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Convenient and Efficient Synthesis of Functionalized Oligopyridine Ligands Bearing Accessory Pyrromethene-BF_2 Fluorophores

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The synthesis of stable and highly luminescent pyridine-, bipyridine-, phenanthroline-, bipyrimidine-, and terpyridine-based ligands bearing one or two 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (bodipy) modules has demonstrated the advantages of three different protocols which have been adapted in light of the chemical stability of the alkyne-grafted starting building blocks and the chemical reactivity of the bromo-substituted starting materials. A classical method of condensation of aldehydes or acid chlorides with Kryptopyrrole has been used for direct linkage of a bodipy to the oligopyridinic platform. For the phenylethynyl-linked molecules, direct coupling between the bodipy-phenyliodo and the stable 4′-ethynyl-2,2′:6′,2″-terpyridine, 6,6″-diethynyl-2,2′:6′,2″-terpyridine, 5-ethynyl-2,2′-bipyridine, 5,5′-diethynyl-2,2′-bipyridine, 6,6′-diethynyl-2,2′-bipyridine, and 5,5′-diethynyl-2,2′-bipyrimidine substrates is feasible and is promoted by Pd catalysts and sonication. This procedure provides the advantages of efficiency, versatility, and rapidity. A second set of experimental conditions is required to produce the 4-substituted pyridine, 3,8-disubstituted-1,10-phenanthroline, and 5,5″-disubstituted-2,2′:6′,2″-terpyridine derivatives. Cross coupling of a bodipy-phenylethynyl molecule with the bromo-substituted partners takes place smoothly with the pyridine but with low yields in the other cases due to the efficient formation of the homocoupled diphenylbutadiyne bodipy compounds. A third convenient protocol enabled the preparation of these target molecules in a one-pot reaction where the deprotection of the alkyne was conducted in situ by a phase-transfer process with aqueous NaOH and with $Et_3BnN^+Cl^-$ as mediator and the cross-coupling reaction realized in the benzene phase with $[Pd(PPh_3)_4]$ as catalyst and CuI as co-reagent. The nascent acid was quenched in the aqueous phase. This method is much more efficient when a trimethylsilyl protecting group is used instead of a propargylic alcohol. The pyridino-bodipy bases were alkylated smoothly in good yields in the presence of methyl iodide. The photophysical and electrochemical properties for these new molecules have been investigated and are discussed in terms of substitution patterns of the bipyridine and terpyridine platforms. In the pyridinium salt **18**, the fluorescence from the first singlet excited state at $\lambda_{em} = 547$ nm is totally quenched at the expense of a low-lying charge-transfer emitting state located at $\lambda_{em} = 660$ nm.

Introduction

The search for molecular materials with novel luminescence and electrochemical properties is a thriving subject undergoing rapid development.[1−3] This widespread interest stems from their potential applications in diverse areas such as light-emitting films,[4] electroluminescent materials,[5] and molecular probes.[6] Recently, for example, multicomponent arrays based on new lu-

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minescent materials have been employed as the key components of supramolecular devices capable both of performing photochemical light energy conversion and of storage of information at the molecular level.[7−9] Importantly, properties of the final device depend on both the particular structures of the active chemical centers and the ways in which different centers may be linked together.

Among the many laser dyes available in the literature, pyrromethene-BF_2 complexes[10,11] are attractive because of their exceptional optical properties. The applicability of a dye as a laser depends on properties including its photostability, solubility, solvatochromism, molar absorptivity, and luminescence quantum yields. Most noteworthy of the pyrromethene-BF_2 dyes are the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes (bodipy[12]), because the fluorescence properties can be tailored and tuned by a variety of different substitution patterns not only on the organic core but also on the pyrrole side.[13−15] The well-defined molecular structure makes it easier to establish firm structure−property relationships. Thus, major efforts have been devoted to the engineering of new bodipy structures and the investigation of their salient physical and spectroscopic properties.[16]

The availability of more sophisticated bodipy dyes offers the potential to tackle specific problems linked to (i) sensing of protons[17] or various cations[18,19] by optoelectronic switching, (ii) light-harvesting in porphyrin-based arrays,[20] and (iii) Stokes' shift discrimination in energy transfer based on molecular cassettes.[21] We have previously argued that the grafting of a terpyridine subunit to an indacene fluorophore will induce special sensing properties,[22] and such neutral pigments may also be interesting for the preparation of molecularly well-organized thin films, which could find application as light-emitting diodes or transistors.[4] Nevertheless, relatively few hybrid derivatives bearing dual bodipy and oligopyridine fragments are yet known, due largely to difficulties in synthesizing the prerequisite starting materials and elaborating molecules with different conjugated linkers. Although, it is known that two bodipy units may be attached to the 4,4′ positions of 2,2′-bipyridine,[23] it has only been shown so far that the fluorescence of this compound can be effectively modulated by cation binding. Under specific conditions, what has been argued to be an intramolecular photoinduced oxidative electron-transfer process strongly quenches the bright green fluorescence of the boradiazaindacene. Here, we present a complete description and characterization of a family of related but hitherto unknown molecules, which by virtue of their concise and flexible synthesis in addition to their physicochemical and electrochemical properties are promising candidates as effective molecular-scale sensors and light-emitting materials.

