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Boradipyrromethenecyanines

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Keywords: BODIPY compounds / Boron dipyrromethene dye / Merocyanine / Polymethine dye / Long-wavelength dye / Heterocycles

A series of *meso*-polymethine-substituted BODIPY compounds have been synthesized by the reaction of *meso*-methyl-3,5-diphenylboradipyrromethene with a number of hemicyanine derivatives. The dyes obtained exhibit intense long-wavelength absorption, but weak fluorescence. Upon protonation of the dyes the long-wavelength band disappears and the intensity of the short-wavelength band increases significantly. It has been shown that the properties of the dyes obtained, which we call boradipyrromethenecyanines, are closely related to those of merocyanine dyes rather than those of boron dipyrromethenes.

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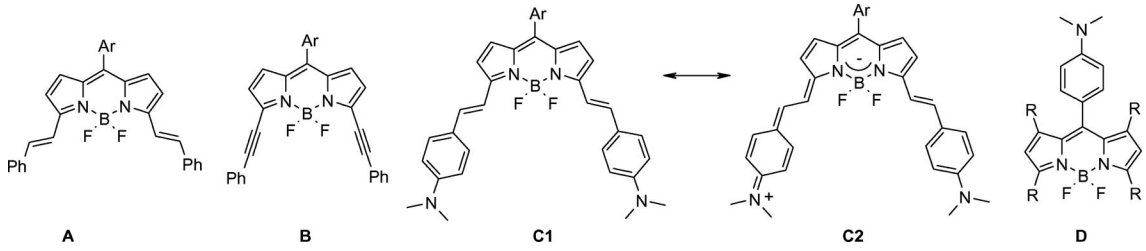
Introduction

Boradipyrromethene dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes, BODIPY, BDP) have attracted considerable attention over the past two decades. The ever increasing interest in this type of compound is due to their excellent thermal, chemical, and photochemical stability, high molar absorptivity, high fluorescence quantum yields, insensitivity to solvent polarity and pH, long excited-state lifetimes, a large two-photon cross-section for multiphoton excitation, lack of ionic charge, and good solubility.[1] However, the absorption maxima of the majority of BODIPYs are below 600 nm. Long-wavelength dyes are important for both basic and applied research[2] and therefore many synthetic approaches exist for modifying the BODIPY core to give structures that absorb at longer wavelengths. One of the most promising approaches to the modification of BODIPY is its peripheral functionalization with conjugated chromophores.

For example, distyryl-substituted derivatives **A** exhibit a bathochromic shift of the absorption maximum of 79 nm compared with diphenyl-substituted analogues (see Scheme 1). The bathochromic shift of phenylethynyl analogues **B** is somewhat smaller, however, both **A** and **B** are typical BODIPYs and demonstrate high fluorescence quantum yields that are fairly insensitive to the nature of the solvent.[3] The introduction of additional 4-(dialkylamino) substituents into **A** (structure **C**[4]) results in even more pronounced spectral changes, with bathochromic shifts of around 80 nm. The structures **C** exhibit very small solvatochromism and considerable positive solvatofluorochromism. The fluorescence intensity increases significantly with decreasing solvent polarity. Protonation of the dialkylamino groups in **C** leads to optical properties that are very similar to those of **A**. Although the charge-separated mesomeric form **C2** is typical of merocyanine dyes, the properties of the structures **C** (e.g., easy protonation, weak solvatochromism, and relatively low molar absorptivity) as a whole do not correspond to those of merocyanines. Thus, the dialkylamino groups in structures **C** provide considerable spectral changes, but do not change the color of the



Scheme 1.

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BODIPY core. Therefore in this case they cannot be referred to as true "end groups" as defined in the ideology of polymethine dyes.

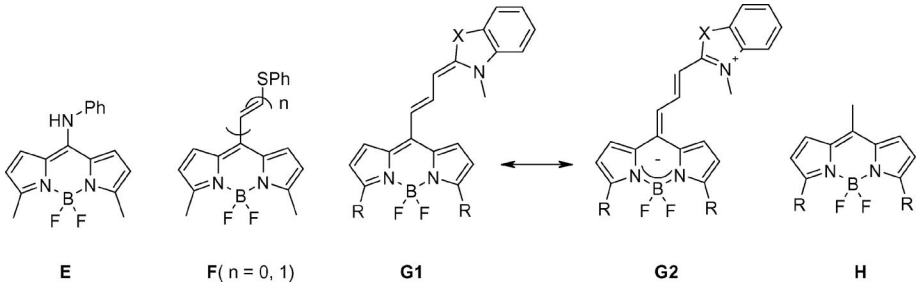
This statement is even more evident for structures **D**.[3a,4b,5] In this case the dialkylamino group leads to a small hypsochromic shift of the BODIPY absorption maximum. The fluorescence quantum yields are quenched in polar solvents but not in nonpolar media. Protonation of the dialkylamino groups in **D** results in both a small bathochromic shift of the BODIPY absorption maximum and the appearance of fluorescence. For steric reasons the conjugation of the dialkylaminophenyl fragment with the BODIPY chromophore in **D** is rather inefficient, but fluorescence quenching occurs in the planar structure **E**[6] (see Scheme 2). Compounds of type **F** (n = 0, 1) were also described in this report. Thus far this is the only example of a *meso*-vinyl-substituted BODIPY reported in the literature. Introduction of an additional vinyl unit into the *meso* position of BODIPY does not influence its absorption maximum, but leads to a bathochromic shift of 26 nm in the emission spectrum.

