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Design, Synthesis, and Spectral Luminescent Properties of a Novel Polycarbocyanine Series Based on the 2,2-Difluoro-1,3,2-dioxaborine Nucleus

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The natures of the chromophores in symmetric polymethine dyes derived from 2,2-difluoro-1,3,2-dioxaborine have been investigated. Ab initio quantum chemical calculations demonstrated that the presence of dioxaborine end residues stabilizes the frontier levels of the corresponding polymethine dye and makes electron-density distribution over the oxygen atoms in the chelate ring more even than in the analogous dye structure with boron-free acyclic end groups. A series of novel symmetric polycarbocyanines and a tricarbocyanine series with variously bridged polymethine chromophores have been synthesized from hitherto unknown pyrimidino-annelated dioxaborines. The absorption, fluorescence and ^{13}C NMR spectroscopic data point to the polymethinic type of electron-density distribution in the 2,2-difluoro-1,3,2-dioxaborine polymethine dye molecules. The fundamental options for controlling the spectral properties of these dyes by modification of their polymethine chains have been evaluated. One of the new compounds synthesized is remarkable among the known open-chain polymethine dyes for its record high fluorescence quantum yield.

Introduction

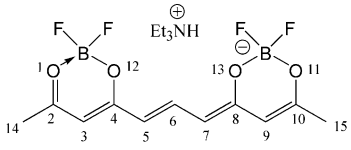
Since the second half of the last century, it has been known that 2,2-difluoro-1,3,2-dioxaborines bearing a methyl or methylene group at position 4 of the heterocycle can form deeply coloured polymethine dyes (PDs).[1–6] A special interest in π-conjugated systems derived from 2,2-difluoro-1,3,2-dioxaborines has stemmed from their peculiar electronic and spectral luminescent properties, such as high hyperpolarizabilities,[7,8] wide ranges (from UV to near IR wavelengths) and high intensities of absorption[1,2,4–12] and fluorescence,[10–13] photosensitizing activities towards photoconducting materials[3,4] and metallic silver,[13] and large two-photon cross sections.[13] The wide application of 2,2-difluoro-1,3,2-dioxaborines has been reviewed.[14,15]

An effective instrument for the design of PDs with specified parameters is offered by structural variation in the polymethine chains (PCs) and heterocyclic end groups.[16] This approach calls for a deep insight into the relationships between the electronic structures and the spectral properties of the symmetric PDs concerned. However, the literature devoted to 2,2-difluoro-1,3,2-dioxaborine PDs is mostly focused on synthetic[1–6,8] and some colour[12,17] respects, as well as on various physical properties.[7,8,13,15,17] The natures of the chromophore systems and the general colour regularities have so far remained unexplored.

This study, based on the nonempirical ab initio method (UHF/6–31G**), addresses the effect of the ring-forming BF_2 moiety on the frontier level positions and the electron-density distributions in the molecules of symmetric carbocyanines with variously derivatized 2,2-difluoro-1,3,2-dioxaborine end residues. A novel polycarbocyanine series has been synthesized from previously unknown pyrimidino-annelated 2,2-difluoro-1,3,2-dioxaborines, and the spectral properties of the dyes obtained have been investigated.

Results and Discussion

The simplest symmetric 2,2-difluoro-1,3,2-dioxaborine PD **1**, with its first absorption maximum found at λ_{max} = 519 nm in CH_3CN, was synthesized by us starting from the boron complex of acetylacetone:[17]



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Dyes of this kind are regarded as oxonoles: that is, oxygen analogues of cyanine dyes bearing delocalised negative charges.[6] A classical example of an oxonol, with much the same absorption region (λ_{max} = 547 nm) is provided by

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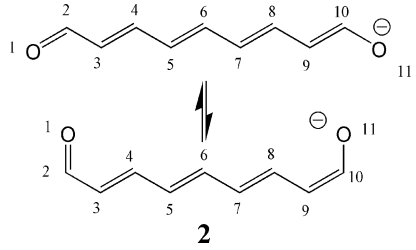
structure **2**.[16] It is clear that the chromophores of dyes **1** and **2** include the same number of atoms and that the main long-wavelength transitions are localized along the conjugation chains connecting oxygen atoms 1 and 11. To estimate the effect of the dioxaborine rings on the electronic structure of dye **1**, its frontier level positions, and the S_0–S_1 transition energy, we performed ab initio calculations for PD **1** and oxonole **2**.



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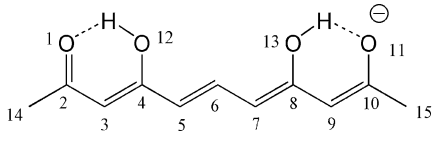
The relevant characteristics were also calculated for the virtual oxonole **3**, representing a structure intermediate between PDs **1** and **2**: like dioxaborine dye **1**, it contains hydroxy groups at positions 4 and 8, but six-membered dioxaborine rings are simulated with analogous chelate rings arising from intramolecular H-bonding.



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The previously reported computational data for the 2,2-difluoro-1,3,2-dioxaborine nucleus concerned only 4,5,6-trisubstituted and other functionalized derivatives.[14,18] The calculation results listed in Table 1 suggest that the presence of the dioxaborine rings leads to a notable lowering of the highest occupied molecular orbital (HOMO) of PD **1** in relation to oxonoles **2** and **3** (by 1.83 and 1.51 eV, respectively).

Table 1. The HOMO and LUMO energies for PDs **1**, **2** and **3** calculated by the ab initio MO method at the UHF/6–31G** level of theory.

Dye	E_{HOMO} [eV]	E_{LUMO} [eV]
1	–4.27	4.37
2	–2.44	5.22
3	–2.76	5.65

The stabilization of the lowest unoccupied molecular orbital (LUMO) of PD **1** relative to the simple oxonole **2** and its substituted analogue **3** is not so significant (the corresponding downward energy shifts amount to 0.85 and 1.28 eV). As can be seen from Figures 1 and 2, the dioxaborine rings also cause an essential equalization of the HOMO coefficients and charges on oxygen atoms 1 and 12 (and, accordingly, 11 and 13) in comparison with those in the model dye **3**. Contrary to this, the charge distribution and the frontier level positions for model oxonole **3**, which lacks the BF_2 groups, were found to resemble those for anionic dye **2** (see Figures 1 and 2). In relation to isolated keto and hydroxy groups, the electron density is distributed somewhat more evenly in the oxygen atom pairs 1/12 and 11/13, but this equalization is much less pronounced than in the dioxaborine derivative **1**. The hydroxy substituents at positions 4 and 8 in dye **3**, though stabilized by the intramolecular hydrogen bond, merely widen the energy gap (from 7.66 to 8.41 eV), due to their positive inductive effect, in accordance with the Foerster–Dewar–Knott rule.[19]

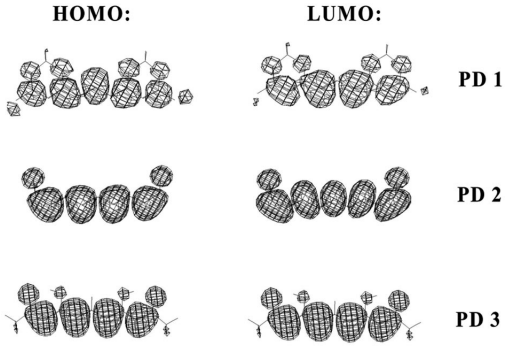


Figure 1. HOMO and LUMO shapes for PDs **1**, **2** and **3** calculated by the ab initio MO method at the UHF/6–31G** level of theory.