Results and Discussion

As depicted in Scheme 1, the Kryptopyrrole **1**[24] is readily condensed with acyl chlorides or, under acidic conditions, with carbaldehydes. In the first case, the relatively stable pyrromethene salt can be isolated and crudely purified prior to its conversion to the desired target materials according to Scheme 1. In the second case, DDQ is required for the oxidation of dipyrromethane to dipyrromethene. Here, a one-pot sequence of condensation, oxidation, and boron complexation afforded better yields. The last step required treatment with boron trifluoride etherate in the presence of triethylamine. In general, when an acyl chloride was used for the condensation procedure, the intermediate protonated species were much more stable than the neutral dipyrromethene compounds and the isolated yields were mostly higher, though no general trends could be drawn concerning the efficiency of those condensations.[16] For molecules **2**−**4** (Scheme 1), low yields (8−13%) were obtained and it is likely that under the reaction conditions either the starting materials or the intermediates (ketopyrrole, dipyrromethene) are unstable.

Previous studies of donor−acceptor complexes based on polyethynyl-bis-terpyridine ligands have shown that the photophysical characteristics are ultimately governed by the topology of the ligands and the chemical nature of the spacer.[25] Alkynyl connectors are particularly useful for favoring electronic communication and extending the conjugation length. This is especially true when the connection is through the para position of the central pyridine ring of a terpyridine template.[26] These consid-

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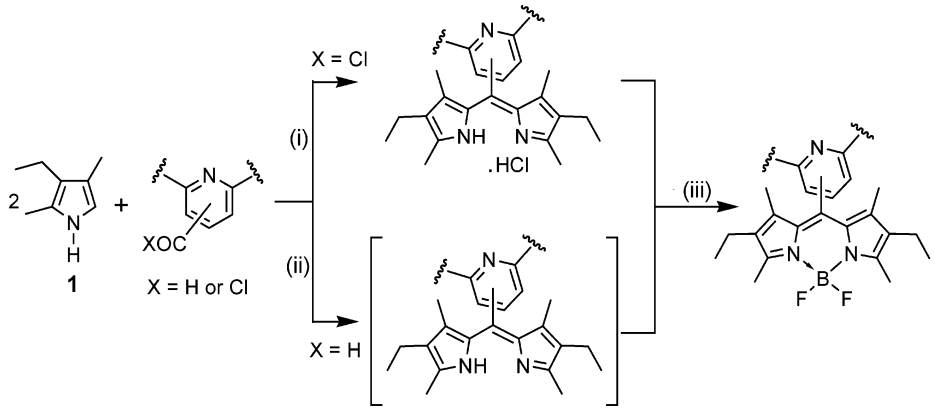
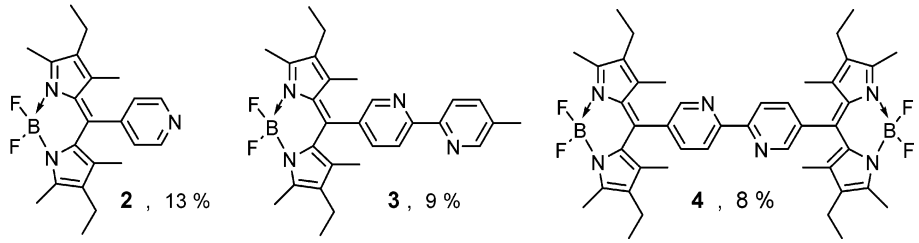
SCHEME 1

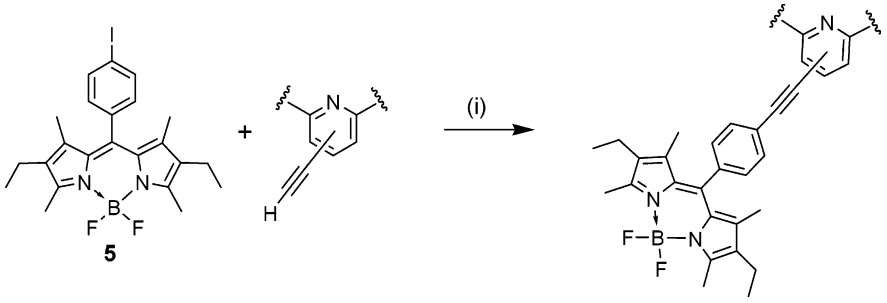


(i) CH_2Cl_2, rt for X = Cl; (ii) TFA or p-TsOH cat.,CH_2Cl_2, rt , DDQ (1 equiv.); (iii) TEA, $BF_3.Et_2O$, toluene, rt.



2 , 13 % **3** , 9 % **4** , 8 %

SCHEME 2



(i) $[Pd(PPh_3)_2Cl_2]$ 6 mol%, CuI 10 mol%, THF, *i*-Pr_2NH, rt, 10 min ultrasounds

erations were the basis of the present investigation of the use of alkynylene bridges to interconnect bodipy fragments to a variety of different chelating subunits including bipyridine, bipyrimidine, phenanthroline, and terpyridine.

After some experimentation, it became obvious that a single strategy could not be adapted to the synthesis of all the target molecules. Particular problems arose in the cases where the starting alkyne-substituted oligopyridines were not sufficiently stable for cross coupling with iodo-substituted bodipy molecule **5**[16] (Scheme 2).

When the terminal alkynes are reasonably stable the cross-coupling reaction catalyzed by low-valent palladium(0) is very fast and efficient under ultrasound irradiation and isolated yields lie in the 68−90% range for single and double substitutions. No major difference in efficiency was observed to depend on the substitution patterns on the 2,2-bipyridine chelate (Chart 1). However, in the case of terpyridine building blocks, the fact that the starting 5,5″-diethynylterpyridine derivative is very unstable meant that the target molecule **17** could only be isolated in low yield (12%). Similarly, for 4,7-diethynyl-1,10-phenanthroline, the final disubstituted compound **14** could not be isolated from an intractable mixture of compounds.