In this paper we report the synthesis and spectral study of a new series of dyes of type **G** that combine the polymethine and dipyrromethene chromophoric fragments. It was our expectation that such a combination of chromophores would have a considerable effect on spectral properties enabling the design of deeply colored dyes.

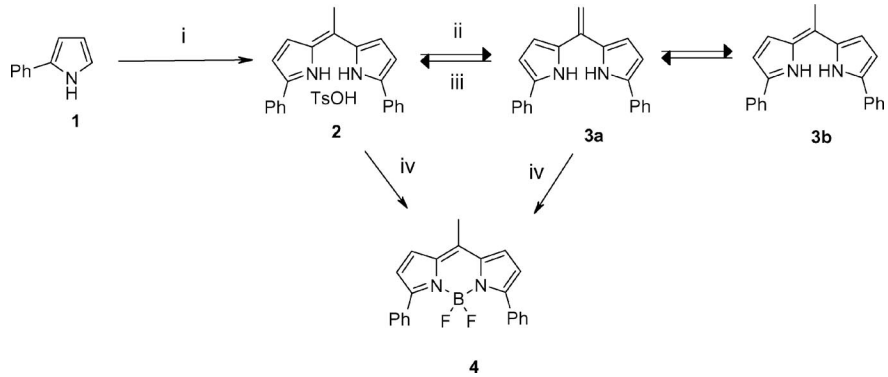
Results and Discussion

The selection of a BODIPY derivative suitable for further derivatization to obtain dyes **G** was based on the following. We assumed that the methyl group in the *meso* position of structure **H** should be active enough for Knoevenagel-type condensations. In addition, the positions next to the *meso*-methyl group should not be substituted to avoid steric problems. Therefore, the readily available 2-phenylpyrrole (**1**)[7] was used in the first synthetic step. As shown in Scheme 3 the salt **2** was prepared by treating **1** with triethyl orthoacetate and *p*-toluenesulfonic acid. This approach is more convenient compared with other reported methods that use chloroacetaldehyde[8] or acetyl chloride.[9]

The salt *p*-toluenesulfonate·**2** partly dissociates in polar solvents, so its ^{1}H NMR spectrum in [D$_6$]DMSO reveals signals of both the protonated form and the free base **3**. The latter was prepared from **2** by the action of triethylamine. Compound **3** is quite stable in ambient conditions, in contrast to some alkyl-substituted dipyrrolylethylenes that are susceptible to oxidation.[8] Compound **3** exists in an equilibrium of two tautomeric forms, an ethylenic form **3a** and a *meso*-methyldipyrromethene form **3b**, which can be observed in the ^{1}H NMR spectra. The ethylenic form prevails in polar [D$_6$]DMSO, whereas the *meso*-methyldipyrromethene tautomer is the major component in CDCl$_3$.



Scheme 2.



Scheme 3. Synthetic route to the key compound **4**. Reagents: i) CH$_3$C(OEt)$_3$, TsOH; ii) Et$_3$N; iii) TsOH; iv) BF$_3$·OEt$_2$, Et$_3$N.

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The reaction of either **3** or **2** with BF_3–OEt_2 in the presence of a base led to the fluorescent boron difluoride complex **4**, a key intermediate in the synthesis of *meso*-polymethine-substituted BODIPY derivatives.

The methyl group in the dye **4** is not highly reactive, however, it is still able to participate in some condensation reactions (Scheme 4). Attempts to prepare the formyl derivatives **5** and **6** failed. Nevertheless, a standard Vilsmeier-type formylation of **4** gave rise to the disubstituted product **7**. Even though diformylation under the given conditions is known,[10] in our case, as well as in the case described in ref.[10b], it turned out to be impossible to stop the reaction at the monoformylation stage. A mixture of the diformylated derivative **7** and the unreacted **4** was formed when the Vilsmeier reagent and **4** were used in a 1:1 or lower ratio. Nevertheless, the monoformylated product **8** was obtained by the reaction of compound **4** with DMF acetal. The reaction of intermediate **8** with aniline resulted in the hemicyanine **6**. However, further synthetic transformations of **6** (e.g., reactions with quaternary salts of heterocycles) were not efficient.