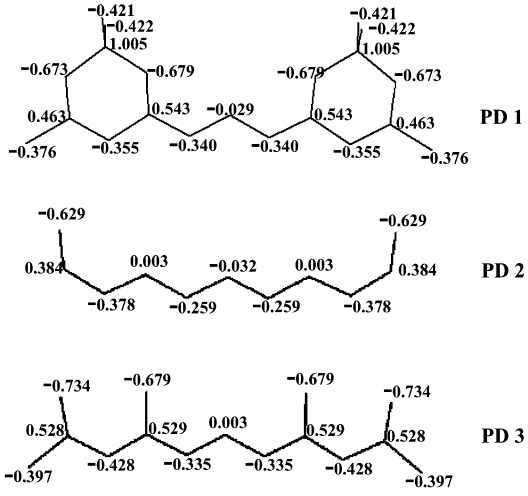
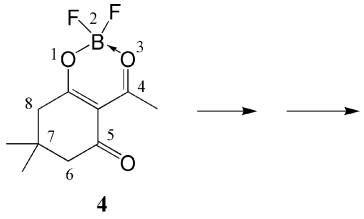


Figure 2. Atomic charges for PDs **1**, **2** and **3** calculated by the ab initio MO method at the UHF/6–31G** level of theory.

As shown by us previously,[17] the boron chelate of 2-acetyldimedone (**4**) reacts with electrophiles to give the symmetric PD **5** as well as its unsymmetrical analogues. Though the exocyclic carbonyl groups conjugated with the dye chromophore produce no auxochromic effect (λ_{max} = 519 nm in CH_3CN both for **1** and for **5**), they make the structures of related dyes more solvolytically stable, due to electron withdrawal from the dioxaborine chelate ring.

On the other hand, it has been demonstrated[12] that bridge groups that make the dioxaborine ring coplanar with the rest of the PD molecule can substantially increase the molar absorption coefficients (ε) and the fluorescence quantum yields (Φ) of such dyes. In this context, it thus appears even more promising, from the spectroscopic point of view, to annelate the dioxaborine chelate ring to the 1,3-dimethyl-



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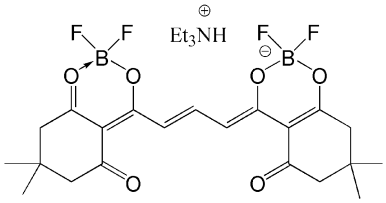

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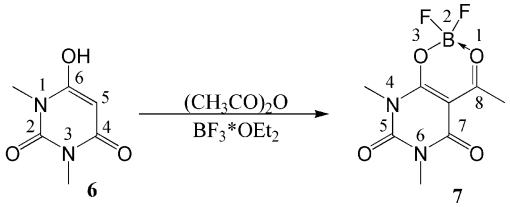
barbituric acid (**6**) residue rather than to dimedone, since the former component has a more planar molecular structure and bears an additional carbonyl group. The desired bicyclic nucleus **7** was obtained by the known procedure,[20] with the strong nucleophilic centre C-5 of the pyrimidine system used for the construction of the boron chelate complex.



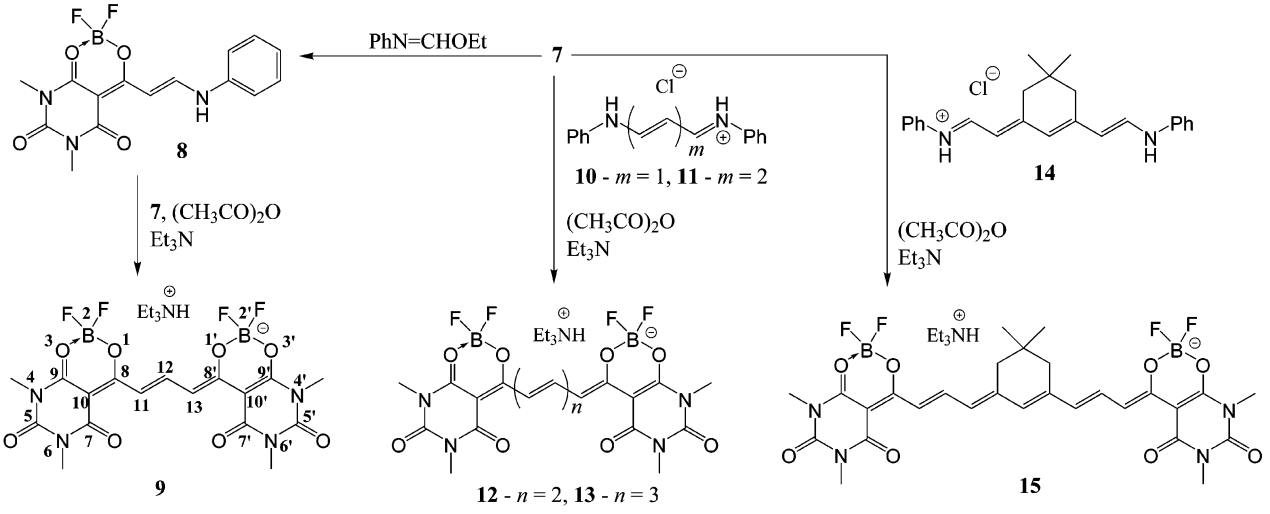
6 **7**

Taking advantage of the highly reactive methyl group at position 8, heterocycle **7** was treated according to conventional cyanine chemistry synthetic schemes; the series of PDs **9**, **12**, **13** and **15** was thus produced with the goals of research into the dyes' electronic structures and spectral properties in relation to variation in PC length (Scheme 1). Table 2 presents the spectral luminescence parameters of the new PDs, together with those of the previously obtained dye **5**. Though the absorption and fluorescence maxima (represented by λ_{max} and λ^{fl}_{max}, respectively) of carbocyanine **9** are only slightly shifted to longer wavelengths in relation to PD **5**, its absorption intensity (ε), fluorescence quantum yield (Φ), and Stokes shift ($\Delta\tilde{\nu}$) are significantly increased. To elucidate the effect of end group topology on the π-electronic properties of 2,2-difluoro-1,3,2-dioxaborine carbocyanines, ab initio calculations for PDs **5** and **9** were carried out (the results are demonstrated in Figure 3).

Table 2. Spectral luminescence properties of PDs **5**, **9**, **12**, **13** and **15**.