It was then found that the grafting reaction might indeed work out the other way around, starting with an ethynyl-substituted bodipy **13b** (Scheme 3). This protocol enabled isolation of derivatives **14** and **17** in 5% and 30% yields, respectively. The key derivative **13a** was prepared from derivative **5** according to a literature procedure.[20a]

The low yield obtained for the synthesis of compound **14** could in part be explained by the fact that 22% of the monosubstituted derivative **15** was isolated. It is surmised that in the phenanthroline case, the grafting of the first substitutent induces a pronounced σ-withdrawing character,[27] which deactivates the second carbon−bromine bond to such an extent that further reaction is slow and competes poorly with an oxidative homocoupling process of **13b**. Indeed, it was observed that the starting material **13b** has a high tendency to produce the di-

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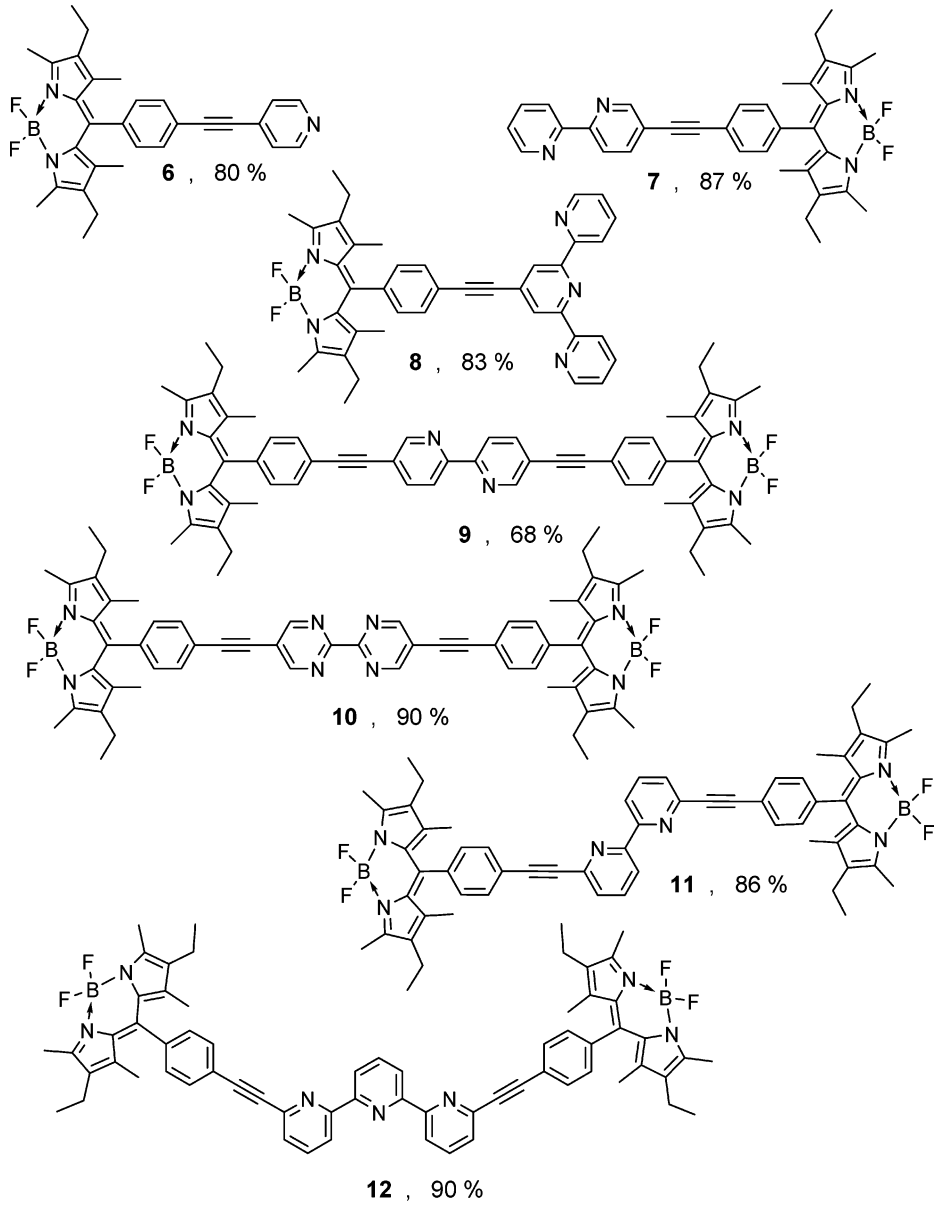
CHART 1



phenylbutadiyne derivative **16** in more than 50% isolated yield in many cases. Strictly anaerobic conditions were used, and it may be that this homocoupling reaction is favored by palladium(0) complexes, as recently suggested for other ethynyl grafted molecules.[28] The use of a pure carbon dioxide atmosphere as previously reported[29] does not significantly reduce the Eglinton−Glaser homocoupling reaction.[30]

After some experimentation, a useful solution was discovered based on a one-pot reaction protocol where in situ deprotection of the alkyne (either from a propargylic alcohol or a trimethylsilane protected alkyne) was realized in a biphasic mixture of benzene and aqueous sodium hydroxide, with 10 mol % of a quaternary ammonium salt as a phase-transfer catalyst (Scheme 4). The cross-coupling reaction between the resulting terminal alkyne and the dibromo-substituted phenanthroline or terpyridine derivatives occurs in the organic phase promoted by palladium(0) and the nascent acid is quenched in the aqueous solution by phase transfer. Previous studies[31,32] provide evidence, consistent with the need to heat the reaction mixture, that the deprotection step is relatively slow while the cross-coupling reaction is fast under these conditions. Thus, in the syntheses of **14** and **17** (Scheme 4), almost no side reaction (including monofunctionalization) could be detected, resulting in very good yields (85−87%). The need to heat at 60 °C probably favors the double substitution process. It is worth pointing out that the most suitable method for the preparation of compound **17** is to use a trimethylsilane protecting group rather than a propargylic one. It is well-

