complex **4a** (1 mmol) and gemicyanine **5a** (1 mmol) in 2.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 75 °C for 1 h, then cooled to a room temperature, by adding ether (50 ml), and allowed to stand for 2 h. The precipitate was filtered off, washed with ether (2 × 25 ml), dissolved in the CH_2Cl_2 (30 ml), and solids were filtered off. To the filtrate was added ether (70 ml), and the mixture was allowed to stand for 4 h. Precipitate was filtered off, washed with ether (2 × 25 ml), washed with water (3 × 30 ml); ^{1}H NMR (DMSO-d_6): δ 1.73 (t, $3\mathit{CH_3}CH_2N^+H$, $J = 7.5$ Hz), 3.09 (q, $3CH_3\mathit{CH_2}N^+H$, $J = 9.4$ Hz), 3.65 (s, $2CH_2$), 5.88 (d, $H_\alpha + H_\gamma$, $J = 13.8$ Hz), 7.42–7.68 (m, 8HAr), 8.37 (t, H_β, $J = 13.5$ Hz), 8.92 (s, $3CH_3CH_2N^+\mathit{H}$).

*3.6. Triethylammonium-4-[3-(2,2-difluoro-5H,6H-naphtho-[1,2-d]-1,3,2-dioxaboratine-4-ylidene)-1-propenyl]-2,2-difluoro-5H,6H-naphtho-[2,1-e]-3,1,2-oxaoxoniaboratine (**2b**)*

To a mixture of boron complex **4b** (1 mmol) and gemicyanine **5b** (1 mmol) in 1.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 60 °C for 15 min and then cooled to a room temperature,

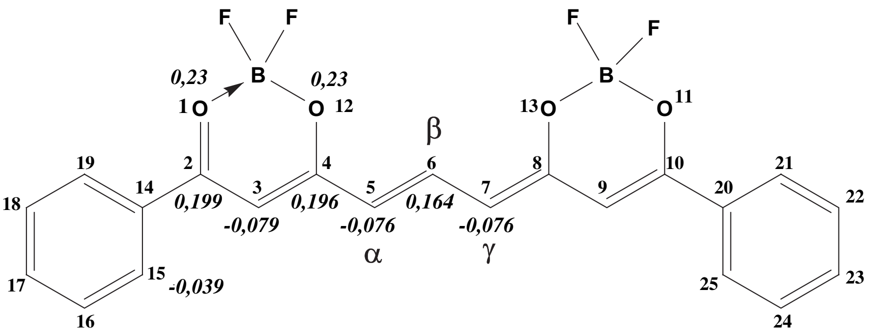


Fig. 6. The ground-state atomic π-charges of the dye **1**.

by adding ether (50 ml), and allowed to stand for 4 h. The precipitate was filtered off, washed with ether (2 × 25 ml). The crystalline product was dissolved in the CH_2Cl_2 (20 ml), and solids were filtered off. To the filtrate was added ether (70 ml), and the mixture was allowed to stand for a night. Precipitate was filtered off, washed with ether (3 × 25 ml); ^{1}H NMR ($CDCl_3$): δ 1.50 (t, $3CH_3CH_2N^+H$, $J = 7.2$ Hz), 2.62 (t, $2CH_2CH_2$, $J = 7.8$ Hz), 2.90 (t, $2CH_2CH_2$, $J = 7.8$ Hz) 3.42 (q, $3CH_3CH_2N^+H$, $J = 6.6$ Hz), 5.96 (d, $H_\alpha + H_\gamma$, $J = 13.2$ Hz), 7.15–7.40 (m, 6HAr), 7.96 (d, 2HAr, $J = 7.2$ Hz), 8.64 (t, H_β, $J = 13.5$ Hz), 8.99 (s, $3CH_3CH_2N^+H$).

*3.7. Triethylammonium-7-[(2,2-difluoro-4-phenyl-5H,6H-cyclopenta[e]-1,3,2-dioxaboratine-7-yl)methylidene]-2,2-difluoro-4-phenyl-5H,6H,7H-cyclopenta[d]-3,1,2-oxaoxoniaboratine (**3a**)*

To a mixture of boron complex **6a** (1 mmol) and gemicyanine **7a** (1 mmol) in 2.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 60 °C for 20 min and then cooled to a room temperature, by adding ether (50 ml), and allowed to stand for 2 h. The precipitate was filtered off, washed with ether (2 × 25 ml). The crystalline product was dissolved in the CH_2Cl_2 (50 ml), and solids were filtered off. To the filtrate was added ether (150 ml), and the mixture was allowed to stand for 4 h. Precipitate was filtered off, washed with ether (2 × 25 ml); ^{1}H NMR (DMSO-d_6): δ 1.10 (t, $3CH_3CH_2N^+H$, $J = 7.5$ Hz), 2.90–3.05 (m, $3CH_3CH_2N^+H + 2CH_2CH_2$), 7.35–7.87 (m, 10HAr + H_β), 8.97 (s, $3CH_3CH_2N^+H$).

*3.8. Triethylammonium-8-[(2,2-difluoro-4-phenyl-5H,6H,7H-cyclohexa[e]-1,3,2-dioxaboratine-8-yl)methylidene]-2,2-difluoro-4-phenyl-5H,6H,7H,8H-cyclohexa[d]-3,1,2-oxaoxoniaboratine (**3b**)*

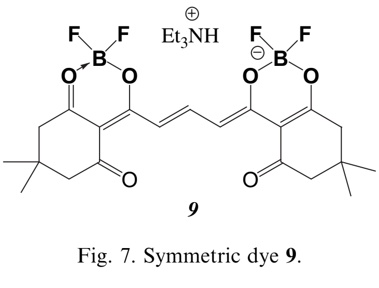
To a mixture of boron complex **6b** (1 mmol) and gemicyanine **7b** (1 mmol) in 1.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 60 °C for 15 min and then cooled to a room temperature, by adding ether (50 ml), and allowed to stand for 2 h. The precipitate was filtered off, washed with ether (2 × 25 ml) and crystallized from isopropanol; ^{1}H NMR (DMSO-d_6): δ 1.11 (t, $3CH_3CH_2N^+H$, $J = 7.7$ Hz), 1.53 (m, $2CH_2CH_2CH_2$), 2.44 (m, $2CH_2CH_2CH_2$), 2.67 (m, $2CH_2CH_2CH_2$), 3.02 (q, $3CH_3CH_2N^+H$), 7.37–7.62 (m, 10HAr), 8.68 (m, H_β), 8.81 (s, $3CH_3CH_2N^+H$).

*3.9. Triethylammonium-4-[2-(2,2-difluoro-4-phenyl-5H,6H-cyclopenta[e]-1,3,2-dioxaboratine-7-yl)ethenyl]-2,2-difluoro-5H-indeno-[2,1-e]-3,1,2-oxaoxoniaboratine (**8a**)*

To a mixture of boron complex **6a** (1 mmol) and gemicyanine **5a** (1 mmol) in 1.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 100 °C for 20 min, and then cooled to a room

Table 3
^{1}H NMR chemical shifts of β-protons and π-charges on β-carbons in the dye PC

Dye	δH_β (ppm)	q_β
3a	7.741	0.100
Thiacarbocyanine	7.790	0.134
2a	8.365	0.161
Indocarbocyanine	8.450	0.175
9	9.041	0.231



9

Fig. 7. Symmetric dye **9**.

Table 4
Characterization data for dyes **2**, **3**, **5**, **7**, and **8**

Dye	Mp (°C)	Yield (%)	Empirical formula	Elemental analysis (%)			
					C	H	N
2a	241	65	$C_{29}H_{31}B_2F_4NO_4$	Calcd	62.74	5.63	2.52
				Found	62.95	5.61	2.60
2b	225	58	$C_{31}H_{35}B_2F_4NO_4$	Calcd	63.84	6.05	2.40
				Found	63.56	6.10	2.38
3a	229	69	$C_{31}H_{35}B_2F_4NO_4$	Calcd	63.84	6.05	2.40
				Found	63.89	6.25	2.43
3b	176	88	$C_{33}H_{39}B_2F_4NO_4$	Calcd	64.84	6.43	2.29
				Found	64.99	6.51	2.33
5a	231	68	$C_{18}H_{14}BF_2NO_2$	Calcd	66.50	4.34	4.31
				Found	66.55	4.34	4.40
5b	212	62	$C_{19}H_{16}BF_2NO_2$	Calcd	67.29	4.76	4.13
				Found	67.60	4.96	4.12
7a	205	71	$C_{19}H_{16}BF_2NO_2$	Calcd	67.29	4.76	4.13
				Found	67.35	4.76	4.28
7b	230	60	$C_{20}H_{18}BF_2NO_2$	Calcd	68.02	5.14	3.97
				Found	67.80	5.10	4.02
8a	>310	84	$C_{30}H_{33}B_2F_4NO_4$	Calcd	63.30	5.84	2.46
				Found	63.39	5.87	2.51
8b	220	77	$C_{32}H_{37}B_2F_4NO_4$	Calcd	64.35	6.24	2.35
				Found	64.55	6.32	2.38

temperature, by adding ether (50 ml), and allowed to stand for 2 h. The precipitate was filtered off, washed with ether (2 × 25 ml). The dye was dissolved in the CH_2Cl_2 (20 ml), and solids were filtered off. To the filtrate was added ether (70 ml), and allowed to stand for 4 h. Precipitate was filtered off, washed with ether (2 × 25 ml), washed with water (3 × 30 ml); ^1H NMR (DMSO-d_6): δ 1.17 (t, $3\mathit{CH_3}CH_2N^+H$, $J = 7.2$ Hz), 2.72 (m, $-\mathit{CH_2}CH_2-$), 3.00 ($-CH_2\mathit{CH_2}-$), 3.09 (q, $3CH_3\mathit{CH_2}N^+H$), 3.65 (s, $-CH_2-$), 5.59 (d, H_α, $J = 13.5$ Hz), 7.40–7.60 (m, 9HAr), 8.05 (d, H_β, $J = 13.5$ Hz), 8.88 (s, $3CH_3CH_2N^+\mathit{H}$).

3.10. *Triethylammonium-4-[2-(2,2-difluoro-4-phenyl-5H,6H,7H-cyclohexa[e]-1,3,2-dioxaboratine-8-yl)ethenyl]-2,2-difluoro-5H,6H-naphtho-[2,1-e]-3,1,2-oxaoxoniaboratine (**8b**)*

To a mixture of boron complex **6b** (1 mmol) and gemicyanine **5b** (1 mmol) in 1.5 ml acetic anhydride was added triethylamine (0.2 ml). The mixture was heated at 60 °C for 20 min and then cooled to a room temperature, by adding ether (50 ml), and allowed to stand for 2 h. The precipitate was filtered off, washed with ether (2 × 25 ml). The dye was dissolved in the CH_3CN (20 ml), and solids were filtered off. To the filtrate was added ether (70 ml), and allowed to stand for 4 h. Precipitate was filtered off, washed with ether (2 × 25 ml); ^1H NMR (DMSO-d_6): δ 1.17 (t, $3\mathit{CH_3}CH_2N^+H$, $J = 7.2$ Hz), 1.63 (m, $CH_2\mathit{CH_2}CH_2$), 2.44 (m, $\mathit{CH_2}CH_2\mathit{CH_2}$), 2.62 (t, $CH_2\mathit{CH_2}$, $J = 7.2$ Hz), 2.87 (t, $\mathit{CH_2}CH_2$, $J = 7.2$ Hz), 3.09 (q, $3CH_3\mathit{CH_2}N^+H$), 5.84 (d, H_α, $J = 13.8$ Hz), 7.27–7.80 (m, 9HAr), 8.58 (d, H_β, $J = 13.5$ Hz), 8.88 (s, $3CH_3CH_2N^+\mathit{H}$).

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