Dye	λ_{max} [nm] ($\varepsilon\cdot10^{-5}$, $M^{-1}cm^{-1}$) CH_3CN	λ_{max} [nm] ($\varepsilon\cdot10^{-5}$, $M^{-1}cm^{-1}$) CH_2Cl_2	λ^{fl}_{max} [nm] CH_2Cl_2	$\Delta\tilde{\nu}$ [cm^{-1}]	Φ
5	519 (1.756)	525 (1.553)	535	356	0.11
9	525 (2.095)	530 (1.693)	546	553	0.31
12	625 (2.221)	630 (2.028)	651	512	0.82
13	725 (1.613)	735 (1.766)	760	448	0.43
15	838 (1.111)	844 (1.283)			

In PD **5**, the sp^3-hybridized carbon atoms in the cyclohexane rings cause nonplanarity of the dye structure, so that the non-chelated carbonyl groups are turned out of the plane of the polymethine chromophore by 18°. In spite of the deplanarization, the atoms of the twisted carbonyl groups have nonzero HOMO coefficients, thus implying a certain degree of conjugation with the PC. PD **9** is characterized by a more planar structure, as its pyrimidine moiety lies in the chromophore plane. The carbonyl groups at positions 5 and 5′, as well as the nitrogen atoms at positions 4 and 4′, are also involved in the first electronic transition. It is likely that the enhanced absorption and fluorescence intensity observed on going from PD **5** to **9** is partially at-



Scheme 1. Synthesis of a series of PDs: **9**, **12**, **13** and **15**.

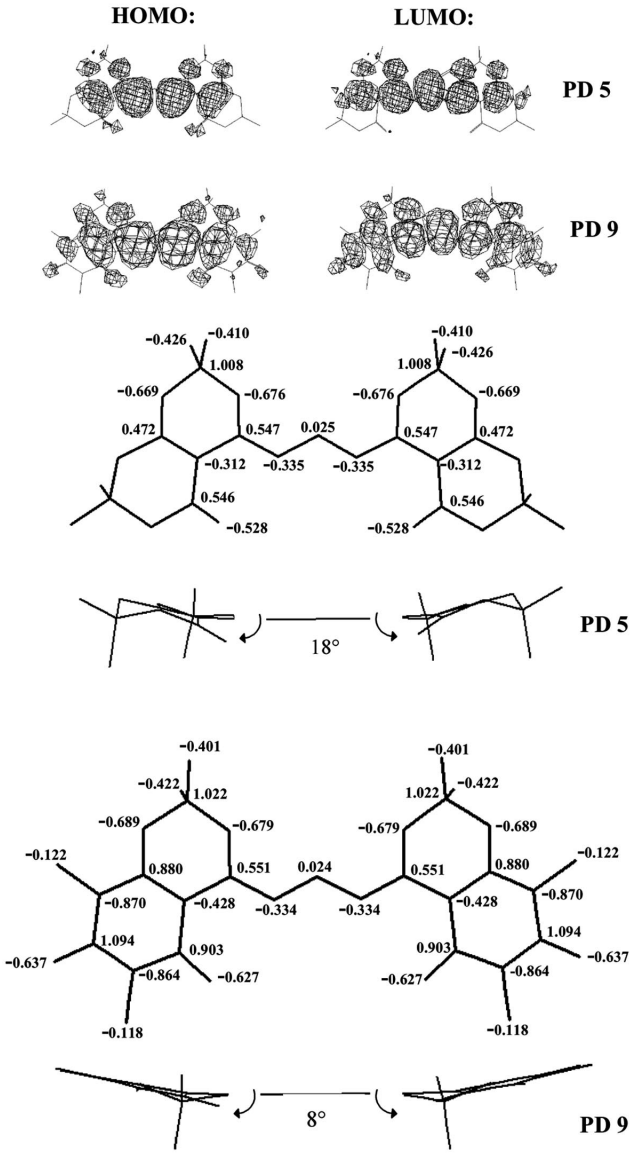


Figure 3. HOMO and LUMO shapes, atomic charges and molecular projections (side views) for dioxaborine PDs **5** and **9** calculated by the ab initio MO method at the UHF/6–31G** level of theory.

tributable to the better conjugation between the heterocyclic end residues and the PC in the latter molecule, whereas the larger Stokes shift of PD **9** can be attributed to the electron effect of the nitrogen atoms in the pyrimidine moiety. The effect of the end group structure on the dye frontier MO energies is illustrated in Table 3.

Table 3. HOMO and LUMO energies for PDs **5** and **9** calculated by the ab initio MO method at the UHF/6–31G** level of theory.

Dye	E_{HOMO} [eV]	E_{LUMO} [eV]
5	–4.52	4.08
9	–4.77	3.87

Comparison of the data listed in Tables 1 and 3 suggests that the annelation of the simple dioxaborine residues (in PD **1**) with the alicyclic moieties (as in PD **5**) and then with the heterocyclic nucleus (as in PD **9**) results in increasing stabilization of the dye frontier levels: when passing from **1** to **5** and then to **9**, the initial HOMO energy is lowered by 0.25 eV in each modification, while the corresponding values for the LUMOs amount to 0.29 and 0.21 eV.

The electronic structures of carbocyanines **5** and **9** approach the polymethinic type, as evidenced by the vinylene shifts of close to 100 nm (the typical value for symmetric PDs), as well as by the alternation of positive and negative atomic charges in the chromophore, supported both by the quantum chemical computational results for the two dyes (see Figure 3) and by the ^{13}C NMR spectroscopic data for PD **9** (see Table 4).

Table 4.[a] The chemical shifts of the ^{13}C NMR signals and the corresponding ab initio calculated charges on the carbon atoms in the chromophore of PD **9**.

Carbon atom number	δ [ppm]	q
9	173.3	0.880
10	90.0	–0.428
8	165.3	0.551
11	108.2	–0.334
12	152.9	0.024

[a] The data for half of the symmetric main chromophore are listed. For the δ values of the other carbon atoms see Exp. Sect.

It can be seen from Table 4 that the calculated charges correlate qualitatively with the chemical shifts of the ^{13}C NMR signals from the carbon atoms in the PC. A positive charge on a C atom in the dye chromophore corresponds to its chemical shift in the ^{13}C NMR spectrum being between 153 and 173 ppm, while a negative charge of a chromophore C atom corresponds to its chemical shift in the ^{13}C NMR spectrum being close to 100 ppm. A discrepancy for the atom C-12 may arise from the overestimated C–H bond polarization typical of the computational method used.