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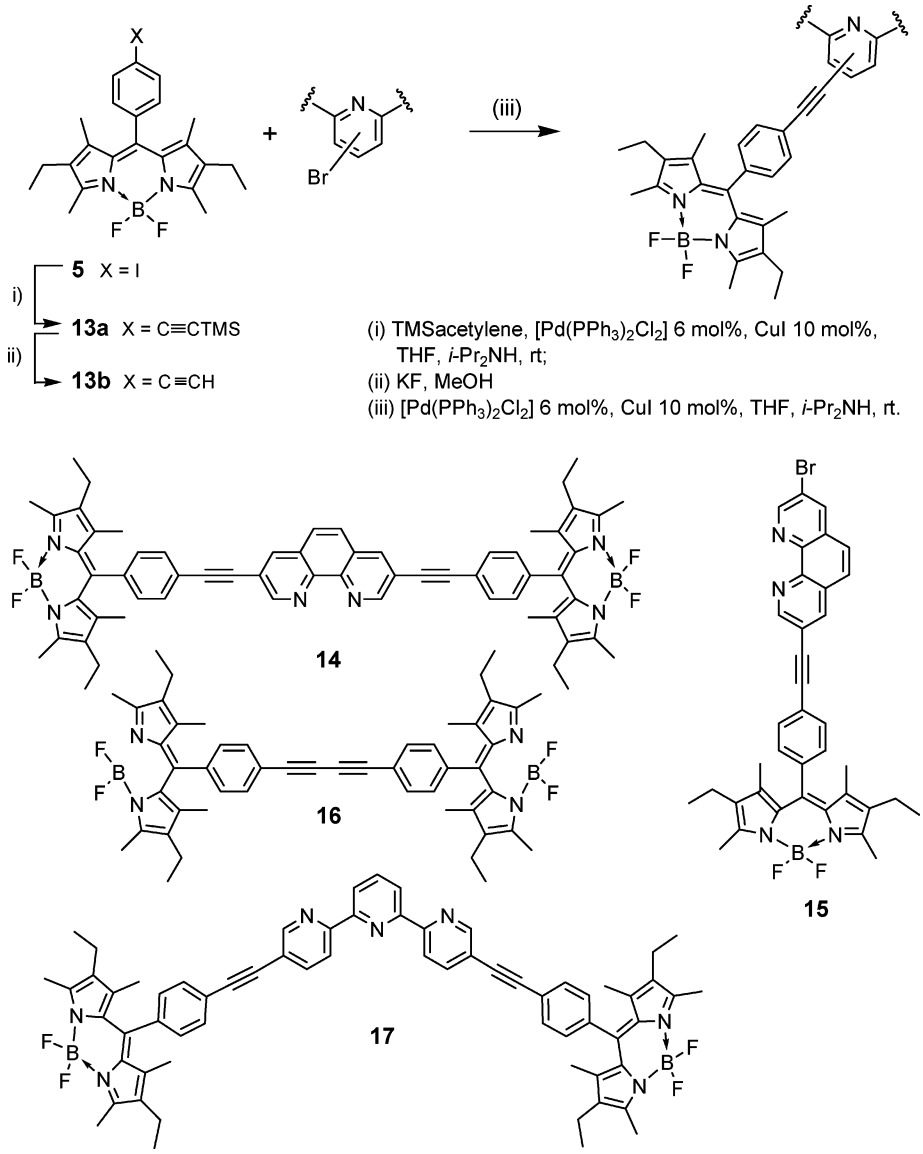
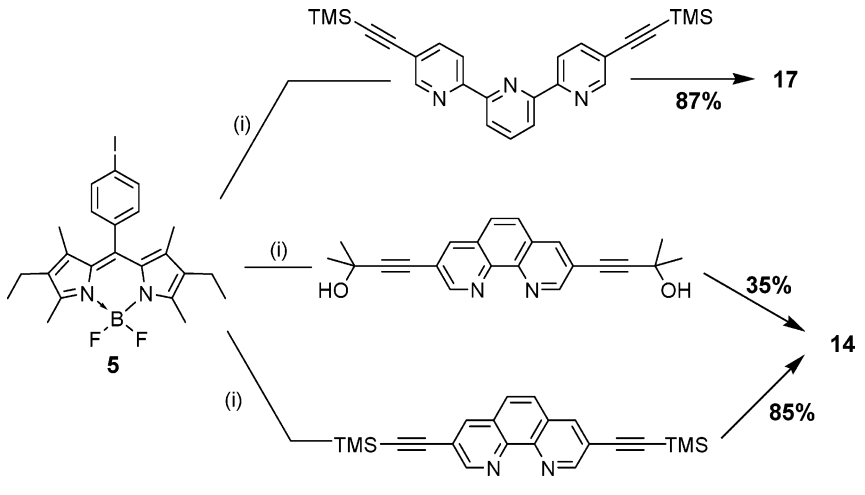
SCHEME 3

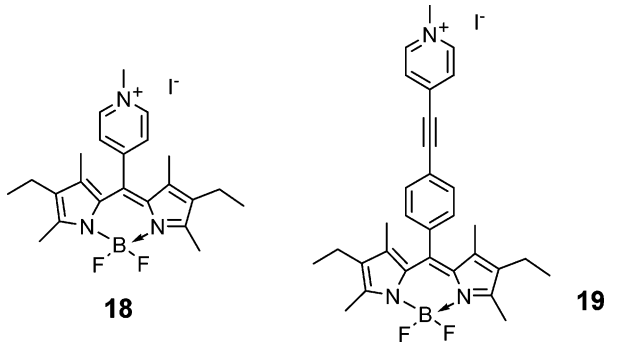


SCHEME 4



known that the deprotection of a propargylic function is difficult and requires high-temperature conditions.[33] Furthermore, propargylic groups could be involved in C−C bond cleavage reactions promoted by low-valent

CHART 2



palladium(0) and be responsible for the low yields.[34] Though not separately identified, many side products accompanied the 35% yield of **14** obtained with use of the inferior protection method.