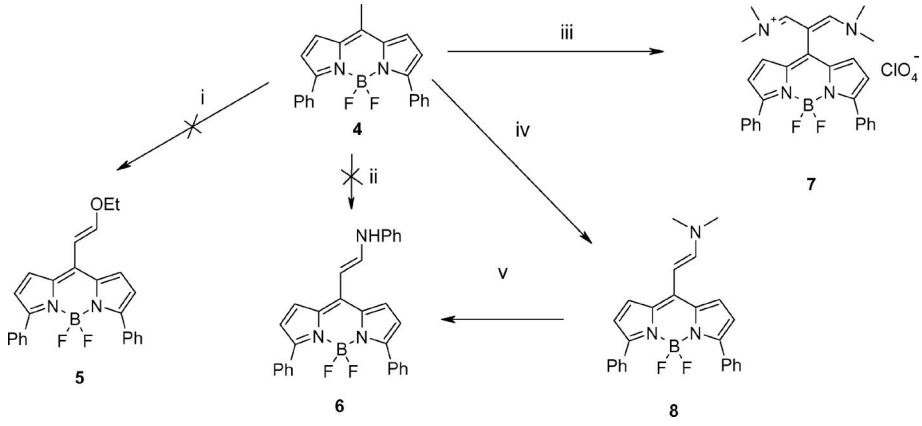
An attempt to prepare the styryl derivative **9** by the reaction of BODIPY derivative **4** with *p*-(dimethylamino)benzaldehyde failed (Scheme 5). At the same time, the reactions of **4** with more active phenyliminovinyl derivatives of heterocycles of low and medium basicity (e.g., 4-pyran, indoline, benz[*c*,*d*]indole, and benzothiazole) proceeded smoothly to give the corresponding dyes **11**–**15** in good yields (Scheme 5). The reaction of **4** with phenyliminobutadienyl-substituted indolenine yielded the vinylogue dye **12b**. In principle, it is possible to obtain other butadienyl derivatives of this type; in fact, they were observed in the reaction mixtures, but were not isolated as individual compounds. The reaction of **4** with a 2-(anilidovinyl)quinoline derivative proved more complicated. In this case a mixture of dyes was obtained and the desired dye **14** was isolated by column chromatography. In an attempt to condense **4** with a 4-substituted analogue to produce **16**, the latter lost the borondifluoride fragment to form salt **17**. Apparently, in the case of the reaction of **4** with the 2-(phenyliminovinyl)quinoline derivative, a dye of this type was also formed as a side-product. This is perhaps due to the low electron-withdrawing ability of the terminal boradipyrromethene nucleus, which makes the betaine mesomeric form **G2** unfavorable. The contribution of the **G2** form increases with increasing electron-donating effect of the second terminal nucleus, whereas the stability of the boron complex decreases. The unfavorable formation of the anionic form of the dipyrromethene nucleus is probably the main obstacle in the synthesis of symmetrical dyes of type **10** (at least for given substituents).

In the case of a terminal pyran nucleus with weak electron-donating properties (dye **11**) a broad band with only a small short-wavelength shoulder is observed in the absorption spectrum in acetonitrile (Figure 1, Table 1). The absorption band becomes narrower and more intense with increasing electron-donating ability of the second terminal nucleus. This behavior is typical of merocyanine dyes that contain weak electron-acceptor terminal nuclei[11] and is a result of an increase in the polarization of the donor–acceptor system through the increasing electron-donating properties of another nucleus, that is, the increased contribution of the mesomeric form **G2**. The opposite trend is observed at short wavelengths.

Dichloromethane and DMF are the optimal solvents for evaluating the solvatochromic properties of the dyes from the standpoint of solvent polarity with a minimum of other effects.[11] The data obtained with these solvents are given in Table 1.

Positive and negative solvatochromism is observed for the long- and short-wavelength absorption bands, respectively (Table 1, Figure 2). Extension of the polymethine chain (dyes **12a** and **12b**) leads to a bathochromic shift of the long-wavelength absorption band by 98 nm in DMF, although the band becomes less intense.

The starting boron difluoride complex **4** shows a narrow fluorescence band and a high quantum yield, which is typical of BODIPYs (see Figure 3 and Table 1). BODIPY derivative **7** also exhibits good fluorescent properties. However, the BODIPY derivatives **6** and **8** do not fluoresce because of photoinduced electron transfer, which has also been reported for similar systems.[12] As expected, acidifica-



Scheme 4. Reagents: i) $CH(OEt)_3$, Ac_2O; ii) PhN=CHOEt, Ac_2O; iii) $POCl_3$, DMF, $HClO_4$; iv) $(CH_3)_2NCH(OCH_3)_2$, Ac_2O; v) $PhNH_2$.

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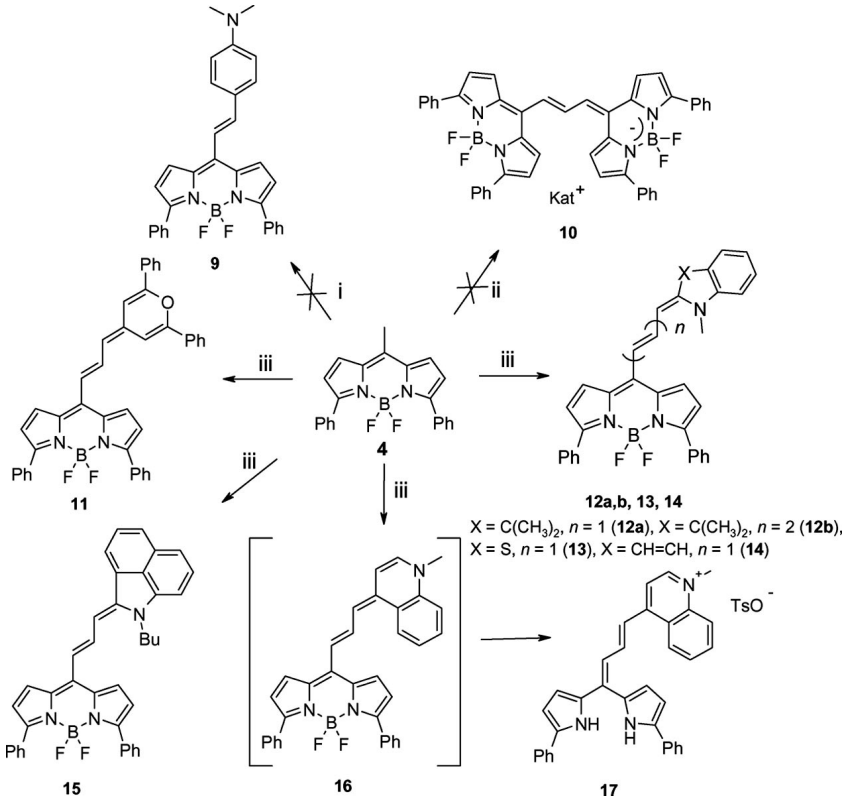

Scheme 5. Reagents: i) *p*-(dimethylamino)benzaldehyde, Ac_2O; ii) $CH(OEt)_3$ or PhN=CHOEt, Ac_2O, Et_3N; iii) Het=(CH–CH)$_n$=NPh, TsOH, Ac_2O, Et_3N.

tion of solutions of **6** and **8** leads to bathochromic shifts in the absorption spectra of 2 and 55 nm, respectively, and to the appearance of fluorescence. In the case of compound **8**, the fluorescence vanishes quickly and the solution turns yellow. This process is irreversible, which we assume is a result of a hydrolytic cleavage of the boron complex and/or the enamine fragment.

Similarly, polymethine-substituted BODIPYs as well as their enamine-type analogues are weakly fluorescent, particularly in polar solvents. However, in contrast to the standard BODIPYs, the polymethine-substituted BODIPYs behave differently upon protonation; the long-wavelength absorption band completely disappears and an increase in the intensity of the short-wavelength band is observed (Fig-

Table 1. Optical properties of the prepared compounds.

Dye	CH_2Cl_2			CH_3CN			DMF		
	λ_{abs} [nm] (ε)·[10^{-3} M^{-1} cm^{-1}][cm^{-1}]	fwhm [cm^{-1}]	λ_{em} [nm] (Φ_f)	λ_{abs} [nm] (ε)·[10^{-3} M^{-1} cm^{-1}]	fwhm [cm^{-1}]	λ_{em} [nm] (Φ_f)	λ_{abs} [nm] (ε)·[10^{-3} M^{-1} cm^{-1}]	fwhm [cm^{-1}]	λ_{em} [nm] (Φ_f)
4	544 (57)	1631	577 (64)	536 (35)	1732		543 (47)	1684	
6		2904		53 2 (65)	2915		543 (65)	2923	
7	306 (49)		604 (32)	305 (48)			305 (50)		
	572 (54)	1635		564 (54)	1685		572 (54)	1738	
8	501 (67)	3155		501 (57)	3159		501 (58)	3163	
11	674 (66)	4306	–	692 (65)	4531	–	712 (69)	4403	–
12a	562 (40)		712 (0.6)	547 (31)		720 (<0.1)	557 (34)		736 (<0.1)
	661 (108)	1631		671 (111)	1656		682 (116)	1634	
12b	587 (38)			572 (29)			582 (27)		
	743 (98)	1683		771 (116)	1915		784 (107)	1777	
13	558 (33)		726 (0.5)	539 (26)		727 (<0.1)	549 (25)		729 (<0.1)
	679 (110)	2289		683 (116)	1595		693 (105)	1558	
14	560 (23)		745 (0.4)	534 (17)		743 (<0.1)	548 (21)		754 (<0.1)
	710 (125)	1432		705 (117)	1403		718 (128)	1334	
15	610		–	597 (23)		–	614 (24)		–
	737 (73)	2353		752 (74)	2184		762 (78)	2071	

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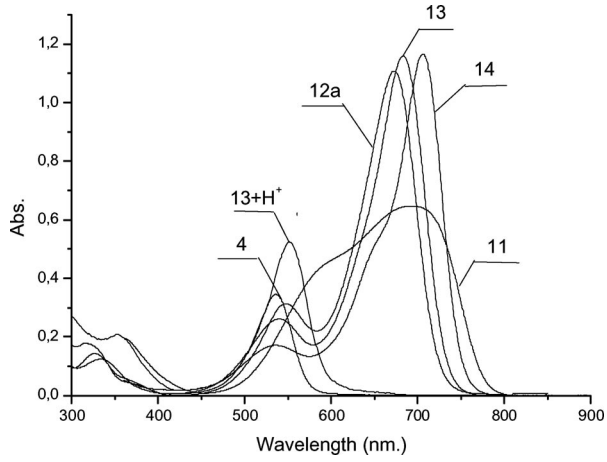

Figure 1. Absorption spectra of compounds **4** and **11**–**14** in acetonitrile ($C = 1 \times 10^{-5}$ M).