Analysis of absorption band shapes and, in particular, halfwidths (S) for PDs **9**, **12**, **13** and **15** (see Figure 4 and Table 5) reveals a gradual weakening of the main spectral maxima for tricarbo- and tetracarbocyanines, together with a band broadening on going from dichloromethane to the more polar acetonitrile. The absorption band of the tetracarbocyanine **15** demonstrates an extended short-wavelength tail, which can hardly be associated with vibrational transitions. Nor does it result from higher excitations (e.g., the $S_0 \rightarrow S_2$ transition), as evidenced by previous studies[21a,21b] involving fluorescence anisotropy measurements of the fluorescence excitation spectra and two-photon absorption measurements for some cationic PDs.[21a,21b] This feature is due, rather, to the increased contribution of the electronically unsymmetrical resonance structure of the dye, which is favoured by the absorption shift to the near IR region and by the increasing solvent polarity.[21] Importantly, the electron symmetry break for PD **15** occurs at shorter wavelengths than for cationic and anionic PDs,[21] and also for the previously described symmetric tetracarbocyanine with the 2,2-difluoro-1,3,2-dioxaborine end groups.[8]

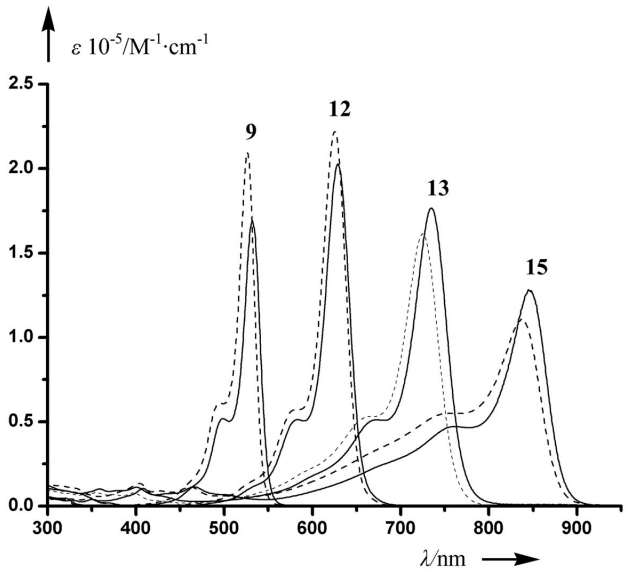


Figure 4. Absorption spectra for PDs **9**, **12**, **13** and **15** in CH_2Cl_2 (solid lines) and CH_3CN (dashed lines).

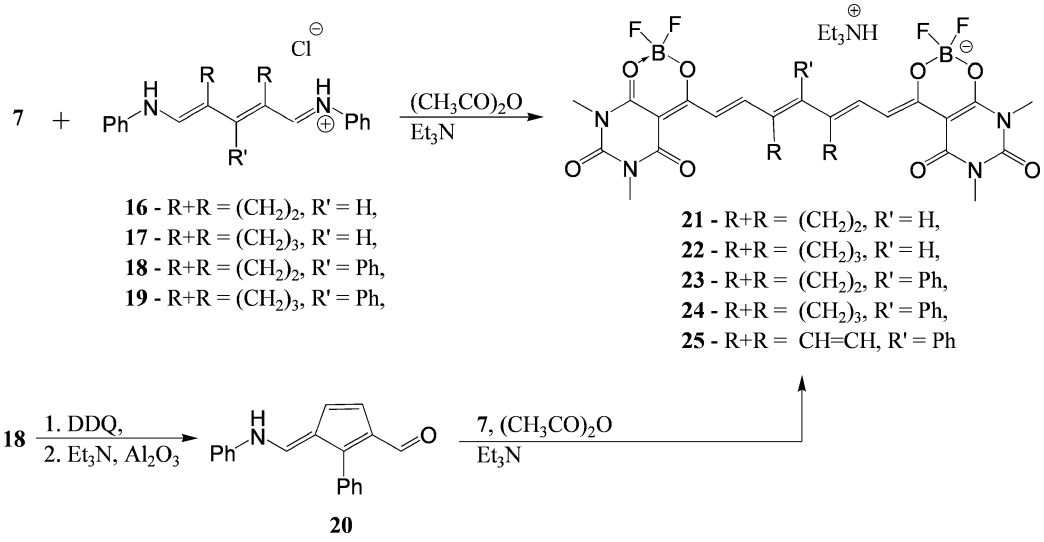
Table 5. Absorption band halfwidths for PDs **9**, **12**, **13** and **15**.

Dye	*n*	*S* [cm^{-1}] (CH_2Cl_2)	*S* [cm^{-1}] (CH_3CN)
9	1	818	764
12	2	812	836
13	3	849	922
15	4	810	1262

To minimize solvation effects, the luminescence properties of the PDs obtained were studied in dichloromethane, a weakly polar solvent. From analysis of the fluorescent measurements for the PD series **9**, **12** and **13** (see Table 2) it follows that, as in the case of cationic PDs,[22] the PC lengthening causes a regular bathochromic shift of the fluorescent maxima λ_{max}^{fl}, as well as the absorption maxima λ_{max}, by a value of about 100 nm, while the Stokes shift reduces on passing from shorter to longer vinylogues. The luminescence efficiencies of cyanines **9**, **12** and **13** also behave like those of cationic dyes. On going from the carbo- to the dicarbocyanine, the Φ value increases to a record high value among the known open-chain PDs (0.82) and then reduces for tricarbocyanine. The latter effect is probably due to the enhancement of internal conversion, which becomes a significant deexcitation channel for most PDs with the absorption wavelengths over 700 nm.[23]

Introduction of bridge groups into the various positions of the polymethine chromophore is known to be an advantageous approach to PD design, enabling fine and efficient tuning of absorption and luminescence in a specified spectral region.[24] As has been shown previously,[12] cyclizations of different portions of the conjugated chain with the aid of bridge groups makes it possible to vary the positions and intensities of the absorption and fluorescence maxima of dioxaborine carbocyanines. It is noteworthy that the coplanarization of the dioxaborine nucleus and the trimethine chain can cause not only spectral band shifts but also distortions of the chromophore system arising from bridge-induced steric hindrance. As a result, the fluorescence quantum yields of bridged dioxaborine carbocyanines can decrease drastically. Thus, in order to study a possibly "pure" effect of various bridge groups on the colour of dioxaborine PDs, with the minimized bridge-induced geometry perturbations, we synthesized tricarbocyanines **21**–**25** (Scheme 2) in which the end heterocyclic nuclei are sufficiently distant from the substituents in the PC.

As shown by the spectroscopic data in Table 6, the effects of cyclic bridge groups on the absorption band positions are much the same for dioxaborine PDs as for cationic dyes.[24] The dimethylene and trimethylene bridge groups, when introduced into the central positions of the PCs (as in PDs **21** and **22**, **23** and **24**) give rise to regular bathochromic shifts of spectral maxima, the former residue causing more pronounced changes. The presence of vinylene groups



Scheme 2. Synthesis of series of PDs **21**–**25**.

Table 6. Spectral luminescence properties of PDs **21**–**25**. The differences in absorption and fluorescent maximum positions, $\Delta\lambda_{max}$ and $\Delta\lambda^{fl}_{max}$, are calculated with reference to open-chain tricarbocyanine **13**.