Finally, to achieve the synthesis of derivatives **18** and **19** (Chart 2), we carried out an alkylation reaction with methyl iodide at room temperature. This reaction is slow and required many days despite the use of a 10-fold excess of the iodide reagent. Nonetheless, both compounds were finally isolated in very good yields. These compounds are interesting because the presence of pyridinium subunits significantly perturbed the redox and optical properties of the luminophore, leading to a significant increase in the Stokes' shift of the emissive state (vide infra).

All the compounds were unambiguously characterized by standard spectroscopic techniques. The ^{1}H NMR spectra display characteristic peaks including two singlets at ca. 1.3 and 2.5 ppm for the two methyl groups and a triplet and quadruplet for the ethyl group of the Kryptopyrrole subunit. This reflects the complete delocalization of the electrons on the indacene core, leading to a 2-fold symmetry. The quasiaromaticity of the boradiazaindacene system is confirmed by the values of the pyrrole quaternary carbon ^{13}C NMR chemical shifts between 120 and 140 ppm. In the case of the acetylenic bridged systems, the triple bond appears as two well-defined peaks between 85 and 95 ppm. The ^{11}B NMR spectra show a characteristic triplet signal at 3.5−3.9 ppm with a coupling constant of ca. 30 Hz, due to coupling with two equivalent fluorine nuclei. The FAB$^+$ mass spectra reveal the high stability of these dyes, with a major molecular peak corresponding to $[M + H]^+$ followed by fragmentation peaks due to the successive loss of the fluorine atoms.

Electrochemical Properties. The solution electrochemical behavior of all molecules was investigated by cyclic voltammetry to probe the electronic effects of the various substituents on the meso position of the bodipy electrophore. Data are collected in Table 1. In most cases, the oxidation of the bodipy fragment to the radical cation (bodipy$^{+\bullet}$) is reversible in dichloromethane and the potential lies within the range of +0.99 to +1.10 V, close to the value for the reference compound **5**. Interestingly, when a pyridine is linked in the para position, either directly or via a phenyl−ethynyl link to the meso position of the bodipy, the oxidation becomes irreversible and a second irreversible oxidation to the dication (bodipy^{2+}) is observed at higher oxidation potential (around +1.4 V) (see compounds **2** and **6** in Table 1 and also Figure 1). The same is true for terpyridine frameworks substituted in the 4′ position of the central pyridine (compounds **8** and **21**) or directly linked in the 6-position (compound

TABLE 1. Solution Electrochemical Properties of the bodipy-polypyridines[a]

compd	$E^{i\,0}_{ox}$, V (ΔE, mV)	$E^{i\,0}_{ox}$, V (ΔE, mV)
2	+1.09 (irrev); +1.46 (irrev)	−1.27 (80)
3	+1.08 (80)	−1.33 (80)
4	+1.05 (60)	−1.31 (80)
5	+1.10 (60)	−1.27 (80)
6	+1.01 (irrev); +1.41 (irrev)	−1.37 (80); −2.10 (60)
7	+1.05 (60)	−1.34 (80)
8	+1.08 (irrev); +1.45 (irrev)	−1.35 (80)
9	+1.00 (70)	−1.34 (70); −1.73 (80)
10	+1.00 (70)	−1.34 (70); −1.44 (70)
11	+1.00 (60)	−1.34 (80)
12	+1.01 (60)	−1.34 (70)
13a	+0.99 (80)	−1.34 (80)
13b	+1.00 (60)	−1.35 (60)
14	+1.06 (62)	−1.34 (60)
15	+0.99 (60)	−1.35 (60)
16	+1.00 (70)	−1.35 (70)
17	+1.00 (60)	−1.37 (80)
18	+0.37[c] (irrev); +0.54[d] (80); +1.13 (70)	−0.79 (70)
19	+0.36[c] (irrev); +0.52[d] (80); +1.07 (70)	−0.88 (70)
20	+1.06 (irrev); +1.44 (irrev)	−1.38 (70)
20[b]	+1.03 (60)	−1.21 (70). −1.98 (90)
21	+1.12 (irrev); +1.51 (irrev)	−1.27 (80)
21[b]	+1.10 (70)	−1.13 (60); −1.73 (70)

[a] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solutions, containing 0.1 M $TBAPF_6$, at a solute concentration range of $1-5 \times 10^{-3}$ M, at 23 °C. Potentials were standardized with ferrocene (Fc) as internal reference and converted to SSCE assuming that $E_{1/2}$ (F_c/F_c^+) = +0.38 V (ΔE_p = 70 mV) vs SSCE. The error in half-wave potentials is ±10 mV. When the redox process is irreversible the peak potential (E_{ap}) is quoted. All waves are monoelectronic unless otherwise specified. [b] Measured in anhydrous CH_3CN. [c] Corresponds to the oxidation of I^- to I_2.[36] [d] This signal might correspond to further oxidation of I_3^- and is also observed under the same conditions from a soluble KI/dicyclohexano-18-crown-6 mixture.

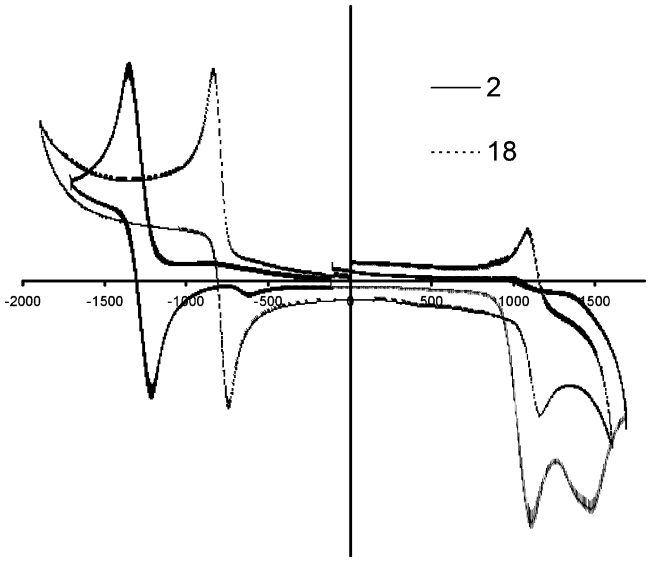


FIGURE 1. Cyclic voltammetry of compounds **2** and **18** (PF_6 form), in CH_2Cl_2 at room temperature, using 0.1 M $^nBu_4PF_6$ as supporting electrolyte.

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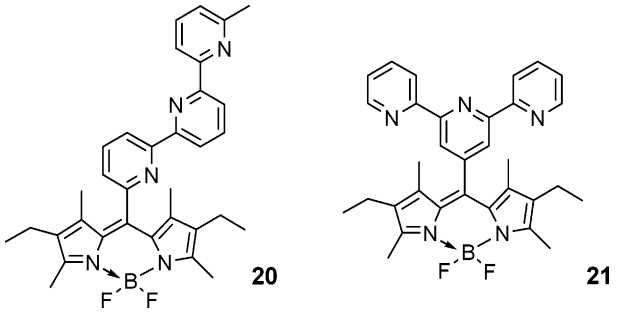
20). In these cases, the use of anhydrous acetonitrile enables observation of a single reversible oxidation to the radical cation at +1.03 and +1.10 V respectively for compounds **20** and **21**, and the second oxidation vanishes from the electrochemical window. This was also found in acetonitrile for derivatives **6** and **8**. It is believed that in acetonitrile the radical cation is stable within the time scale of the cyclic voltammetry. This greater stability than in dichloromethane might be due to a better solvation of bodipy$^{+\bullet}$ and the elimination of the possibility of reacting with dichloromethane to give chlorinated adducts. Interestingly, the observation of the dication in dichloromethane is in keeping with similar processes found with porphyrins.[35] For the pyridinium derivatives **18** and **19** the formation of the bodipy$^{+\bullet}$ was reversible in dichloromethane as the result of the charge effect induced by the alkylation. Additional redox processes are related to the redox activity of I^- and I_3^- present respectively as counteranions and as the result of the electrochemical oxidation of I^- to I_2. These processes disappear on exchanging the anion for PF_6^- and their authenticity was confirmed by carrying out an experiment with KI in the presence of a crown ether to solubilize the salt (see Table 1).

Note that for compound **20** the formation of the radical cation occurs at a ~70 mV lower potential than is found for **21**. In compound **20**, one pyridyl group is bound to the pyridine ring adjacent to the dipyrromethene moiety. In contrast, in compound **21**, two pyridyl rings are bound to the pyridine ring carrying the dipyrromethene fragment. The electron density of the central pyridine ring in **21** is lower than that in **20** because a pyridyl group acts as an electron-withdrawing group. Consequently, the electron density on the indacene fragment is weaker in **21** and its oxidation is more difficult compared to that in **20**. Furthermore, the electron-donating effect of the methyl group present in **20** could also affect the potential required to form the radical cation of the bodipy subunit.

The reduction of the bodipy fragment to the radical anion (bodipy$^{-\bullet}$) was in all cases reversible and lay in the potential range expected for such compounds. Interestingly, a second one-electron reduction wave is observed for the pyridine- (**6**), bipyridine- (**9**), and bipyrimidine- (**10**) based arrays. Due to the pronounced σ-withdrawing effect[37] induced by the ethynyl junction, it is believed that this second reduction does not correspond to the reduction of the bodipy subunit to the dianion but to the radical anion of the pyridine at −2.10 V, the bipyridine at − 1.73 V, and the bipyrimidine at −1.44 V. Such potentials and the sequence of electron affinity are in keeping with previous results found with related polypyridines.[38,39] The reduction of the bodipy to the radical anion in compound **20** is more difficult by ca. 80 mV for compound **21**, as might be expected when a donor group is present and considering the substitution pattern of the pyridine ring directly linked to the indacene core. Using dichloromethane instead of acetonitrile increases this difference to 110 mV and no additional reduction to the terpy$^{-\bullet}$ could be observed (compounds **20** and **21**). Finally, the most spectacular effect results from alkylation of the pyridine rings, causing the one-electron reduction potential to rise by ca. 490 mV compared to that for the neutral molecules (compare compounds **18** and **19**, respectively, with **2** and **6**). Note that the single reduction wave is dielectronic compared to the monoelectronic oxidation of the bodipy to the radical cation (Figure 1). On the basis of previous studies with porphyrin pyridiniums[40,41] it is surmised that this single reduction wave is a superimposition of the reduction located on the bodipy fragment and on the pyridinium. The fact that the reduction of the bodipy is facilitated is likely to be due to the charge withdrawal imposed by the pyridinium group. The overlapping of both processes could be fortuitous but no splitting of the wave is observed with anhydrous DMF or CH_3CN as solvent. It is likely that the single reduction of compound **18** would give a radical easily reduced so that addition of the second electron occurs almost simultaneously.[42] The two-electron reduction of compound **18** is thought to be due to partial localization of the electrons on the two subunits **A** as shown in Chart 4, though **B** is presumably the most stable resonance form. No attempts to isolate and further characterize such interesting compounds have yet been carried out. It is, however, worth noting that highly delocalized, similar derivatives of tripyrrylmethene−boron complexes have been isolated previously.[43]

CHART 3



These characteristics are indicative of a relatively significant coupling between the constituents of these segmented dyes and are auspicious for the perturbation of the redox properties by incoming substrates. Work along these lines is currently in progress.

Optical Properties. Spectroscopic data relevant to the present discussion are collected in Table 2. With the exception of the pyridinium derivatives **18** and **19**, all compounds exhibit absorption patterns typical for bodipy fluorophores.[12−16]

Typical examples are given in Figure 2. In solution, the absorption spectrum shows a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition located around 528 nm with an extinction coefficient depending on the number of appending bodipy

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CHART 4

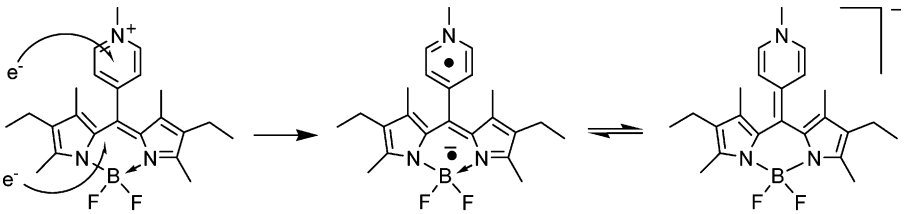

TABLE 2. Spectroscopic[a] Data for the Compounds at 298 K

compd	λ_{abs} (nm)	ϵ ($M^{-1}cm^{-1}$)	λ_F (nm)	Φ_F[b]	τ_F (ns)	k_r[c] ($\times 10^8$ s^{-1})	k_{nr}[c] ($\times 10^7$ s^{-1})
2	528	59 000	547	0.50	3.6	1.40	13.89
3	529	83 000	546	0.69	3.7	1.86	8.38
4	528	141 000	547	0.51	3.7	1.37	13.42
6	527	100 200	544	0.83	4.2	1.97	4.05
7	527	67 000	545	0.89	3.9	2.28	2.82
8	526	123 000	545	0.70	4.1	1.71	7.32
9	527	195 000	544	0.70	3.7	1.89	8.11
10	527	140 000	546	0.62	3.6	1.72	10.50
11	527	160 000	544	0.64	4.1	1.56	8.78
12	526	210 000	545	0.67	3.8	1.76	8.68
13a	528	69 000	542	0.63	4.8	1.31	7.71
13b	528	96 000	544	0.69	4.4	1.57	7.04
14	526	180 000	544	0.78	3.8	2.05	5.79
15	526	38 000	547	0.25	3.3	0.76	22.73
16	529	150 000	545	0.62	3.7	1.67	10.27
17	526	225 000	545	0.48	3.8	1.26	13.68
18	541	26 000	660	0.03	<1		
19	529	77 500	545	0.09	3.6[d]	0.25[d]	25.28[d]
20	529	67 000	552	0.56	4.8	1.16	9.17
21	529	72 000	548	0.87	5.3	1.64	2.45

[a] Determined in dichloromethane solution. [b] Determined in dichloromethane solution, ca. 5×10^{-7} M. With use of Rhodamine 6G as reference with $\Phi = 0.78$ in water and $\lambda_{exc} = 488$ nm[44] (except for **18** where $[Ru(bpy)_3]^{2+}$ was used with $\Phi = 0.028$ in water and $\lambda_{exc} = 452$ nm[45]). All Φ_F are corrected for changes in refractive index. [c] Calculated by using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1 - \Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency. [d] Calculated for the residual singlet emission.

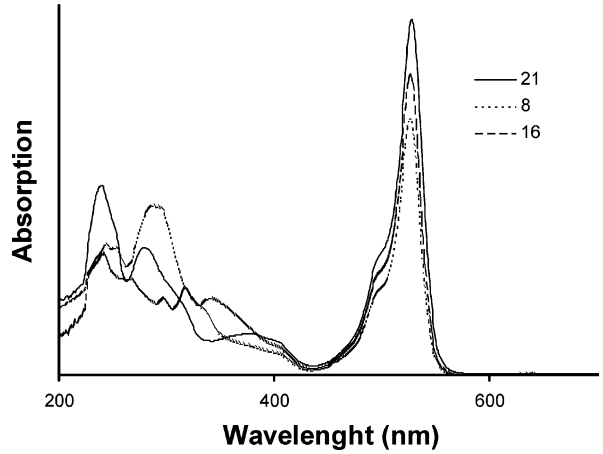

FIGURE 2. Absorption spectra in arbitrary units measured in CH_2Cl_2 at room temperature.

subunits and also on the way these units are connected to the chelating core.

Note that for compounds **6** and **9**, clear hyperchromic shifts were observed compared to derivatives **2** and **4**, respectively. This significant hyperchromic shift induced by the phenylethynyl linkage is also apparent in the terpy series of compounds (compare **8** and **21**). A second weak and broad $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition located at ca. 375 nm was also clearly evident for most of the new species.[46] On the basis of literature data, the peak appearing in the high-energy region may be assigned to spin-allowed $\pi-\pi^*$ transitions centered on the polypyridine part of the ligand.[47] In particular, the band at lower energy (250 nm) should be due principally to transitions involving the phenyl sites and that at higher energy to transitions involving the polypyridine fragments. The absorption band around 320 nm is tentatively assigned to $n-\pi^*$ transitions also involving the polypyridine sites.[48] These transitions are absent from the absorption spectra of derivative **16** (Figure 2). In addition the transitions located around 380 nm are due to the contribution of the $\pi-\pi^*$ transitions located on the alkyne fragment.[49] This absorption band is, as expected, absent for the reference compound **5**. Finally, no long-wavelength charge-transfer (CT) absorption bands are observed for these neutral compounds.[50]

The fluorescence properties were examined under ambient conditions in dichloromethane. The neutral dyes, which are highly soluble in most common solvents, exhibit strong photoluminescence with fluorescence quantum yields being measured using Rhodamine 6G. The highest quantum yields were found for ligands **7** and **10**, which have the highest oscillator strength for the corresponding absorption, induced by the monosubstitution of the bipyridine core in **7** and the presence of four nitrogen atoms in compound **10**. No marked difference in the quantum yield was found by changing the substitution patterns in the bipyridine series (e.g. compare **9** and **11**) or in the terpyridine series (e.g. compare **12** and **17**). The decrease in ϕ_{lum} observed for the bromo derivative **15** is possibly due to a heavy atom effect favoring an effective spin−orbit coupling, resulting in a nonemissive low-lying excited state.[51] The weak Stokes shifts of about 600 cm^{-1} for the series of bodipy fluorophores are in keeping with a singlet emitting state. Excitation spectra performed under similar conditions perfectly match the absorption spectra. A typical example (Figure 3) shows that the emitted light originates from a single excited state with

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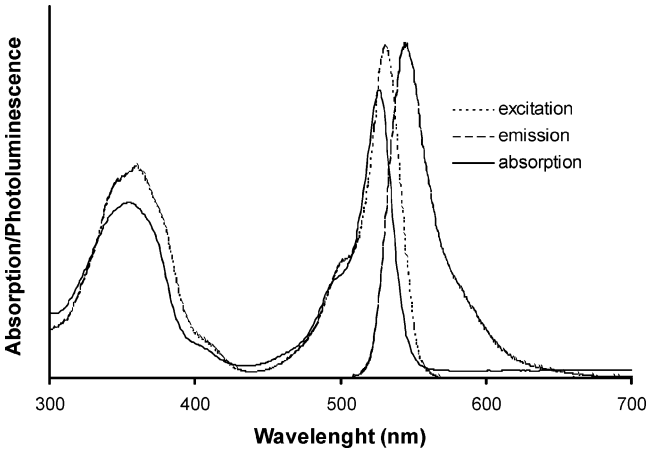

FIGURE 3. Absorption, emission, and excitation spectra measured for compound **9**, in CH_2Cl_2 at room temperature.

almost no contribution of a possible CT transition, despite the fact that these molecules contain both electron-donating groups such as bodipy/phenyl and electron-accepting fragments such as bodipy and polypyridine fragments. The absence of any significant dynamic quenching of the luminescence by molecular oxygen excludes the presence of an emissive triplet excited state. Furthermore, the fluorescence decay profiles could be described by a single-exponential fit giving raise to fluorescence lifetimes in the order of ca. 5 ns, in accordance with a singlet excited state. In fact, the radiative rate constants of 2×10^{-8} s^{-1} are the same within experimental errors (Table 2). The nonradiative rate constants are significantly higher for **15** compared to the others, which may be attributed either to the higher conformational flexibility induced by the terpyridine backbone or to the interaction with an energetically low-lying localized state. In addition, no significant solvatochromic effect was observed in the absorption and fluorescence spectra, confirming weak polarization of the ground and excited states. More importantly, the fluorescence spectrum shows good mirror symmetry with the lowest energy absorption transition (Figure 3), confirming that these transitions are due to the same state. These photophysical data are in accordance with related functionalized boron−dipyrromethene dyes.[52]

Considering both the absorption and fluorescence properties of the dyes, the most interesting optical properties were found for the cationic dyes **18** and **19**. No fluorescence was observed from the $S_0 \rightarrow S_1$ transition for **18**, at the expense of a pronounced red-shifted emission at 660 nm in dichloromethane. The strong Stokes' shift at about 3300 cm^{-1} is contrary to the previous cases where a standard Stokes' shift of ca. 600 cm^{-1} is found. In dioxane, acetone, and acetonitrile a hypsochromic shift of 980 cm^{-1} was found (Figure 4). The excitation spectrum of **18** perfectly matches the absorption spectrum (Figure 5) in the solvents used. For **19**, a residual steady-state fluorescence attributed to the $S_0 \rightarrow S_1$ transition persists with a quantum yield of 9% compared to 83% in derivative **6**. Unfortunately, the CT emissive band is not clearly seen but it could be much

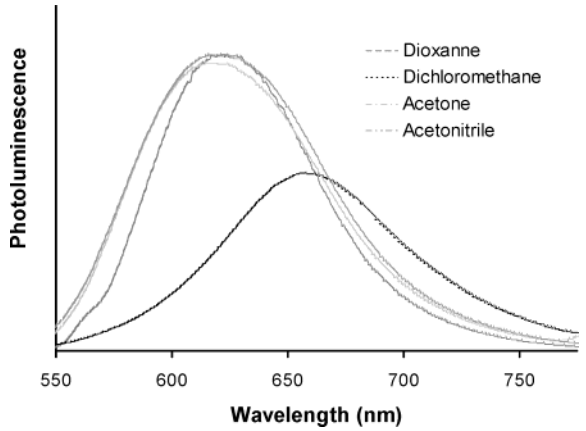

FIGURE 4. