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Synthesis, crystal structures and spectroscopic characterizations of two difluoroboradiaza-*s*-indacene dyes

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Abstract

Two new 8-(4-dimethylaminophenyl) substituted boron-dipyrromethene (BDP) dyes: 1,2,6,7-tetraethyl-4,4-difluoro-3,5-dimethyl-8-(4-dimethylaminophenyl)-4-bora-3*a*,4*a*-diaza-*s*-indacene (5) and 4,4-difluoro-1,2,3,5,6,7-hexamethyl-8-(4-dimethylaminophenyl)-4-bora-3*a*,4*a*-diaza-*s*-indacene (6) have been synthesized and their crystal structures are determined by X-ray diffraction analysis. The torsion angles of 8-phenyl ring and the indacene plane are 79.61° for **5** and 87.56° for **6**, respectively. The absorption and steady-state fluorescence properties in different solvents have been investigated. The fluorescence quantum yields of the two dyes are lower in more polar solvents, which can be ascribed to the intramolecular charge transfer from the aniline to the BDP unit. Protonation of the aniline moiety at low pH in MeOH–H_2O (1:1 v/v) solution causes a large fluorescence enhancement. The pK_a values calculated from the pH dependent fluorescence emission spectra are 3.14 for **5** and 3.09 for **6**, respectively. They are suitable as pH probes excitable with visible light.

Keywords: Boron–dipyrromethene; Fluorescence; Crystal structure; pH probe

1. Introduction

4,4-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (boron-dipyrromethene, BDP) dyes are strongly fluorescent materials that possess many valuable photophysical properties, such as high photostability, high absorption coefficients, high fluorescent quantum yield and they are photoexcitable with visible light [1]. They have found numerous applications in many different areas, such as laser dyes [2–8], fluorescent sensors [9–16], optical devices [17–23] and molecular probes for biochemical research [24]. Recently, an increasing number of BDP-based fluorescent probes have been synthesized for proton or metal ion detections [3,9]. BDP-based fluorophores bearing dialkyl-aminophenyl [25–28], phenolic [29], naphtholic and calyx [4]-arene [30] subunits at *meso*-position have been investigated as pH sensors as they showed fluorescence off/on switching behavior upon protonation/deprotonation. However, the crystal structures of BDP dyes reported so far are still rare [2,31–38]. Herein we describe the crystal structures of two newly synthesized BDP dyes: 1,2,6,7-tetraethyl-4,4-difluoro-3,5-dimethyl-8-(4-dimethylaminophenyl)-4-bora-3*a*,4*a*-diaza-*s*-indacene (**5**) and 4,4-difluoro-1,2,3,5,6,7-hexamethyl-8-(4-dimethylaminophenyl)-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6**). Their absorption and steady-state fluorescence properties have been investigated.

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2. Experimental

2.1. Instruments

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. Melting points were measured with a Reichert Thermometer apparatus without correction. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at ambient temperature. NMR chemical shifts are expressed in ppm relative to TMS as the internal standard. The MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager De pro spectrometer. UV–visible spectra were carried out on a UV-3100 spectrophotometer. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a xenon arc lamp as the light source. The fluorescence quantum yields (ϕ_f) were determined relative to rhodamine 6G in water ($\lambda_{ex} = 488$ nm, $\phi_f = 0.76$) using dilute solutions with an absorbance below 0.1 at the excitation wavelength (λ_{ex}) [39]. Fluorimetric titration measurements were done in MeOH–H_2O (1:1 v/v) by gradually adding microlitre of H^+ ($c = 10^{-3}$ M of $HClO_4$) to the dye solution ($c = 10^{-7}$ M).

Table 1
Crystal data and structure refinement for **5** and **6**

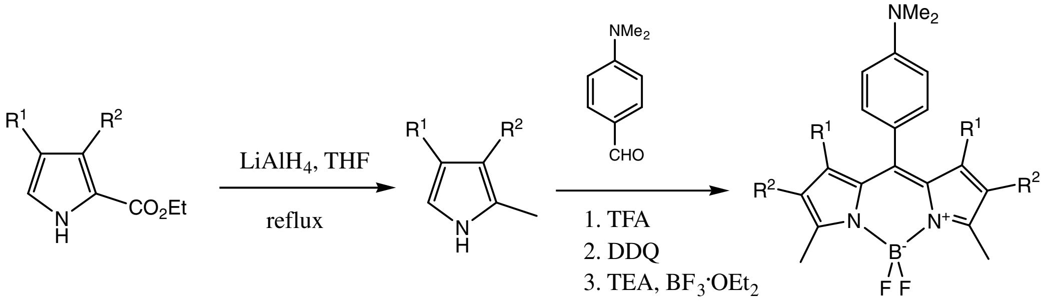
	5	**6**
Empirical formula	$C_{27}H_{36}BF_2N_3$	$C_{23}H_{30}BF_2N_3O$
F_w	451.40	413.31
Crystal size (mm)	0.22 × 0.26 × 0.28	0.24 × 0.24 × 0.32
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Z	4	4
a/Å	19.290(6)	17.747(4)
b/Å	13.721(5)	13.633(3)
c/Å	11.075(4)	11.676(3)
α(deg)	90	90
β(deg)	122.447(5)	129.747(4)
γ(deg)	90	90
V/Å^3	2473.7(15)	2172.0(9)
ρ (calc) (g/cm^3)	1.212	1.264
μ_{calc}(mm^{-1})	0.081	0.089
T (K)	293(2)	293(2)
F(000)	968	880
Transmission factors (max; min)	0.98; 0.97	0.98; 0.98
Scan type	ϕ and ω	ϕ and ω
Θ range for data collection (°)	1.94–26.00	2.11–26.00
Total reflections	2417	2127
Measured reflections (R(int))	1548 (0.044)	1515 (0.028)
Absorption correction	semi-empirical	semi-empirical
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Parameters refined	156	147
R_1,wR_2	0.0612, 0.1109	0.0587, 0.1009
Goodness-of-fit on F^2	1.056	1.504
Largest diff. peak and hole/(eÅ^{-3})	0.17 and−0.39	0.30 and −0.29

2.2. Reagents and materials

All syntheses were carried out under nitrogen. Unless otherwise noted, all reagents or solvents were of analytical grade and were used as received. Dry CH_2Cl_2 was obtained by refluxing and distilling over CaH_2 under nitrogen. Dry THF was distilled from sodium/benzophenone. Triethylamine was obtained by simple distillation. The solvents used for photophysical measurement were of spectroscopic grade and used without further purification.

2.3. Crystal structure determination

Single crystals of **5** (0.22 × 0.26 × 0.28) and **6** (0.24 × 0.24 × 0.32) were obtained by slow diffusion of methanol into the corresponding solutions in $CHCl_3$ at room temperature and were glued to a thin glass fiber with adhesive, respectively. The unit cell parameters and data were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan mode. The data were corrected for Lorenz and polarization effects. The two structures were solved by the direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding on their attached positions. All calculations and molecular



1: R^1 = Et, R^2 = Et
2: R^1 = CH_3, R^2 = CF_3

3: R^1 = Et, R^2 = Et
4: R^1 = CH_3, R^2 = CH_3

5: R^1 = Et, R^3 = Et
6: R^1 = CH_3, R^3 = CH_3

Scheme 1. Synthetic procedures for compounds **5** and **6**. DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

graphics were carried out on a computer using the SHELXTL-2000 program package [33]. Crystallographic data for **5** and **6** are summarized in Table 1.

CCDC-297327 for **5** and CCDC-297326 for **6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

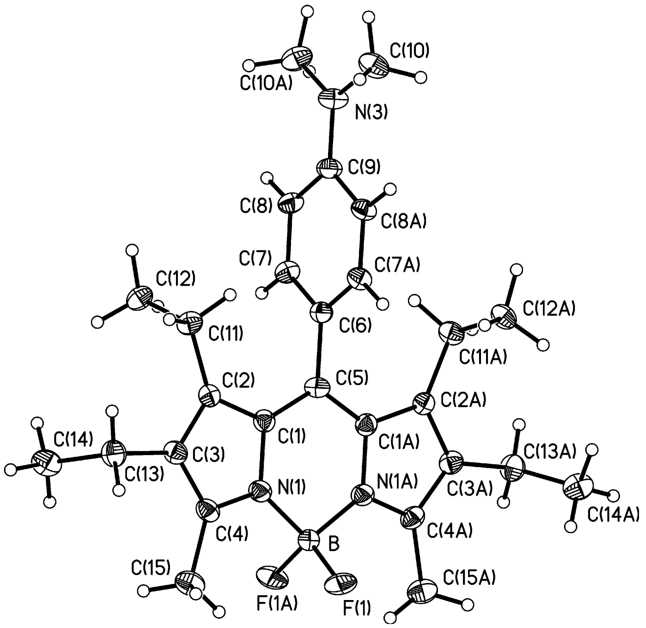


Fig. 1. ORTEP view of the molecular structure of **5** with thermal ellipsoids shown at 30%.

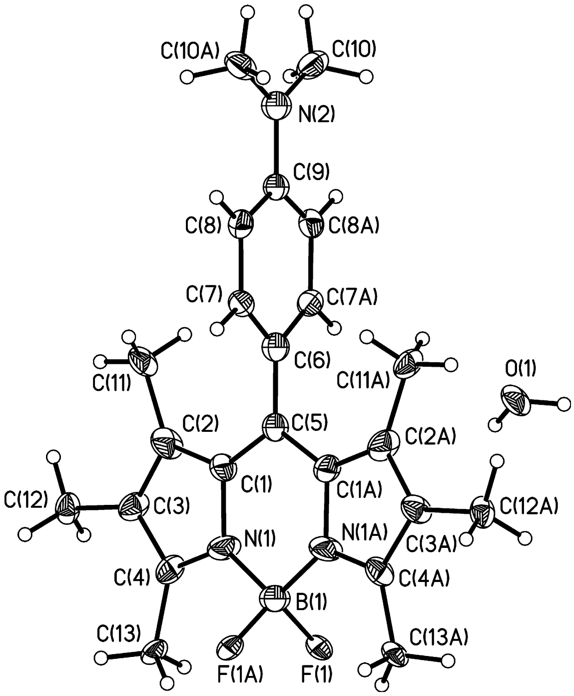


Fig. 2. ORTEP view of the molecular structure of **6** with thermal ellipsoids shown at 30%.

3. Results and discussion

3.1. Synthesis of 1,2,6,7-tetraethyl-4,4-difluoro-3,5-dimethyl-8-(4-dimethylaminophenyl)-4-bora-3a,4a-diaza-s-indacene (5) and 4,4-difluoro-1,2,3,5,6,7-hexamethyl-8-(4-dimethylaminophenyl)-4-bora-3a,4a-diaza-s-indacene (6)

The synthetic routes for **5** and **6** are outlined in Scheme 1. Ethyl 3,4-diethylpyrrole-2-carboxylate (**1**) and ethyl 3-(trifluoromethyl)-4-methylpyrrole-2-carboxylate (**2**) were prepared according to published procedures [40,41]. Our purpose to introduce the electron-withdrawing CF_3 group to pyrrole is to tune the redox properties of the resulting BDP dye. However, reduction of **2** with excess of $LiAlH_4$ in dry THF under reflux for 3 h gave 2,3,4-trimethylpyrrole

Table 2
Selected bond lengths (Å) and bond angle (°) of **5** and **6**

5		**6**	
Bond lengths			
F(1)–B	1.387(3)	F(1)–B	1.407(3)
N(1)–B	1.552(3)	N(1)–B	1.516(3)
N(1)–C(1)	1.383(3)	N(1)–C(1)	1.403(3)
N(1)–C(4)	1.338(4)	N(1)–C(4)	1.340(3)
N(3)–C(9)	1.370(4)	N(2)–C(9)	1.422(4)
N(3)–C(10)	1.420(3)	N(2)–C(10)	1.490(3)
C(1)–C(2)	1.439(4)	C(1)–C(2)	1.380(3)
C(1)–C(5)	1.403(3)	C(1)–C(5)	1.418(2)
C(2)–C(3)	1.384(3)	C(2)–C(3)	1.381(3)
C(2)–C(11)	1.497(3)	C(2)–C(11)	1.516(3)
C(3)–C(4)	1.399(3)	C(3)–C(4)	1.380(3)
C(3)–C(13)	1.517(4)	C(3)–C(13)	1.537(3)
C(4)–C(15)	1.493(3)	C(4)–C(15)	1.501(3)
C(5)–C(6)	1.478(4)	C(5)–C(6)	1.400(4)
C(6)–C(7)	1.391(2)	C(6)–C(7)	1.388(3)
C(7)–C(8)	1.358(3)	C(7)–C(8)	1.388(3)
C(8)–C(9)	1.407(3)	C(8)–C(9)	1.332(3)
Bond angles			
F(1)–B–F(1A)	109.4(3)	F(1)–B–F(1A)	104.8(3)
F(1)–B–N(1)	110.65(9)	F(1)–B–N(1)	111.16(9)
F(1)–B–N(1a)	109.62(10)	F(1)–B–N(1a)	110.22(10)
N(1)–B–N(1a)	106.9(3)	N(1)–B–N(1a)	109.2(3)
C(1)–N(1)–C(4)	109.3(2)	C(1)–N(1)–C(4)	107.29(16)
C(1)–N(1)–B	125.3(2)	C(1)–N(1)–B	124.98(19)
C(4)–N(1)–B	125.4(2)	C(4)–N(1)–B	127.67(19)
C(9)–N(3)–C(10)	120.70(13)	C(9)–N(2)–C(10)	118.24(12)
N(1)–C(1)–C(2)	107.3(2)	N(1)–C(1)–C(2)	107.18(17)
N(1)–C(1)–C(5)	120.9(2)	N(1)–C(1)–C(5)	120.49(18)
N(1)–C(4)–C(3)	109.2(2)	N(1)–C(4)–C(3)	110.49(18)
N(1)–C(4)–C(15)	123.0(2)	N(1)–C(4)–C(15)	123.00(17)
C(2)–C(1)–C(5)	131.8(2)	C(2)–C(1)–C(5)	132.3(2)
C(1)–C(5)–C(1A)	120.5(2)	C(1)–C(5)–C(1A)	119.7(2)
C(1)–C(5)–C(6)	119.76(14)	C(1)–C(5)–C(6)	120.15(12)
C(5)–C(6)–C(7)	121.50(13)	C(5)–C(6)–C(7)	123.52(13)
C(1)–C(2)–C(3)	106.1(2)	C(1)–C(2)–C(3)	108.91(19)
C(1)–C(2)–C(3)	108.2(2)	C(1)–C(2)–C(3)	106.12(17)
C(2)–C(3)–C(13)	127.0(2)	C(2)–C(3)–C(13)	128.01(19)

(**4**). 2-Methyl-3,4-diethyl pyrrole (**3**) was obtained by the reduction of **1** with excess of $LiAlH_4$ under the same conditions. Compounds **5** and **6** were prepared according to a published procedure [17] by condensation of 4-dimethylaminophenyl aldehyde with **3** or **4** using trifluoroacetic acid (TFA) as a catalyst. After oxidation with 2,3-dichloro-5, 6-dicyano-1,4-benzoquinone (DDQ) and treatment with triethylamine and boron trifluoride etherate, the crude product was purified by silica-gel column chromatography and recrystallized from $CHCl_3$/hexane. Compound **5**: Orange red crystals; 34% yield; mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.71 (t, 6H), 1.05 (t, 6H), 1.66–1.71 (q, 4H), 2.29–2.34 (q, 4H), 2.54 (s, 6H), 3.04 (s, 6H), 6.90 (m, 2H), 7.15 (m, 2H); MALDI-TOF MS: *m*/*z*: 451.96 (M^+); Anal. Calcd for $C_{27}H_{36}BF_2N_3$: C, 71.84; H, 8.04; N, 9.31. Found: C, 71.95; H, 8.07; N, 9.51; UV–vis ($CHCl_3$) λ_{max}/nm 377, 491 and 523. Compound **6**: Orange red crystals; 45% yield; mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.38 (s, 6H), 1.87 (s, 6H), 2.53 (s, 6H), 3.08 (s, 6H), 6.90 (m, 2H), 7.10 (m, 2H); MALDI-TOF MS: *m*/*z*: 395.38 (M^+); Anal. Calcd for $C_{23}H_{28}BF_2N_3$: C, 69.88; H, 7.14; N, 10.63. Found: C, 69.96; H, 7.09; N, 10.55; UV–vis ($CHCl_3$) λ_{max}/nm 376, 492 and 520.

3.2. Structural descriptions for 5 and 6

The molecular conformations of **5** and **6** are shown in Figs. 1 and 2, respectively. Selected geometrical parameters of **5** and **6** are listed in Table 2.

Compounds **5** and **6** are crystallized in the monoclinic space group *C*2/c. The bond length of B–N for **5** (1.552(3) Å) is relatively longer than that of **6** (1.516(3) Å), whereas the bond length of B–F for **5** (1.387(3) Å) is shorter than that of **6** (1.407(3) Å). The N–B–N bond angle of **5** (106.9(3)°) is relatively smaller than that of **6** (109.2(3)°), while the F–B–F bond angle of **5** (109.4(3)°) is longer than that of **6** (104.8(3)°). These data are in good agreement with the corresponding values of BF_2N_2 tetrahedron configurations in their analogues [2].

The bond length of N(1)–C(4)/N(1A)–C(4A) is 1.338(4) Å for **5** and 1.340(3) Å for **6**, which is significantly shorter than the bond length of N(1)–C(1)/N(1A)–C(1A) (1.383(3) Å) for **5** and (1.403(3) Å) for **6**. The central six-membered ring containing B–N1–C1–C5–C1A–N1A is almost coplanar with the adjacent five-membered rings with the average deviation from the mean plane being 0.02 Å for **5** and 0.0194 Å for **6**, indicating strong π-electron delocalization within the indacene plane. The two fluorine atoms in the two compounds occupy apical positions relative to the mean plane of the indacene ring system. The *meso*-phenyl ring is almost perpendicular to the indacene plane with torsion angles being 87.56° and 79.61° for **5** and **6**, respectively.

The molecular packing in the crystal structure of **5** and **6** is given in Figs. 3 and 4. All the molecules are parallel to each other with head-to-tail orientation. The *meso*-phenyl ring of one molecule is nearly orthogonal to the indacene plane of the other molecule, therefore no π–π stacking interactions can be observed.

3.3. Absorption and fluorescent spectroscopy of 5 and 6

The absorption and steady-state fluorescence emission spectra of **5** and **6** in hexane are given in Fig. 5. The absorption spectra of **5** and **6** have similar band features

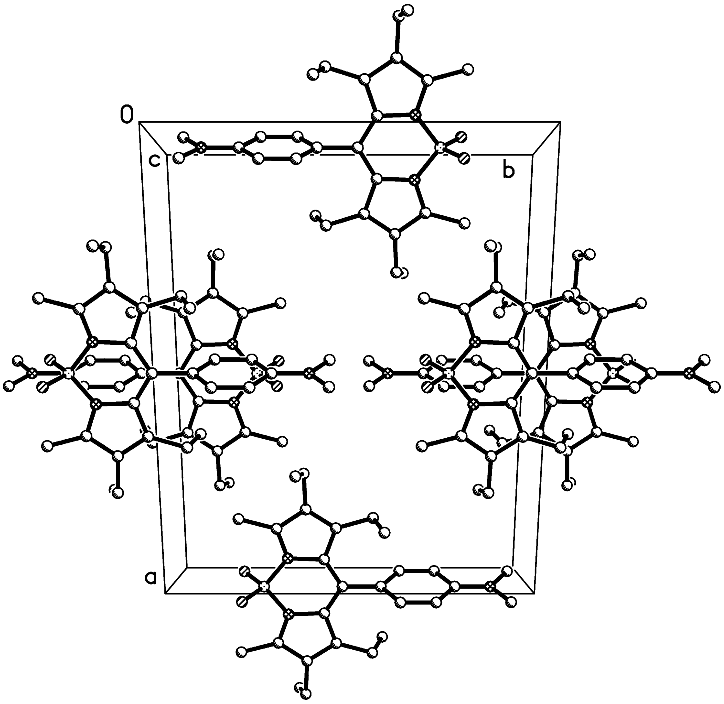


Fig. 3. Molecular packing in the crystal structure of **5** along the *a*-axis.

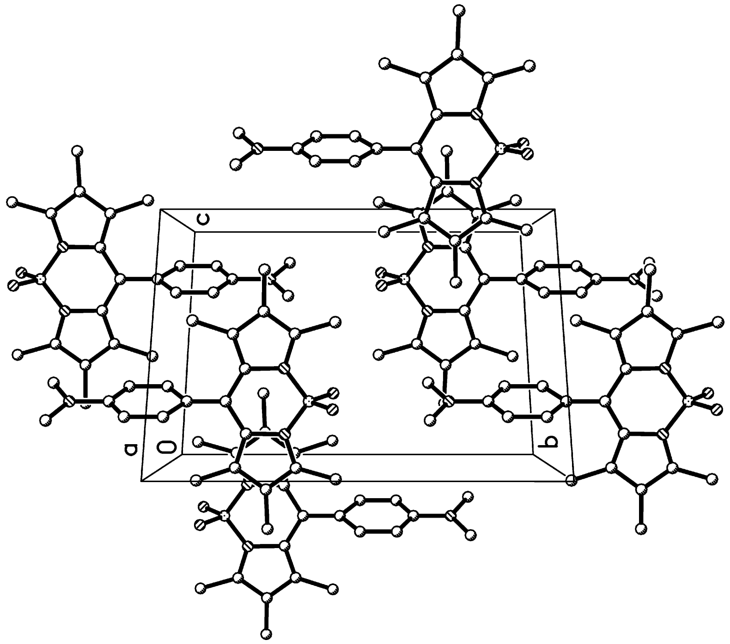


Fig. 4. Molecular packing in the crystal structure of **6** along the *c*-axis.

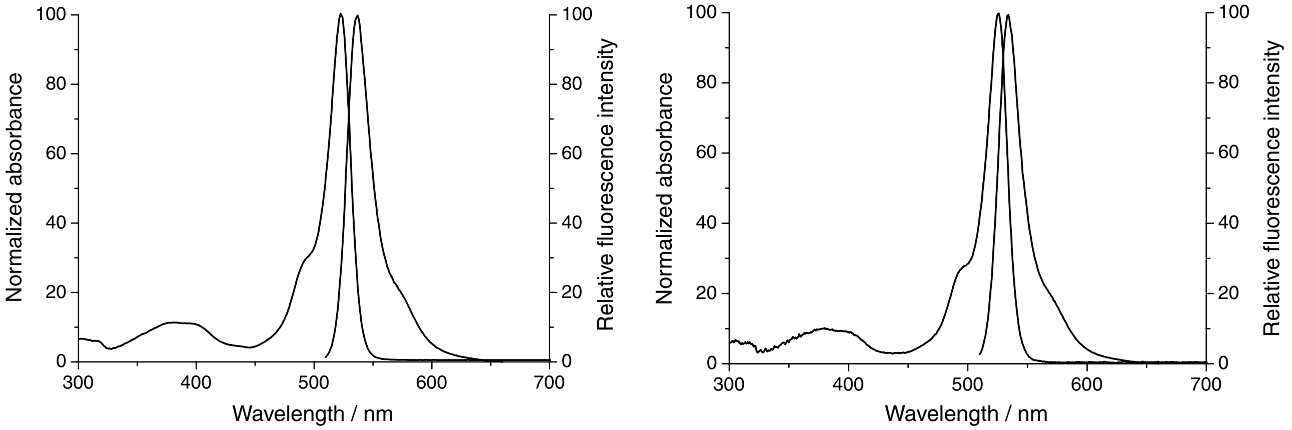


Fig. 5. The UV–vis absorption and fluorescence emission spectra of **5** (left) and **6** (right) in hexane ($\lambda_{ex} = 495$ nm).

with a strong, narrow band centered at 520–523 nm and a shoulder on the high-energy side centered at about 493 nm, which is typical for the conventional BDP derivatives carrying only alkyl substituents on the indacene core. In addition, a considerably weaker and broad absorption band is observed at about 380 nm, which can be ascribed to the $S_0 \rightarrow S_2$ transition [17]. The absorption maximum of **5** and **6** is not affected by the solvent polarity (Table 3). The fact that the absorption spectra of **5** and **6** are similar to those of the classical BDP dyes indicates the absence of donor-acceptor interaction in the ground state, which is due to the decoupled structure between the indacene plane and *meso*-subunit as has been observed in their crystal structures.

In contrast to the absorption spectra, the emission behaviors of **5** and **6** are solvent dependent (Table 3). In nonpolar solvent hexane, the emission spectra of **5** and **6** display mirror symmetry to their absorption spectra (Fig. 5) with high fluorescence quantum yields (Table 3). Increasing the solvent polarity to methanol, the emission intensities of **5** and **6** are heavily quenched, while the maximum of the bands are slightly shifted to the red. The ϕ_f values of **5** and **6** are very low in acetonitrile and methanol. This is due to the activation of an excited-state intramolecular charge transfer (ICT) from the *meso*-aniline donor to the BDP fluorophore [42]. Gradually adding H^+ to their solutions in MeOH–H_2O (1:1 v/v), the emission intensity increases significantly while the emission maxima centered at 540 nm remain unchanged (Fig. 6). Protonation of the tertiary amine function [9] drastically changes the electron-donating properties of the aniline group and is

Table 3
Absorption and emission properties of **5**, **6** in different solvents

BDP	Solvent	λ_{abs} (max/nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (max/nm)	ϕ_f
5	Hexane	523	115000	537	0.64
	CH_2Cl_2	523	81800	533	0.43
	MeCN	523	131000	541	0.007
	MeOH	522	127000	540	0.005
6	Hexane	520	78000	535	0.71
	CH_2Cl_2	520	184000	535	0.50
	MeCN	520	222000	534	0.012
	MeOH	521	169000	539	0.004

expected to switch off the ICT to the boron-dipyrromethene moiety. The ground-state acidity constant K_a values of **5** and **6** are determined by fluorimetric titration as a function of pH using the fluorescence emission spectra (Fig. 7). Nonlinear curve fitting Eq. (1) to the fluorescence data (F) recorded as a function of pH yield values of n (the stoichiometry of H^+ binding to the aniline), K_a, the fluorescence signals F_{max} and F_{min} at maximal and minimal $[H^+]$, respectively. Fitting Eq. (1) to the steady-state fluorescence data F with n, K_a, F_{max} and F_{min} as freely adjustable parameters gives values of n close to 1, indicating that one proton is bound per aniline molecule. Therefore, n is kept fixed at 1 in the final curve fitting, from which the estimated values of pK_a are obtained as 3.14 for **5** and 3.09 for **6**, respectively. Such a high proton-induced fluorescence enhancement makes **5** and **6** into very sensitive fluorescent probes for pH measurements.

$$F = \frac{F_{max}[H^+]^n + F_{min}K_a}{K_a + [H^+]^n} \quad (1)$$

4. Conclusion

In summary, we have prepared and determined the structures of two new difluoroboradiaza-*s*-indacene dyes containing an electron-donating aniline entity at the *meso*-position. In the polar solvent MeOH/H_2O, both compounds exhibit a large fluorescent enhancement upon increasing the acidity of the solution. They can

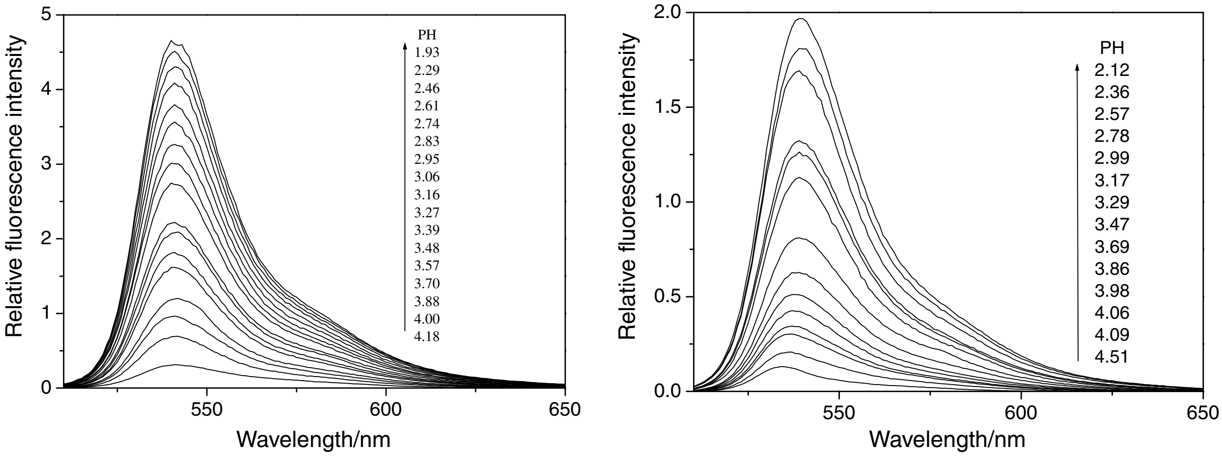


Fig. 6. Fluorescence emission spectra ($\lambda_{em} = 488$ nm) of **5** (left) and **6** (right) in MeOH–H_2O (1:1 v/v) as a function of pH.

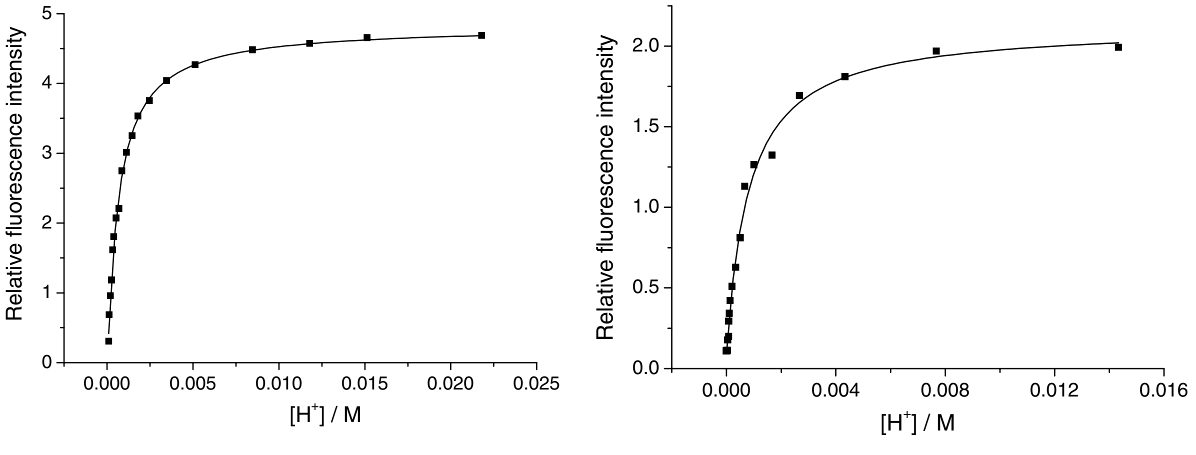


Fig. 7. Fluorescence titration curve of **5** (left) and **6** (right) in MeOH–H_2O (1:1 v/v) as a functional of $[H^+]$ ($\lambda_{em} = 540$ nm, $\lambda_{ex} = 488$ nm). The solid line represents the best fit of Eq. (1) with $n = 1$.

be used as fluorescent pH probes excitable at visible light.

Acknowledgements

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