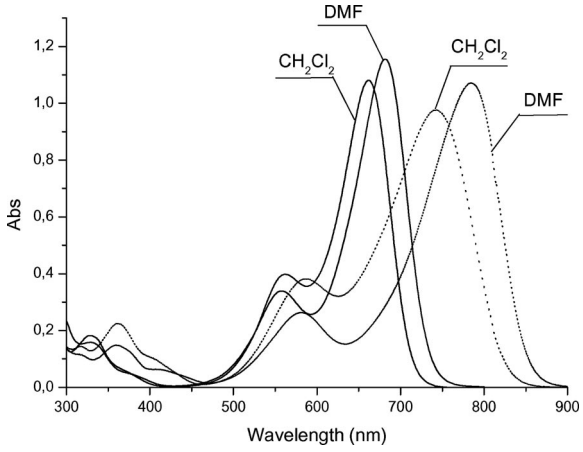

Figure 2. Absorption spectra of compounds **12a** (solid line) **and 12b** (dotted line) ($C = 1 \times 10^{-5}$ M).

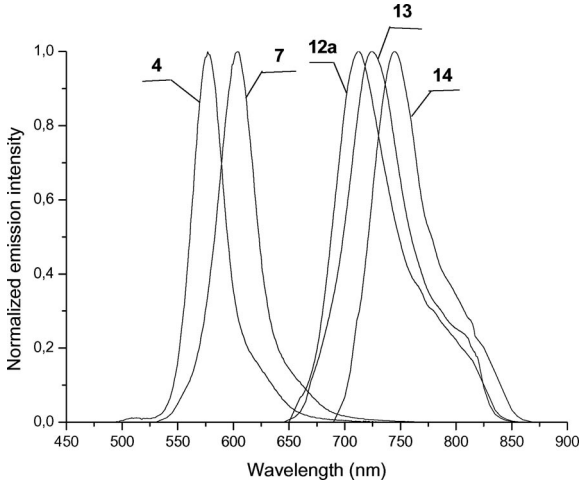

Figure 3. Normalized emission spectra of the dyes **4**, **7**, and **12a**–**14** in CH_2Cl_2.

ure 1). At the same time, no fluorescence appears in these dyes upon protonation.

The optical properties of the cationic dye **17** cannot be discussed in direct comparison with those of the boron difluoride complexes **11**–**15** because it is a different type of dye. Such dyes have not been investigated systematically;[9] however, their properties will be reported in the due course.

Conclusions

The reported compounds **11**–**15** are specific polymethine merocyanine dyes, even though they can be formally referred to as BODIPY derivatives. The merocyanine nature of these dyes manifests itself in the existence of two characteristic bands in their absorption spectra. The long-wavelength band belongs to the polymethine fragment and is more intense than the short-wavelength band that stems from the dipyrromethene unit. This is also confirmed by the spectral changes that occur upon protonation of these dyes, that is, the long-wavelength band disappears and the short-wavelength absorption increases. The prepared dyes show intense long-wavelength absorption and weak fluorescence. These dyes have only a few known formal analogues, the cyanine-like chromophoric systems that contain another dye as a terminal nucleus.[13] By reference to conventional cyanine nomenclature,[14] we refer to them as boradipyrromethenecyanines.

Experimental Section

General: The absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. ^{1}H (300 MHz, 25 °C, TMS as internal standard) and ^{13}C NMR (75 MHz, $CDCl_3$ as internal standard) spectra were obtained with a Varian VXR-300 spectrometer. LC–MS measurements were performed with a liquid chromatography–mass spectrometric system consisting of an Agilent 1100 Series HPLC instrument equipped with a diode matrix detector and an Agilent LC/MSD SL mass-selective detector. The atmospheric pressure chemical ionization (APCI) technique with detection of positive ions was used. Fluorescence spectra were recorded with a Solar CM 2203 fluorescence spectrophotometer. Fluorescence quantum yields (Φ) for compounds **4** and **7** were determined relative to Rhodamine 6G ($\Phi = 0.95$, EtOH), whereas for compounds **11**, **12a**, **13**, and **14** they were determined relative to pentamethinedioxaborinate ($\Phi = 0.57$, CH_2Cl_2).[15]

5-Phenyl-2-[1-(5-phenyl-1*H*-pyrrol-2-yl)ethylidene]-2*H*-pyrrolium Tosylate (2): A solution of 2-phenylpyrrole (2.14 g, 15 mmol) and toluene-4-sulfonic acid (1.35 g, 7.8 mmol) in triethyl orthoacetate (8 mL, 45 mmol) was stirred for 30 min at room temp. The solution was diluted with EtOAc (30 mL), filtered, and the precipitated solid was washed with EtOAc and hexane. Yield 2.65 g, 73%; m.p. 212–214 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz; mixture of **2** and **3a** in a ratio of 1:2): δ = 12.68 (s, NH; **2**), 11.14 (s, NH; **3a**), 8.12 (d, J = 7.2 Hz), 7.79 (d, J = 7.8 Hz), 7.74 (d, J = 7.2 Hz), 7.58 (d, J = 7.8 Hz), 7.47 (d, J = 7.2 Hz), 7.44 (d, J = 4.2 Hz), 7.36 (t), 7.1–7.2 (m), 6.54 (s), 6.26 (s), 5.42 (s, CH_2; **2**), 3.02 (s, CH_3; **2**), 2.29 (s, CH_3) ppm. $C_{29}H_{26}N_2O_3S$ (482.60): calcd. C 72.18, H 5.43, N 5.80; found C 72.30, H 5.31, N 5.89.

1,1-Bis(5-phenyl-1*H*-pyrrol-2-yl)ethene (3): Triethylamine (0.5 g, 5 mmol) was added to a solution of compound **2** (0.97 g, 2 mmol)

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in EtOH (15 mL) and the reaction mixture was stirred for 30 min at room temp. The crude product was filtered and washed with EtOH. Yield 0.46 g, 74%; m.p. 142–144 °C. Form **3a**: ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 11.18 (s, 2 H, NH), 7.74 (d, J = 7.8 Hz, 4 H, ArH), 7.35–7.39 (m, 6 H), 6.55 (s, 2 H, pyrrole H), 6.27 (s, 2 H, pyrrole H), 5.43 (s, 2 H, CH_2) ppm. Form **3a**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 13.96 (br. s, 1 H, NH), 7.88 (d, J = 7.2 Hz, 4 H, ArH), 7.36–7.48 (m, 6 H, ArH), 7.20 (d, J = 4.2 Hz, 2 H, pyrrole H), 6.84 (d, J = 4.2 Hz, 2 H, pyrrole H), 2.56 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 106.7, 107.3, 111.0, 124.6, 126.3, 129.1, 132.3, 133.0, 133.1, 133.2 ppm. LC–MS: m/z = 311 [M + H]$^+$.

4,4-Difluoro-8-methyl-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (4): Triethylamine (1.94 g, 15 mmol) was added to compound **3** (1.45 g, 3 mmol) in BF_3·OEt_2 (6 mL) and the reaction mixture was stirred for 15 min at room temp. Then the reaction the mixture was diluted with CH_2Cl_2. The mixture was washed with water (4 × 50 mL) and the organic layer was separated, dried with Na_2SO_4, and the solvents evaporated to dryness. Yield 0.98 g, 91%; m.p. 231–233 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 7.79–7.82 (m, 4 H, ArH), 7.72 (d, J = 4.5 Hz, 2 H, pyrrole H), 7.44–7.47 (m, 6 H, ArH), 6.83 (d, J = 4.5 Hz, 2 H, pyrrole H), 2.76 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.5, 120.7, 127.7, 128.5, 129.8, 133.1, 137.1, 142.2, 158.6 ppm. LC–MS: m/z 340 [M – 19]$^+$.

4,4-Difluoro-3,5-diphenyl-8-[2-(phenylamino)ethenyl]-4-bora-3a,4a-diaza-*s*-indacene (6): Aniline (0.37 g, 4 mmol) and acetic acid (0.5 mL) were added to a solution of compound **8** (0.082 g, 0.2 mmol; prepared as described below) in CH_2Cl_2 (5 mL) and the reaction mixture was allowed to stand overnight. Then the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water (4 × 30 mL) and the organic layer was separated, dried with Na_2SO_4, and the solvents evaporated to dryness. The residue was purified by chromatography on silica gel (eluent hexane/EtOAc, 4:1, then hexane/EtOAc, 1:1). Yield 0.07 g, 76%. ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ = 11.31 (d, J = 12 Hz, 1 H, NH), 8.46 (t, J = 12.3 Hz, 1 H, CH), 7.69 (d, J = 7.2 Hz, 4 H, ArH), 7.33–7.45 (m, 13 H), 6.75 (d, J = 12 Hz, 1 H, CH), 6.61 (d, J = 4.5 Hz, 2 H, pyrrole H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 101.3, 117.6, 123.0, 124.9, 128.3, 129.2, 130.3, 132.8, 134.4, 140.2, 145.5, 149.3, 150.2 ppm. LC–MS: m/z 442 [M – 19]$^+$.

2-(4,4-Difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacen-8-yl)-3-(dimethylamino)propenylidene(dimethyl)ammonium Perchlorate (7): The Vilsmeier complex was prepared by the dropwise addition of freshly distilled $POCl_3$ (0.27 g, 17.5 mmol) to dry *N*,*N*-dimethylformamide (5 mL) with stirring and cooling in an ice bath. The complex was warmed to room temperature and then was added dropwise to a stirred solution of compound **4** (0.18 g, 0.5 mmol) in dry DMF (3 mL). The mixture was stirred at 60 °C until completion of the reaction (50–60 min). The mixture was poured into ice–water and extracted with CH_2Cl_2 (3 × 25 mL). The combined extracts were washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was dissolved in *i*PrOH (25 mL). Perchloric acid (3 mL) was added to the solution and left to stand overnight. The crude product was filtered and washed with *i*PrOH. Yield 0.1 g, 34%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.22 (s, 2 H, CH), 7.85–7.87 (m, 4 H, ArH), 7.44–7.47 (m, 6 H, ArH), 7.17 (d, J = 3.8 Hz, 2 H, pyrrole H), 6.75 (d, J = 3.8 Hz, 2 H, pyrrole H), 3.44 (s, 6 H, 2 CH_3), 2.97 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 49.3, 122.8, 128.9, 130.6, 131.4, 132.1, 138.4, 159.8, 165.1 ppm. LC–MS: m/z 551 [M – 19]$^+$.

4,4-Difluoro-8-[2-(dimethylamino)ethenyl]-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (8): *N*,*N*-Dimethylformamide dimethyl acetal (0.5 g, 4.2 mmol) was added to compound **4** (0.36 g, 1 mmol) in Ac_2O (2 mL) and the reaction mixture was heated at reflux for 2–3 min. After cooling to room temperature, the crude product was filtered and washed with AcOH. Yield 0.29 g, 70%; m.p. 249–251 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.22 (d, J = 12 Hz, 1 H, CH), 7.63 (d, J = 7.2 Hz, 4 H, ArH), 7.25–7.37 (m, 8 H), 6.49 (d, J = 3.9 Hz, 2 H, pyrrole H), 6.40 (d, J = 12 Hz, 1 H, CH), 3.42 (s, 3 H, CH_3), 3.30 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 39.1, 46.6, 97.9, 116.0, 127.7, 128.2, 129.0, 135.0, 146.1, 14.4, 159.4 ppm. $C_{25}H_{22}BF_2N_3$ (413.27): calcd. C 72.63, H 5.33, N 10.17; found C 72.47, H 5.51, N 10.26. LC–MS: m/z 394 [M – 19]$^+$.

General Procedure for the Synthesis of Dyes 11, 12a,b, 13–15, and 17: Triethylamine (0.65 mmol) was added to compound **4** (0.5 mmol) and the corresponding hemicyanine (0.65 mmol) in Ac_2O (2 mL) and the reaction mixture was heated at reflux for 2–3 min. After cooling to room temperature, the crude product was filtered and washed with AcOH.

8-[3-(2,6-Diphenylpyran-4-ylidene)propenyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (11): Yield 0.14 g, 44%; m.p. 163–165 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.32 (t, J = 12.9 Hz, 1 H, CH), 8.11 (d, J = 7 Hz, 2 H, ArH), 8.02 (d, J = 7 Hz, 2 H, ArH), 7.74 (d, J = 6.6 Hz, 5 H, ArH), 7.55–7.58 (m, 8 H, ArH), 7.27–7.45 (m, 8 H, ArH), 6.72 (d, J = 3.9 Hz, 2 H, pyrrole H), 6.37 (d, J = 12.3 Hz, 1 H, CH) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 104.8, 106.2, 110.0, 118.2, 118.9, 119.1, 121.3, 125.7, 126.0, 128.5, 128.9, 129.3, 129.4, 129.6, 131.2, 131.9, 132.1, 133.9, 134.5, 142.6, 143.1, 145.1, 152.7, 155.5, 155.7 ppm. LC–MS: m/z 596 [M – 19]$^+$.

8-[3-(1,3,3-Trimethylindolin-2-ylidene)propenyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (12a): Yield 0.16 g, 60%; m.p. 242–244 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.31 (t, J = 12.9 Hz, 1 H, CH), 7.69 (d, J = 7.2 Hz, 4 H, ArH), 7.51 (d, J = 6.6 Hz, HetH), 7.14–7.39 (m, 12 H), 6.63 (d, J = 3.9 Hz, 2 H, pyrrole H), 6.38 (d, J = 12.9 Hz, 1 H, CH), 3.56 (s, 3 H, NCH_3), 1.65 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.3, 29.7, 47.2, 99.7, 107.9, 117.2, 118.1, 121.9, 122.3, 123.7, 128.0, 128.3, 129.2, 133.9, 134.3, 139.4, 143.8, 144.7, 153.3, 166.5 ppm. LC–MS: m/z 522 [M – 19]$^+$.

8-[4-(1,3,3-Trimethylindolin-2-ylidene)-1,3-butadienyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (12b): Yield 0.18 g, 64%; m.p. 215–217 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.82 (d, J = 6.9 Hz, 4 H, ArH), 7.54 (t, J = 14.1 Hz, 1 H, CH), 7.2–7.42 (m, 13 H), 6.95 (t, J = 8.1 Hz, 1 H, CH), 6.87 (d, J = 14.4 Hz, 1 H, CH), 6.74 (d, J = 8.1 Hz, 1 H, CH), 6.58 (d, J = 3.9 Hz, 2 H, pyrrole H), 6.37 (t, J = 12.3 Hz, 1 H, CH), 3.25 (s, 3 H, NCH_3), 1.64 (s, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 28.4, 29.5, 46.7, 97.9, 107.2, 118.7, 120.0, 121.3, 121.8, 125.1, 125.5, 128.0, 128.3, 128.6, 129.3, 133.7, 134.7, 139.4, 140.5, 142.6, 144.3, 148.1, 154.5, 162.9 ppm. LC–MS: m/z = 567 [M]$^+$.

8-[3-(3-Methyl-3*H*-benzothiazol-2-ylidene)propenyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (13): Yield 0.16 g, 62%; m.p. 226–229 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.09 (t, J = 13.2 Hz, 1 H, CH), 8.02 (d, J = 8 Hz, 1 H, HetH), 7.76 (d, J = 8.1 Hz, 1 H, HetH), 7.66 (d, J = 6.9 Hz, 4 H, ArH), 7.57 (t, J = 8.1 Hz, 1 H, HetH), 7.26–7.45 (m, 8 H), 7.12–7.18 (m, 3 H), 6.84 (d, J = 13.2 Hz, 1 H, CH), 6.52 (d, J = 4.2 Hz, 2 H, pyrrole H), 3.89 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 34.0, 104.0, 114.1, 114.8, 116.3, 119.3, 123.5, 125.6, 125.9, 127.7, 128.2,

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128.5, 129.0, 129.4, 133.3, 135.0, 140.9, 142.5, 146.9, 147.7, 165.3 ppm. LC–MS: m/z = 512 $[M - 19]^+$.

8-[3-(1-Methyl-1*H*-quinolin-2-ylidene)propenyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (14): The product was purified by chromatography on silica gel (100 mesh, $CHCl_3$) to give the pure dye. Yield 0.07 g, 26%; m.p. >250 °C. ^1H NMR ($[D_6]$DMSO, 300 MHz): δ = 8.51 (t, J = 13.2 Hz, 1 H, CH), 8.19 (m, 2 H, HetH), 8.06 (d, J = 9.3 Hz, HetH), 7.95 (d, J = 7.8 Hz, 1 H, HetH), 7.83 (t, J = 7.5 Hz, 1 H, HetH), 7.65 (d, J = 7.2 Hz, 4 H, ArH), 7.55 (t, J = 6.9 Hz, 1 H, HetH), 7.32 (t, J = 7.8 Hz, 4 H, ArH), 7.18–7.28 (m, 3 H), 7.13 (d, J = 3.6 Hz, 2 H, pyrrole H), 6.91 (d, J = 12.9 Hz, 1 H, CH), 6.46 (d, J = 3.6 Hz, 2 H, pyrrole H), 4.11 (s, 3 H, CH_3) ppm. LC–MS: m/z = 507 $[M - 19]^+$.

8-[3-(1-Butyl-1*H*-benzo[*c*,*d*]indol-2-ylidene)propenyl]-4,4-difluoro-3,5-diphenyl-4-bora-3a,4a-diaza-*s*-indacene (15): The product was dissolved in CH_2Cl_2 and purified by flash column chromatography (CH_2Cl_2). Yield 0.18 g, 60%; m.p. 245–247 °C. ^1H NMR ($[D_6]$-DMSO, 300 MHz): δ = 8.53 (t, J = 12.5 Hz, 1 H, CH), 8.08 (d, J = 6.9 Hz, 1 H, HetH), 8.02 (d, J = 8.1 Hz, 1 H, HetH), 7.75–7.8 (m, 6 H), 7.52–7.59 (m, 6 H), 7.37–7.45 (m, 6 H), 7.23 (d, J = 6.3 Hz, 1 H, CH), 6.81 (d, J = 12.6 Hz, 1 H, CH), 6.75 (d, J = 4.2 Hz, 2 H, pyrrole H), 4.17 (q, 2 H, CH_2), 1.8 (q, 2 H, CH_2), 1.48 (q, 2 H, CH_2), 0.96 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 14.3, 20.3, 30.7, 43.2, 79.7, 118.9, 124.7, 125.8, 128.5, 128.7, 129.2, 134.0, 151.9 ppm. LC–MS: m/z 572 $[M - 19]^+$.

1-Methyl-4-[4,4-bis(5-phenyl-1*H*-pyrrol-2-yl)-1,3-butadienyl]quinolinium *p*-Toluenesulfonate (17): Yield 0.08 g, 23%; m.p. >250 °C. UV/Vis (CH_3CN + 5% AcOH): λ_{max} (ε) = 620 nm (39000 $M^{-1}cm^{-1}$). ^1H NMR ($[D_6]$DMSO, 300 MHz): δ = 11.76 (s, 2H NH), 8.91 (d, J = 6 Hz, 1 H, ArH), 8.78 (d, J = 15 Hz, 1 H, CH),8.31 (d, J = 9 Hz, 1 H, ArH), 8.08–8.22 (m, 2 H), 7.75–8.02 (m, 7 H), 7.39–7.5 (m, 5 H), 7.25–7.33 (m, 3 H), 7.11 (d, J = 6 Hz, 2 H, pyrrole H), 6.8 (d, J = 12 Hz, 2 H, pyrrole H), 6.58 (s, 1 H, ArH), 6.48 (s, 1 H, ArH), 4.4 (s, 3 H, CH_3), 2.3 (s, 3 H, CH_3) ppm.

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