

Nikolay Vologdin*, Sylvain Achelle, Sébastien Gauthier, Bertrand Caro and Françoise Robin-le Guen

New 8-substituted BODIPY-based chromophores: synthesis, optical and electrochemical properties

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Abstract: BODIPY-based chromophores, in which an electron withdrawing difluoro-boraindacene fragment is connected via position 8 to different donor fragments, were synthesized. Their electrochemical and photophysical properties were studied. All compounds exhibit a quasi-reversible oxidation corresponding to the formation of a BODIPY π -radical cation at around 0.8 V vs. $\text{FeCp}_2^+/\text{FeCp}_2$ that is slightly sensitive to the nature of the electron donating group. A reversible reduction is observed around -1.6 V vs. $\text{FeCp}_2^+/\text{FeCp}_2$ corresponding to the formation of the BODIPY π -radical anion. Cyclic voltammetry analysis of a γ -methylenepyran substituted BODIPY indicates the formation of redox bistable system with high bistability. In dichloromethane solution, the chromophores exhibit an intense absorption band around 502 nm and an emission in the 516–528 nm range. A significant emission quench is observed in case of amino and γ -methylenepyran substituents.

Keywords: bistable redox systems; BODIPY; fluorescence; Sonogashira reaction.

Introduction

Over the past two decades, the difluoroboraindacene (BODIPY) fluorophores have drawn an increased interest due to their unusual properties [1–3]. The BODIPY derivatives are versatile fluorophores as their properties can easily be tuned by molecular modification [4–8]. Moreover, the BODIPY fluorophores have robust photophysical properties, such as strong absorption of visible

light, high fluorescence quantum yield, good photostability [1, 2, 9, 10] and can be used for numerous applications such as biological labeling and medical imaging [11–14], photosensitizers for photodynamic therapy [15], molecular switches [16], photovoltaic devices [17, 18], artificial photosynthetic antenna-reaction center assemblies [19] and fluorescent sensors for metal [20–23] or viscosity [24]. In addition, BODIPY derivatives show amphoteric redox behavior [1, 2]. This property makes the BODIPY fragment an interesting component of organic molecules containing an electron donor and an electron acceptor connected by conjugated bridge. Recently, several articles related to BODIPY-based push-pull systems have been published [25–30]. In most cases, the 2,6-, 3,5-, and 4,4'-disubstituted molecules have been described, and in these systems, the BODIPY fragment has been used as a bridge between the donor and acceptor parts of the molecule [25–28] and sometimes as the donor [28] or acceptor part [28–30]. However, 8-substituted BODIPY compounds in which the difluoroboraindacene fragment acts as the electron-withdrawing part has been less studied [31–34]. On the basis of these previous results, we have decided to prepare a series of new BODIPY-based dyads in which the electron-withdrawing difluoroboraindacene fragment is connected to different donor fragments via position this paper, we present the synthesis of such molecules and the preliminary studies of their properties.

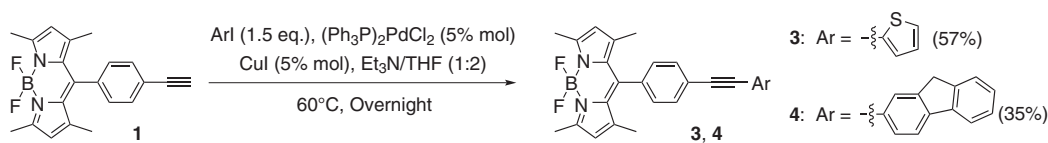
Results and discussion

Target compounds were obtained by Sonogashira cross-coupling reaction starting from the ethynyl precursor **1** [35] or the iodo analogue **2** [36]. Since, the BODIPY fragment has an electron withdrawing nature, we chose several electron donating groups for the creation of dyads. Thiophene and fluorene derivatives **3** and **4** were obtained by the reaction of substrate **1** and 2-iodothiophene or 2-iodofluorene, respectively, in moderate yield (Scheme 1). Compounds **5–8** were obtained in moderate to good yields starting from iodo derivative **2** (Scheme 2).

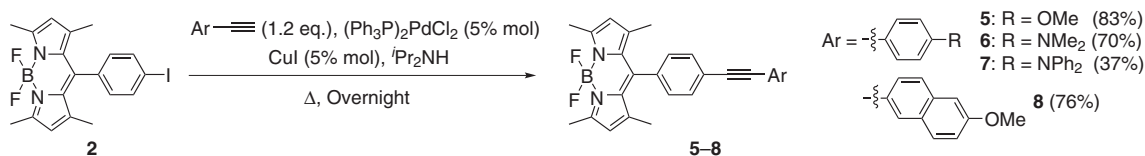
We were also interested in a similar synthesis of a chromophore bearing a γ -methylenepyran fragment

*Corresponding author: Nikolay Vologdin, Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F-22302 Lannion Cedex, France, e-mail: nvologdin@gmail.com

Sylvain Achelle, Sébastien Gauthier, Bertrand Caro and Françoise Robin-le Guen: Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F-22302 Lannion Cedex, France



Scheme 1



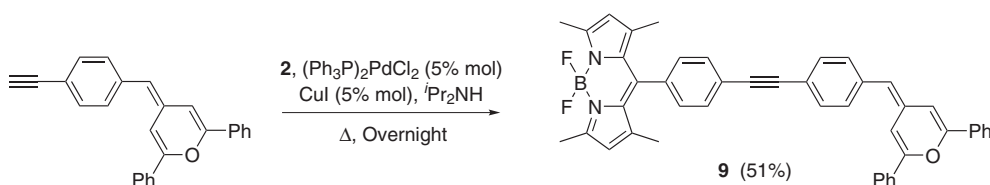
Scheme 2

as a proaromatic electron donating part. Indeed, this fragment displays a significantly increased aromatic character upon intermolecular charge transfer (ICT). In this context, the transformations of γ -methylenepyrans to pyryliums upon ICT are particularly attractive as push-pull structures [37, 38]. Moreover, π -conjugated structures incorporating γ -methylenepyrans as a building block have been described as interesting redox systems [39, 40]. The chromophore **9** was synthesized by the Sonogashira cross-coupling reaction of **2** and 4-(4-ethynylbenzylidene)-2,6-diphenyl-4*H*-pyran [41] (Scheme 3).

All products were characterized by NMR and mass spectroscopy. Unlike the 2,4-methylpyrrole and 1,3,5,7,8-pentamethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

[42] that exhibit proton singlets in their ^1H NMR spectra at 2.09, 2.25 ppm and at 2.41, 2.52 ppm for the protons of methyl groups in position 2,4 and 1,3,5,7, respectively, the molecules **3–9** display signals shifted up-field around 1.4 ppm for the protons of the methyl groups in positions 1,7. Such shielding indicates that the planes of BODIPY and the substituent in position 8 are not coplanar [43]. This geometry favors charge separation and slows down charge recombination that leads to high quantum yields of fluorescence [44].

The electrochemical properties of compounds **3–6** and **8–9** were investigated by cyclic voltammetry in dichloromethane in the presence of NBu_4BF_4 as a supporting electrolyte (Figure 1 and Table 1). The potentials are given in reference to the $\text{FcCp}_2^+/\text{FcCp}_2$ couple.



Scheme 3

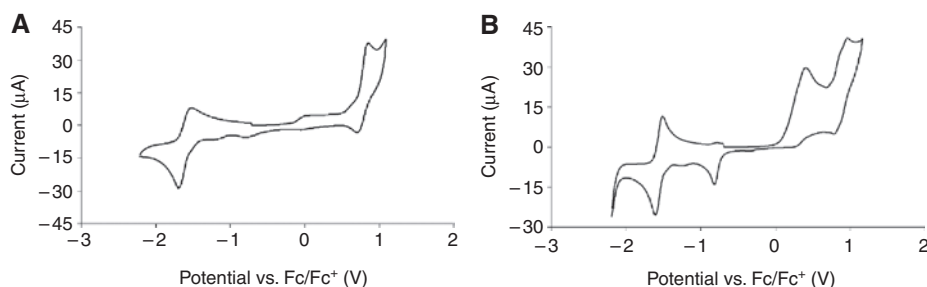


Figure 1 Cyclic voltammogram of (A) BODIPY **3** and (B) BODIPY **9** in dichloromethane in the presence of NBu_4BF_4 ($T = 293\text{ K}$, $c = 2 \times 10^{-3}\text{ M}$, $v = 0.1\text{ V s}^{-1}$, working electrode: Pt).

Table 1 Electrochemical data for BODIPY derivatives, (E vs. $\text{FcP}_2^+/\text{FcP}_2$) in dichloromethane with NBu_4BF_4 as a supporting electrolyte at $0.1 \text{ V} \times \text{s}^{-1}$.

$E_{\text{pa}}(1)^a$	$E_{\text{pa}}(2)^a$	$E_{1/2}(3)^b, (\Delta E_{1/2}/\text{mV})$	$E_{\text{pc}}(4)^c$	$E_{1/2}(5)^b(\Delta E_{1/2}/\text{mV})$
3		0.78 V, (147)		– 1.61 V, (162)
4		0.81 V, (168)		– 1.57 V, (99)
5		0.81 V, (189)		– 1.60 V, (78)
6	0.43 V	0.94 V ^(a)		– 1.56 V, (84)
8		0.90 V, (140)		– 1.59 V, (155)
9	0.40 V	0.87 V, (98)	– 0.81 V	– 1.56 V, (175)

^aIrreversible peak.

^bquasi-reversible peak.

^cIrreversible peak on the reverse cathodic scan.

Compounds **3–5** and **8–9** show a single electrochemically quasi-reversible peak on oxidative scans that is ascribed to the formation of the BODIPY π -radical cation. The oxidation potentials of BODIPY moiety in these compounds are within the same range ($0.78 \text{ V} < E_{1/2} < 0.89 \text{ V}$). On the BODIPY **6** two successive irreversible one-electron oxidation peaks can be resolved and assigned to the oxidation of the dimethylamino group at 0.43 V and the formation of the BODIPY π -radical cation at 0.94 V, respectively. As shown in Table 1 and Figure 1, all compounds **3–6** and **8–9** present a similar single quasi-reversible peak corresponding to the formation of the BODIPY π -radical anion ($-1.61 \text{ V} < E_{1/2} < -1.56 \text{ V}$), on their reduction scans. In addition to the two peaks already observed for the BODIPY fragment **3–5** and **8**, the BODIPY fragment of compound **9** containing the γ -methylenepyran fragment also shows an irreversible anodic peak at 0.40 V corresponding to the formation of the pyrylium radical cation **9^{•+}** followed by a dimerization reaction leading to a dipyrylium salt (Table 1 and Figure 1B). The reverse scan exhibits an irreversible cathodic peak at -0.81 V assigned to the reduction of the dipyrylium cation leading to **9** by a C-C cleavage reaction.

Both observations are consistent with results previously reported for other methylenepyran derivatives and show the bistability of the redox system ($\Delta E = 1.21 \text{ V}$) [37–40, 45].

The UV/Vis and photoluminescence (PL) spectroscopic data of BODIPY derivatives **2–9** measured in dichloromethane are presented in Table 2. The spectra of compound **5** are exemplified in Figure 2.

All compounds exhibit a strong S_0-S_1 transition close to 502 nm with high absorption coefficient ($88.4\text{--}113 \text{ mM}^{-1} \times \text{cm}^{-1}$) assigned to the boradiazaindacene chromophore [25, 47]. At higher energy, a broad band around 306–394 nm is attributed to the S_0-S_2 transition of the BODIPY moiety [48, 49]. The energy bands at 250–297 nm may be related to the substituted phenylethynyl system [50]. When comparing compounds **3–9** with 1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, it appears that the addition of donor substituents in position 8 leads to the slight hypsochromic shift of the BODIPY S_0-S_1 transition band (1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (CH_2Cl_2) – 505 nm [51] and compounds **3–9** (CH_2Cl_2) – 502 nm). Neither the nature of the donor substituent nor the nature of the solvent leads to significant changes of the UV/Vis spectra. This feature is characteristic of 8-substituted BODIPY chromophores [52] and can be explained by the decrease of electronic coupling between the donor and acceptor part of molecules in the ground-state configuration due to non-coplanar geometry. All compounds exhibit emission in the range $\lambda = 516\text{--}528 \text{ nm}$. Compared with unsubstituted BODIPY moieties, the significant emission quenching is observed for all obtained compounds (Φ_F (BODIPY in CH_2Cl_2) = 0.80 [53]). Almost total quenching of BODIPY fluorescence is observed in the case of amino derivatives **6** and **7** and pyranilidene chromophore **9**. Two different reasons accounting for such fluorescence quenching in the presence of donor substituents have been suggested [32, 52]. First, the twisted intramolecular charge transfer (TICT)

Table 2 Optical spectroscopy data for BODIPY derivatives.

	$\lambda_{\text{abs}}, \text{nm}^a (\epsilon, \text{mM}^{-1} \times \text{cm}^{-1})$	$\lambda_{\text{em}}, \text{nm}^a$	Φ_F^b	Stokes shift, cm^{-1}
2	269 (5.8), 329 (8.3), 502 (101)	519	0.41	652
3	306 (32.1), 502 (88.4)	519	0.24	652
4	260 (16.7), 318 (57.2), 501 (91.8)	519	0.28	692
5	297 (35.6), 359 (9.1), 502 (89.7)	517	0.27	578
6	258 (22.0), 339 (48.5), 502 (98.0)	516	< 0.01	540
7	353 (46.1), 501 (103)	528	0.06	1021
8	256 (36.2), 316 (43.3), 502 (103)	518	0.28	615
9	281 (43.1), 394 (67.4), 501 (113)	516	< 0.01	580

^aAll spectra were recorded in dichloromethane solutions at room temperature at $c = 1.0\text{--}9.0 \times 10^{-6} \text{ M}$.

^bFluorescence quantum yield ($\pm 10\%$) determined relative to 9,10-diphenylethynylanthracene in cyclohexane ($\Phi_F = 1.00$) as standard [46].

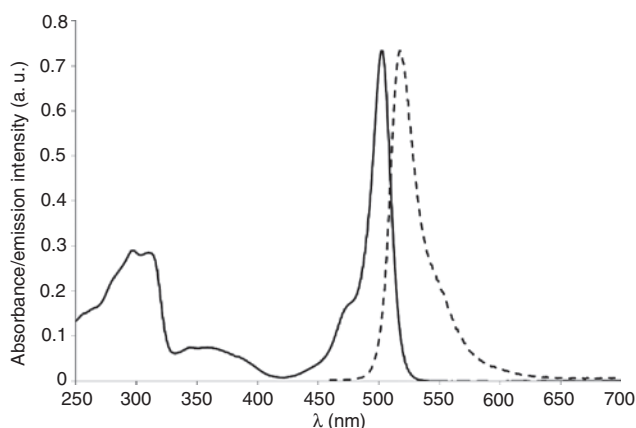


Figure 2 Absorption (solid line) and emission (dashed line) spectra of compound 1 in dichloromethane ($c = 8.4 \times 10^{-6}$ M).

is characterized by a dual fluorescence with large Stokes shift, in addition to the emission from the locally excited state [54] and a red shift of the emission band upon transition from a non-polar solvent to a polar solvent [55]. The second reason is the photo-induced electron transfer (PeT) [52]. In our case, the fluorescence quenching is most likely due to PeT because of the absence of dual fluorescence and significant emission solvatochromism observed when the spectra are recorded in *n*-heptane or acetonitrile (for compound **6**, the emission maxima are observed at 518 nm and 514 nm in heptane and acetonitrile, respectively).

Conclusion

Chromophores containing difluoro-boraindacene part as an electron-withdrawing fragment and different electron-donating groups connected with a phenylethynylene bridge via the position 8 of the BODIPY core were synthesized. It was found that BODIPY and the substituent in position 8 are not co-planar. This geometry leads to the decrease of electronic coupling between the donor and the acceptor parts of the molecules in the ground-state configuration. The nature of the donor substituent and the solvent has no influence on UV/Vis spectra of these compounds. On the other hand, the presence of donor substituents causes the fluorescence quenching, probably due to photo-induced electron transfer. Compounds with such properties could be used as fluorescent probes and in light-emitting diodes.

Experimental

All air- and moisture-sensitive reactions were carried out in flame-dried glassware and cooled under nitrogen. ^1H NMR spectra

(300 MHz) and ^{13}C NMR spectra (75 MHz) were acquired in CDCl_3 at room temperature on a Bruker AC-300 spectrometer (300 MHz). Acidic impurities in CDCl_3 were removed by treatment with anhydrous K_2CO_3 . High resolution mass analyses were performed at the 'Centre Régional de Mesures Physiques de l'Ouest' (CRMPO, University of Rennes1) on a Bruker MicroTOF-Q II apparatus using ESI/ASAP. UV/vis spectra were recorded with a Uvikon xm Secomam spectrometer using standard 1-cm quartz cells. Fluorescence spectra were recorded using a Spex Fluoro Max-3 Jobin-Yvon Horiba apparatus. Compounds were excited at their absorption maxima at the longest-wavelength absorption band. The Φ_F values were calculated using 9,10-diphenylethynylanthracene in cyclohexane as standard [42]. Stokes shifts were calculated by considering the lowest energy absorption band.

General procedures for Sonogashira cross-coupling reaction

Procedure A A mixture of an aryl iodide (1.5 mmol), $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (35 mg, 0.05 mmol, 5% mol.) and CuI (10 mg, 0.05 mmol, 5% mol.) in $\text{Et}_3\text{N}/\text{THF}$ (5 mL/10 mL) was stirred for 15 min and then treated with compound **1** (348 mg, 1 mmol). The mixture was heated to overnight, concentrated and the residue was purified by silica gel column chromatography with the eluent indicated below.

Procedure B A mixture of compound **2** (451 mg, 1.0 mmol), $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (35 mg, 0.05 mmol, 5% mol.) and CuI (10 mg, 0.05 mmol, 5% mol.) in 15 mL of diisopropylamine was stirred for 15 min, treated with an arylacetylene (1.2 mmol) and then heated under reflux overnight. After concentration, the residue was purified by column chromatography using the eluent indicated below.

8-(4-(Thiophen-2-ylethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (3) This compound was obtained using procedure A; chromatography eluent petroleum ether/ CH_2Cl_2 (1 : 1); yield 244 mg (57%); mp > 260°C; ^1H NMR: δ 1.43 (s, 6H); 2.56 (s, 6H); 5.99 (s, 2H); 7.04 (dd, 1H, $J_1 = 3.8$ Hz, $J_2 = 5.1$ Hz); 7.28 (d, 2H, $J = 8.5$ Hz); 7.32–7.35 (m, 2H); 7.64 (d, 2H, $J = 8.5$ Hz); NMR: δ 14.6 (CH_3), 84.1 (C), 92.3 (C), 121.4 (CH), 122.8 (C), 123.9 (C), 127.2 (CH), 127.8 (CH), 128.3 (CH), 132.1 (CH), 132.3 (CH), 135.1 (C), 140.8 (C), 143.0 (C), 155.8 (C). HR-MS. Calcd for $\text{C}_{25}\text{H}_{22}\text{BF}_2\text{N}_2\text{S}$ [$\text{M} + \text{H}$] $^+$: m/z 431.1559. Found: m/z 431.1560.

8-(4-(9H-Fluoren-2-yl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (4) This compound was obtained using procedure A; chromatography eluent petroleum ether/AcOEt (3 : 2 to 1 : 1); yield 179 mg (35%); mp > 260°C; ^1H NMR: δ 1.45 (s, 6H); 2.56 (s, 6H); 3.94 (s, 2H); 6.00 (s, 2H); 7.29 (d, 2H, $J = 8.1$ Hz); 7.32–7.45 (m, 3H); 7.56–7.60 (m, 2H); 7.68 (d, 2H, $J = 8.1$ Hz); 7.74–7.81 (m, 2H); NMR: δ 13.6 (CH_3), 35.8 (CH_2), 87.6 (C), 90.6 (C), 118.9 (CH), 119.3 (CH), 119.8 (C), 120.4 (CH), 123.4 (C), 124.1 (CH), 126.0 (CH), 126.3 (CH), 127.3 (CH), 129.6 (CH), 131.3 (CH), 133.8 (C), 134.1 (CH), 139.9 (C), 140.0 (C), 141.3 (C), 142.1 (C), 142.3 (C), 142.6 (C), 154.8 (C). HR-MS. Calcd for $\text{C}_{34}\text{H}_{28}\text{BF}_2\text{N}_2$ [$\text{M} + \text{H}$] $^+$: m/z 513.2308. Found: m/z 513.2306.

8-(4-(4-Methoxyphenylethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (5) This compound was obtained using procedure B; chromatography eluent petroleum ether/AcOEt (9 : 1); yield 377 mg (83%); mp > 260°C; ^1H NMR: δ 1.43 (s, 6H); 2.56 (s, 6H); 3.84 (s, 3H); 5.99 (s, 2H); 6.90 (d, 2H, $J = 8.7$ Hz); 7.28 (d, 2H, $J = 8.7$ Hz); 7.49 (d, 2H, $J = 8.7$ Hz); 7.64 (d, 2H, $J = 8.7$ Hz);

NMR: δ 14.6 (CH₃), 55.3 (CH₃), 87.4 (C), 90.9 (C), 114.1 (CH), 114.9 (C), 121.3 (CH), 124.5 (C), 128.2 (CH), 131.3 (C), 132.1 (CH), 133.1 (CH), 134.6 (C), 141.0 (C), 155.7 (C), 160.0 (C). HR-MS. Calcd for C₂₈H₂₅¹¹BF₂KN₂O [M + K]⁺: m/z 493.1660. Found: m/z 493.1659.

8-(4-(4-N,N-Dimethylaminophenylethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (6) This compound was obtained using procedure B; chromatography eluent petroleum ether/CH₂Cl₂ (1 : 1 to pure CH₂Cl₂); yield 327 mg (70%); mp > 260°C; ¹H NMR: δ 1.44 (s, 6H); 2.55 (s, 6H); 3.00 (s, 6H); 5.98 (s, 2H); 6.67 (d, 2H, J = 8.7 Hz); 7.24 (d, 2H, J = 8.7 Hz); 7.42 (d, 2H, J = 8.7 Hz); 7.62 (d, 2H, J = 8.7 Hz); NMR: δ 14.6 (CH₃), 40.2 (CH₃), 86.8 (C), 92.3 (C), 109.4 (C), 111.8 (CH), 121.3 (CH), 125.1 (C), 128.1 (CH), 131.3 (C), 131.9 (CH), 132.8 (CH), 134.0 (C), 141.2 (C), 150.3 (C), 155.6 (C). HR-MS. Calcd for C₂₉H₂₈¹¹BF₂KN₃ [M + K]⁺: m/z 506.1876. Found: m/z 506.1979.

8-(4-(4-N,N-Diphenylaminophenylethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (7) This compound was obtained using procedure B; chromatography eluent petroleum ether/CH₂Cl₂ (1 : 1); yield 219 mg (37%); mp > 260°C; ¹H NMR: δ 1.44 (s, 6H); 2.55 (s, 6H); 5.99 (s, 2H); 7.02 (d, 2H, J = 8.7 Hz); 7.14–7.05 (m, 6H); 7.32–7.27 (m, 6H); 7.39 (d, 2H, J = 8.7 Hz); 7.63 (d, 2H, J = 8.7 Hz); NMR: δ 14.6 (CH₃), 87.9 (C), 91.2 (C), 115.4 (C), 121.3 (CH), 122.0 (CH), 123.7 (CH), 124.5 (C), 125.1 (CH), 128.2 (CH), 129.4 (CH), 132.1 (CH), 132.6 (CH), 134.5 (C), 143.0 (C), 147.1 (C), 148.3 (C), 155.7 (C). HR-MS. Calcd for C₃₉H₃₂¹¹BF₂KN₃ [M + K]⁺: m/z 630.2289. Found: m/z 630.2291.

8-(4-((6-Methoxynaphthalen-2-yl)ethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (8) This compound was obtained using procedure B; chromatography eluent petroleum ether/CH₂Cl₂ (7 : 3 to 1 : 1); yield 383 mg (76%); mp > 260°C; ¹H NMR: δ 1.44 (s, 6H); 2.55 (s, 6H); 3.93 (s, 3H); 5.98 (s, 2H); 7.18–7.12 (m, 2H); 7.28 (d, 2H, J = 8.7 Hz); 7.55 (dd, 1H, J_1 = 8.7 Hz, J_2 = 1.5 Hz); 7.68 (d, 2H, J = 8.7 Hz); 7.74–7.72 (m, 2H); 7.94 (s, 1H); NMR: δ 14.6 (CH₃), 53.4 (CH₃), 88.3 (C), 91.4 (C), 105.9 (CH), 117.7 (C), 119.6 (CH), 121.4 (CH), 124.4 (C), 127.0 (CH), 128.2 (CH), 128.5 (C), 129.4 (CH), 131.5 (CH), 132.3 (CH), 134.4 (C), 134.8 (C), 143.0 (C), 155.8 (C), 158.5 (C). HR-MS. Calcd for C₃₂H₂₇¹¹BF₂KN₂O [M + K]⁺: m/z 543.1816. Found: m/z 543.1815.

8-(4-((4-((2,6-Diphenyl-4H-pyran-4-ylidene)methyl)phenyl)ethynyl)phenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (9) This compound was obtained using procedure B (a mixture of THF/NEt₃ was used as solvent instead of HNiPr₂); chromatography eluent petroleum ether/CH₂Cl₂ (3 : 2 to 2 : 3); yield 341 mg (51%); mp > 260°C; ¹H NMR: δ 1.45 (s, 6H); 2.57 (s, 6H); 5.93 (s, 1H); 6.00 (s, 2H); 6.44 (s, 1H); 7.02 (s, 1H); 7.29 (d, 2H, J = 8.3 Hz); 7.38–7.46 (m, 8H); 7.53 (d, 2H, J = 8.3 Hz); 7.67 (d, 2H, J = 8.3 Hz); 7.75–7.82 (m, 4H); NMR: δ 14.6 (CH₃), 88.9 (C), 91.4 (C), 102.0 (CH), 108.6 (CH), 113.5 (CH), 119.3 (C), 121.3 (CH), 124.4 (C), 124.6 (CH), 125.0 (CH), 127.6 (CH), 128.2 (CH), 128.7 (CH), 130.4 (C), 131.8 (CH), 132.2 (CH), 133.2 (C), 133.4 (C), 134.8 (C), 139.1 (C), 141.0 (C), 143.0 (C), 151.2 (C), 153.2 (C), 155.7 (C). HR-MS. Calcd for C₄₅H₄₆¹¹BF₂N₂O [M + H]⁺: m/z 669.2883. Found: m/z 669.2866.

Supporting information

¹H NMR and ¹³C NMR spectra of compounds 3–9, UV/Vis and emission spectra of compounds 2–9 in dichloromethane,

emission spectra of compound 7 in heptane and MeCN can be found in the online supplement.

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