Dye	λ_{max} [nm] [ε 10^{-5} M^{-1}·cm^{-1}] CH_3CN	λ_{max} [nm] [ε 10^{-5} M^{-1}·cm^{-1}] CH_2Cl_2	$\Delta\lambda_{max}$ [nm] CH_3CN/CH_2Cl_2	λ^{fl}_{max} [nm] CH_2Cl_2	$\Delta\lambda^{fl}_{max}$ [nm]	$\Delta\tilde{\nu}$ [cm^{-1}]	Φ
21[a]	773	783	48/48	800	40	271	
22	738 (1.896)	746 (1.551)	13/11	768	8	384	0.20
23	778 (2.001)	786 (1.682)	53/51	812	52	407	0.07
24	755 (2.355)	759 (1.656)	30/24	784	24	420	0.09
25	667 (2.077)	677 (1.619)	–58/–58	698	–62	444	0.15

[a] Because of the high lability of dye solutions, spectra were measured only qualitatively.

bound to the same positions in the chromophore (PD **25**) causes absorption and fluorescence maxima to shift hypsochromically. It should be noted that the observed band shifts are almost insensitive to the nature of the solvent and have closely similar magnitudes in absorption and fluorescence spectra. Contrastingly, the band intensities and shapes prove to depend substantially on the solvent parameters. Dye **13** dissolved in dichloromethane exhibits the most intense absorption among the tricarbocyanines under study (see Table 2). In this solvent, the bridge groups and the *meso*-phenyl substituent in the chromophore slightly reduce the molar extinction coefficients of PDs **22**, **23**, **24** and **25** (by 12.2, 4.8, 6.2, and 8.3%, respectively) and the absorption band halfwidths also change negligibly (Figure 5, Table 5 and Table 7). Contrary to this, acetonitrile solutions of the dyes (Figure 6) show increases in absorption intensities on passing from unsubstituted PD **13** to bridged PDs **22**, **23**, **24** and **25** (by 17.5, 24.0, 46.0, and 28.8%, respectively – cf. Table 2 and Table 6). In addition, the dye absorption bands become much narrower on chromophore bridging (cf. Tables 5 and 7). Such a trend may be due to the fact that the bridge groups and the phenyl residue hinder the nucleophilic solvation of the chromophore, which is typical of PD solutions in acetonitrile and normally leads to broadened absorption bands (resulting from the superposition of bands for variously solvated dye forms).

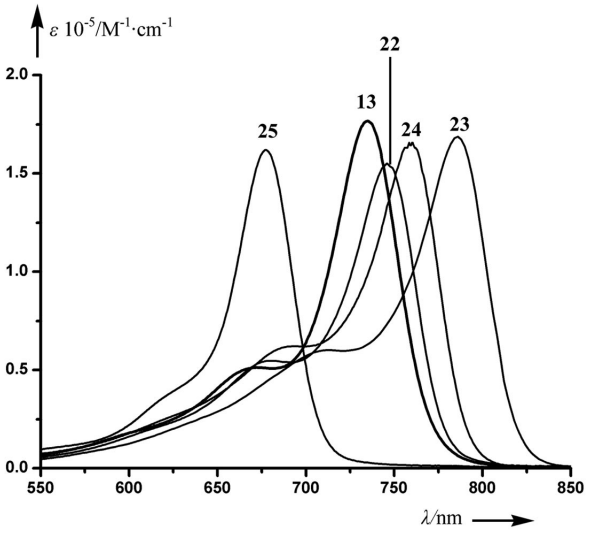


Figure 5. Absorption spectra of tricarbocyanines **13** and **22**–**25** in CH_2Cl_2.

Table 7. Absorption band halfwidths for tricarbocyanines **22**–**25**.

Dye	S [cm^{-1}] (CH_2Cl_2)	S [cm^{-1}] (CH_3CN)
22	866	817
23	858	798
24	893	764
25	877	906

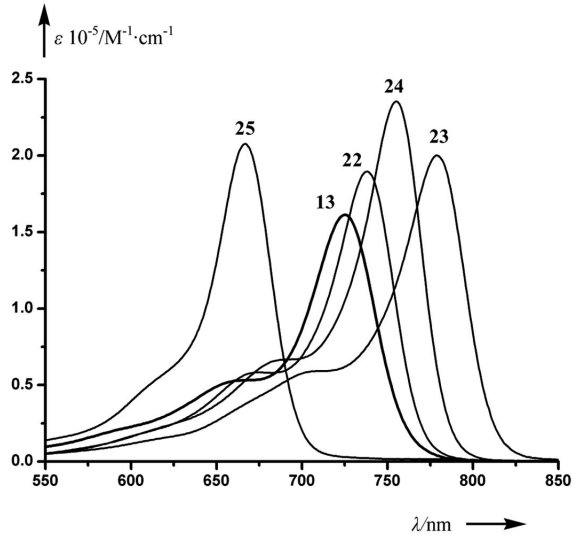


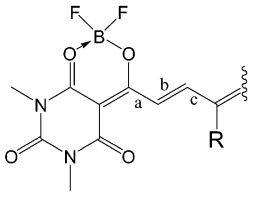
Figure 6. Absorption spectra of tricarbocyanines **13** and **22**–**25** in CH_3CN.

The *meso*-phenyl substituents in tricarbocyanines **23** and **24** act as slight electron acceptors and hence should cause bathochromic shifts, according to the Foerster–Dewar–Knott rule.[19] This effect is only slight in PD **23**, containing the strongly electron-donating dimethylene bridge: the red shifts amount to 5/3 nm (CH_3CN/CH_2Cl_2) for absorption and to 12 nm (CH_2Cl_2) for fluorescence. For comparison, PD **24**, containing the slightly electron-donating trimethyl-

ene bridge, exhibits much stronger bathochromic shifts of absorption and fluorescence, so that the respective values are 17/13 nm (CH_3CN/CH_2Cl_2) and 16 nm (CH_2Cl_2).

Unlike dye absorption intensity in dichloromethane, which is almost insensitive to bridging and substitution effects, fluorescence of bridged and phenyl-substituted PDs **22**, **23**, **24** and **25** in the same solvent is characterized by decreased quantum yields in relation to the open-chain unsubstituted PD **13** (cf. Table 2 and Table 6). It can thus be assumed that the luminescence efficiency falls off because of the electronic factors rather than steric perturbations of the PCs by substituents. To verify this conjecture, we analysed the AM1-calculated bond orders in the PCs of compounds **13**, **22**, **23**, **24** and **25** (see Table 8). As can be seen from the computational results, introduction of a dimethylene and a trimethylene bridge and a phenyl ring (PD **22**, **23** and **24**) into the chromophore leads to bond equalization, with their order tending to 1.5. Therefore, photoisomerizations become less probable in the excited state.

Table 8. AM1-calculated bond orders in the PCs of tricarbocyanines **13**, **22**, **23**, **24** and **25**.



Bond of the dye molecule	**13**	**22**	**23**	**24**	**25**
a	1.322	1.323	1.334	1.325	1.276
b	1.373	1.377	1.361	1.373	1.437
c	1.363	1.344	1.370	1.347	1.273

At the same time, the electron-donating effects of the dimethylene and trimethylene groups and the acceptor effect of the phenyl substitute cause the fluorescence maximum to shift notably to longer wavelengths (about 800 nm). Thus, it is likely that the reduced quantum yields of PDs **22**–**24** are mainly attributable to internal conversion, which is consistent with the fact that the Φ values decrease as the bathochromic effect of the substituent in the PC rises. Introduction of a vinylene bridge results in hypsochromically shifted spectral maxima and hence in a decreased probability of internal conversion. On the other hand, dye **25** exhibits a more pronounced bond alternation in the PC and thus affords more possibilities for photoisomerizations than its unsubstituted counterpart **13**. It is evident that deeper insight into the fluorescence quenching mechanisms for PDs **22**–**25** will require a special study.

Conclusions

In summary, we have investigated the electronic structures and spectral properties of symmetric PDs derived from 2,2-difluoro-1,3,2-dioxaborine. Ab initio calculations performed for anionic PDs **1**–**3** enabled the elucidation of the effects of BF_2 groups on the frontier level positions and electron-density distributions in dioxaborine dye molecules. In relation to the analogous dye structures with boron-free acyclic end groups, dioxaborine PDs have somewhat increased first transition energies and notably stabilized HOMOs and LUMOs. At the same time, the involvement of the BF_2 group in the chelate dioxaborine ring causes charge equalization on the adjacent oxygen atoms but exerts practically no effect on the electron-density distribution in the PC.

To study the design potential for dioxaborine PDs, we synthesized the annelated polycarbocyanine series **9**, **12**, **13** and **15**, as well as the tricarbocyanine series **21**–**25** with the variously bridged chromophores. As shown by enhanced absorption and fluorescence, and by the lower-lying frontier energy levels of PD **9** in relation to PD **5**, the novel heterocyclic nucleus **7** shows much promise in the construction of various π-conjugated systems with favourable hole-blocking and electron-injection behaviour.[18]

The calculated electron-density distribution for PD **9** and its ^{13}C NMR signals, as well as the electronic spectral characteristics of the vinylogous series **9**, **12**, **13** and **15**, point to polymethinic natures of the chromophores in the dioxaborine dyes. Dye **12** exhibits a record high fluorescence quantum yield (0.82) among the known open-chain polymethine dyes.

Modification of the PC in tricarbocyanine **13** by introduction of various substituents leads to the PD series **21**–**25**, with their optical behaviour resembling that of structurally similar cationic PDs.[24] However, bridging of the PC with a vinylene group, as in PD **21**, does not cause fluorescence enhancement, contrary to what has been observed for analogous indotricarbocyanines.[24]

This study demonstrates well that structural variation both of end nuclei and of the PCs of dioxaborine dyes offers the advantage of efficient, wide-ranging control of their optical properties, thus showing much practical promise.

Experimental Section

General: Charge distributions and frontier molecular orbital energies for dyes **1**, **2**, **3**, **5** and **9** were determined for fully optimized ground-state geometries by standard ab initio calculations with the aid of the HyperChem. Package at the Unrestricted Hartree–Fock (UHF) level of theory and with 6–31G** as a basis set.

^1H NMR spectra were obtained with Varian VXR 300 and Bruker Avance DRX 500 instruments at 300 and 500 MHz, respectively (25 °C); the ^{13}C NMR spectrum was obtained with a Varian Gemini 2000 instrument at 100 MHz (25 °C). Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Fluorescence spectra were taken on Cary Eclipse and Hitachi F4010 fluorescence spectrophotometers and were fully corrected. The fluorescence quantum yields (Φ) of the dyes synthesized were determined by the known method[25] relative to Rhodamine 6G (Φ = 0.95 in EtOH)[26] for compounds **5** and **9**, Nile Blue (Φ = 0.27 in MeOH)[27] for compound **12**, indotricarbocyanine (Φ = 0.28 in EtOH)[23,28] for compounds **13**, **22**, **23** and **24** and Rhodamine 800 (Φ = 0.086 in MeOH)[29] for compound **25**.

Boron Complex 7: A mixture of 1,3-dimethylbarbituric acid (**6**, 4.68 g, 30 mmol) and glacial acetic acid (4.5 mL) was heated at reflux until a clear solution was obtained, followed by cooling to room temperature. Boron trifluoride etherate (4.6 mL, 36 mmol) was added, and the reaction mixture was heated at reflux for 1 min. After the system had cooled to room temperature, acetic anhydride (8.5 mL, 90 mmol) was added. The obtained mixture was heated at 95 °C for 4 h, allowed to cool to room temperature and allowed to stand for 2 h. The resulting solid was suspended in diethyl ether (30 mL). The precipitate was filtered off, washed with diethyl ether (3 × 15 mL), and used in the next steps without further purification. Yield 6.7 g (91%); m.p. 172–173 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 3.29 (s, 3 H, NCH_3), 3.22 (s, 3 H, NCH_3), 2.66 (s, 3 H, CH_3) ppm. $C_8H_9BF_2N_2O_4$ (245.98): calcd. C 39.06, H 3.69, N 11.39; found C 39.55, H 3.62, N 11.48.

Hemicyanine 8: A mixture of boron complex **7** (0.49 g, 2 mmol) and *N*-ethoxymethylidenaniline (ethyl isoformanilide, 0.33 g, 2.2 mmol) was heated at 60 °C for 1 h and then allowed to cool to room temperature. The resulting solid was suspended in diethyl ether (25 mL), and the precipitate was filtered off, washed with diethyl ether (2 × 10 mL), and recrystallized from acetic anhydride. Yield 0.56 g (81%); m.p. 227–229 °C (decomp). ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 11.93 [d, ^3J(H,H) = 13.5 Hz, 1 H, NH], 8.75 [t, ^3J(H,H) = 13.5 Hz, 1 H, CH], 7.20–7.52 (m, 5 × H_{Ar} + 1 H), 3.31 (s, 3 H, NCH_3), 3.21 (s, 3 H, NCH_3) ppm. $C_{15}H_{14}BF_2N_3O_4$ (349.10): calcd. C 51.61, H 4.04, N 12.04; found C 52.00, H 3.99, N 12.10.

Carbo-, Dicarbo- and Tricarbocyanines 9, 12, and 13 (General Procedure): Triethylamine (0.2 mL) was added to a thoroughly triturated mixture of boron complex **7** (0.25 g, 1 mmol), hemicyanine **8** (0.35 g, 1 mmol) or malonaldehyde dianil hydrochloride (0.13 g, 0.5 mmol), or glutaconaldehyde dianil hydrochloride (0.14 g, 0.5 mmol) in acetic anhydride (1.5 mL). The mixture was heated at 75 °C for 30 min, and was then allowed to cool to room temperature and to stand for 2 h. The resulting solid was suspended in diethyl ether (30 mL). The precipitate was filtered off, washed with diethyl ether (2 × 15 mL) and (for compounds **12**, **13**) with water (2 × 10 mL), dried, and purified by a specific method.

Carbocyanine 9: Purification by recrystallization from CH_3CN. Yield 0.5 g (84%); m.p. 253–254 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 8.98 [t, ^3J(H,H) = 13.5 Hz, 1 H, CH_β], 7.57 [d, ^3J(H,H) = 13.5 Hz, 2 H, CH_α + CH_γ], 3.48 [q, ^3J(H,H) = 7.0 Hz, 6 H, 3 × $CH_3CH_2N^+H$], 3.40 (s, 6 H, 2 × NCH_3), 3.28 (s, 6 H, 2 × NCH_3), 1.43 [t, ^3J(H,H) = 7.0 Hz, 9 H, 3 × $CH_3CH_2N^+H$] ppm. ^{13}C NMR ([D$_3$]acetonitrile, HMDS): δ = 173.3 (C-9), 165.3 (C-8), 161.1 (C-7), 152.9 (C-12), 151.0 (C-5), 108.2 (C-11), 90.0 (C-10), 48.6 (3 × $CH_3CH_2N^+H$), 29.5 (NCH_3), 28.6 (NCH_3), 9.5 (3 × $CH_3CH_2N^+H$) ppm. $C_{23}H_{31}B_2F_4N_5O_8$ (603.14): calcd. C 45.80, H 5.18, N 11.61; found C 45.23, H 5.23, N 11.72.

Dicarbocyanine 12: The crude dye was dissolved in CH_3CN (7 mL) and the solid was filtered off. Ether (30 mL) was added to the filtrate and the mixture was allowed to stand for 1 h. The precipitate was filtered off and washed with diethyl ether (2 × 15 mL). Yield 0.27 g (87%); m.p. 249–250 °C. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, HMDS): δ = 7.98 [t, ^3J(H,H) = 13.2 Hz, 2 H, 2 × CH], 7.34 [d, ^3J(H,H) = 13.2 Hz, 2 H, 2 × CH], 6.45 [t, ^3J(H,H) = 13.2 Hz, 1 H, CH], 3.29 (s, 6 H, 2 × NCH_3), 3.18 (s, 6 H, 2 × NCH_3), 3.07 [q, ^3J(H,H) = 7.2 Hz, 6 H, 3 × $CH_3CH_2N^+H$], 1.17 [t, ^3J(H,H) = 7.2 Hz, 9 H, 3 × $CH_3CH_2N^+H$] ppm. $C_{25}H_{33}B_2F_4N_5O_8$ (629.18): calcd. C 47.72, H 5.29, N 11.13; found C 47.48, H 5.33, N 11.20.

Tricarbocyanine 13: The dye was purified similarly to dicarbocyanine **12**. Yield 0.25 g (76%); m.p. 168–169 °C. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, HMDS): δ = 7.76 [t, ^3J(H,H) = 13.2 Hz, 2 H, 2 × CH], 7.26–7.35 (m, 3 H, 2 × CH + CH), 6.36 [t, ^3J(H,H) = 13.2 Hz, 2 H, 2 × CH], 3.28 (s, 6 H, 2 × NCH_3), 3.17 (s, 6 H, 2 × NCH_3), 3.07 [q, ^3J(H,H) = 7.2 Hz, 6 H, 3 × $CH_3CH_2N^+H$], 1.17 [t, ^3J(H,H) = 7.2 Hz, 9 H, 3 × $CH_3CH_2N^+H$] ppm. $C_{27}H_{35}B_2F_4N_5O_8$ (655.21): calcd. C 49.49, H 5.38, N 10.69; found C 48.99, H 5.35, N 11.00.

Tetracarbocyanine 15: Triethylamine (0.3 mL) was added to a stirred suspension of compound **14**[24] (0.114 g, 0.3 mmol) in acetic anhydride (1.5 mL). The mixture was stirred until the blue precipitate was dissolved (for about 10 min), and boron complex **7** (0.149 g, 0.6 mmol) was then added. After the system had been stirred for another 30 min, ether (30 mL) was added and the resulting mixture was allowed to stand for 1 h. The precipitate was filtered off, washed with diethyl ether (3 × 15 mL) and water (2 × 10 mL) and dried. The resulting solid was suspended in ethyl acetate (2 mL); the precipitate was filtered off and washed with ethyl acetate (2 × 0.75 mL). Yield 0.035 g (16%); m.p. >310 °C. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile, HMDS): δ = 7.90 [t, ^3J(H,H) = 13.0 Hz, 2 H, 2 × CH], 7.30 [d, ^3J(H,H) = 13.0 Hz, 2 H, 2 × CH], 6.25–6.41 (m, 3 H, 2 × CH + CH), 3.29 (s, 6 H, 2 × NCH_3), 3.19 (s, 6 H, 2 × NCH_3), 3.08 [q, ^3J(H,H) = 7.2 Hz, 6 H, 3 × $CH_3CH_2N^+H$], 2.43 (s, 4 H, 2 × CH_2) 1.18 [t, ^3J(H,H) = 7.2 Hz, 9 H, 3 × $CH_3CH_2N^+H$], 0.97 (s, 6 H, 2 × CH_3) ppm. $C_{34}H_{45}B_2F_4N_5O_8$ (749.38): calcd. C 54.50, H 6.05, N 9.35; found C 54.12, H 6.12, N 9.63.

3-Anilinomethylene-2-phenylcyclopenta-1,4-diene-1-carbaldehyde (20): Compound **18**[24] (1.16 g, 3 mmol) was dissolved in $CHCl_3$ (120 mL) at reflux, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.36 g, 6 mmol) in $CHCl_3$ (100 mL) was added, and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with $CHCl_3$ (3 × 30 mL). The crystalline product was mixed with nitromethane (40 mL) and heated at reflux for 1 h. After cooling to room temperature, it was allowed to stand for 4 h. The solid was filtered off, washed with nitromethane (2 × 10 mL), and suspended in $CHCl_3$ (15 mL) without traces of EtOH. On addition of triethylamine (1 mL), the mixture was stirred for 10 min and purified by column chromatography on aluminium oxide 90 (standardized, Merck) ($CHCl_3$/MeOH 100:0.5). Yield 0.12 g (15%); m.p. 109–110 °C. ^{1}H NMR (500 MHz, [D$_6$]-DMSO, TMS): δ = 11.24 [d, ^3J(H,H) = 11.0 Hz, 1 H, NH], 9.49 (s, 1 H, CHO), 7.68 [d, ^3J(H,H) = 11.0 Hz, 1 H, CH], 7.36–7.51 (m, 7H_{Ar}), 7.28 [d, ^3J(H,H) = 7.3 Hz, 2 × H_{Ar}], 7.17 [t, ^3J(H,H) = 7.3 Hz, 1 × H_{Ar}], 7.02 [d, ^3J(H,H) = 5.0 Hz, 1 H, CH], 6.70 [d, ^3J(H,H) = 5.0 Hz, 1 H, CH] ppm. $C_{19}H_{15}NO$ (273.33): calcd. C 83.49, H 5.53, N 5.12; found C 83.64, H 5.42, N 5.13.

Tricarbocyanines 21–25 (General Procedure): Triethylamine (0.15 mL) was added to a mixture of boron complex **7** (0.185 g, 0.75 mmol) and compound **16**[24] (0.12 g, 0.38 mmol) or compound **17**[24] (0.12 g, 0.38 mmol), or compound **18** (0.15 g, 0.38 mmol) or compound **19**[24] (0.15 g, 0.38 mmol), or aldehyde **20** (0.1 g, 0.38 mmol) in acetic anhydride (1.5 mL). The mixture was heated at 75 °C for 15 min and cooled to room temperature. After addition of ether (30 mL), the mixture was allowed to stand for 1.5 h. The precipitate was filtered off, washed with diethyl ether (3 × 20 mL) and (for compounds **21**–**24**) with water (2 × 10 mL), dried, and purified by a specific method.

Tricarbocyanine 21: The dye was dissolved in CH_3CN (30 mL) and the solid was filtered off. Ether (100 mL) was added to the filtrate and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with diethyl ether (3 × 30 mL). Yield 0.10 g (30%); m.p. >310 °C. ^{1}H NMR (300 MHz, [D$_3$]acetonitrile,

HMDS): δ = 7.68 [d, J(H,H) = 13.5 Hz, 2 H, 2×CH], 7.22 [d, ^3J(H,H) = 13.5 Hz, 2 H, 2×CH], 7.00 (s, 1 H, CH), 3.29 (s, 6 H, 2×NCH_3), 3.19 (s, 6 H, 2×NCH_3), 3.05 [q, ^3J(H,H) = 7.3 Hz, 6 H, 3×$CH_3CH_2N^+H$], 2.71 (s, 4 H, 2×CH_2), 1.17 [t, ^3J(H,H) = 7.3 Hz, 9 H, 3×$CH_3CH_2N^+H$] ppm. $C_{29}H_{37}B_2F_4N_5O_8$ (681.25): calcd. C 51.13, H 5.48, N 10.28; found C 51.18, H 5.44, N 10.11.

Tricarbocyanine 22: The dye was dissolved in CH_3CN (30 mL) and the solid was filtered off. Ether (100 mL) was added to the filtrate and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with diethyl ether (2×25 mL). Yield 0.11 g (32%); m.p. 293 °C. ^{1}H NMR (300 MHz, [D_3]acetonitrile, HMDS): δ = 9.31 (s, 1 H, NH), 7.58 [d, J(H,H) = 13.2 Hz, 2 H, 2×CH], 7.38 [d, ^3J(H,H) = 13.2 Hz, 2 H, 2×CH], 7.14 (s, 1 H, CH), 3.28 (s, 6 H, 2×NCH_3), 3.18 (s, 6 H, 2×NCH_3), 3.07 [q, ^3J(H,H) = 7.2 Hz, 6 H, 3×$CH_3CH_2N^+H$], 2.36 [t, ^3J(H,H) = 6.0 Hz, 4 H, 2×CH_2], 1.76 [q, ^3J(H,H) = 6.0 Hz, 2 H, CH_2], 1.17 [t, ^3J(H,H) = 7.2 Hz, 9 H, 3×$CH_3CH_2N^+H$] ppm. $C_{30}H_{39}B_2F_4N_5O_8$ (695.27): calcd. C 51.82, H 5.65, N 10.07; found C 51.68, H 5.59, N 10.08.

Tricarbocyanine 23: The dye was dissolved in CH_2Cl_2 (20 mL) and the solid was filtered off. Ether (70 mL) was added to the filtrate and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with diethyl ether (2×25 mL). Yield 0.18 g (66%); m.p. >310 °C. ^{1}H NMR (300 MHz, [D_3]acetonitrile, HMDS): δ = 7.45–7.49 (m, 3 H), 7.27–7.31 (m, 4 H), 7.18–7.22 (m, 2 H), 3.24 (s, 6 H, 2×NCH_3), 3.18 (s, 6 H, 2×NCH_3), 3.05 [q, ^3J(H,H) = 7.0 Hz, 6 H, 3×$CH_3CH_2N^+H$], 2.82 (s, 4 H, 2×CH_2), 1.16 [t, ^3J(H,H) = 7.0 Hz, 9 H, 3×$CH_3CH_2N^+H$] ppm. $C_{35}H_{41}B_2F_4N_5O_8$ (757.36): calcd. C 55.51, H 5.46, N 9.25; found C 55.43, H 5.48, N 9.31.

Tricarbocyanine 24: The dye was purified similarly to tricarbocyanine **23**.Yield 0.15 g (52%); m.p. 204–206 °C. ^{1}H NMR (300 MHz, [D_3]acetonitrile, HMDS): δ = 7.36–7.48 (m, 5 H), 7.20 [d, ^3J(H,H) = 13.2 Hz, 2 H, 2×CH], 7.08–7.16 (m, 4 H), 3.26 (s, 6 H, 2×NCH_3), 3.17 (s, 6 H, 2×NCH_3), 3.04 [q, ^3J(H,H) = 7.0 Hz, 6 H, 3×$CH_3CH_2N^+H$], 2.51 (s, 4 H, 2×CH_2), 1.90 (s, 2 H, CH_2), 1.18 [t, ^3J(H,H) = 7.0 Hz, 9 H, 3×$CH_3CH_2N^+H$] ppm. $C_{36}H_{43}B_2F_4N_5O_8$ (771.37): calcd. C 56.05, H 5.62, N 9.08; found C 55.93, H 5.70, N 9.12.

Tricarbocyanine 25: The crude dye was dissolved in CH_3CN (15 mL) at 50 °C and the solid was filtered off. Ether (50 mL) was added to the filtrate and the mixture was allowed to stand for 2 h. The precipitate was filtered off and washed with diethyl ether (2×15 mL). Yield 0.18 g (63%); m.p. >310 °C. ^{1}H NMR (300 MHz, [D_3]acetonitrile, HMDS): δ = 7.86–7.91 (m, 3 H), 7.40–7.52 (m, 4 H), 7.20–7.26 (m, 2 H), 6.79 (s, 2 H, 2×CH), 3.28 (s, 6 H, 2×NCH_3), 3.21 (s, 6 H, 2×NCH_3), 3.01 [q, ^3J(H,H) = 7.2 Hz, 6 H, 3×$CH_3CH_2N^+H$], 1.14 [t, ^3J(H,H) = 7.2 Hz, 9 H, 3×$CH_3CH_2N^+H$] ppm. $C_{35}H_{41}B_2F_4N_5O_8$ (757.36): calcd. C 55.51, H 5.46, N 9.25; found C 55.43, H 5.48, N 9.31.

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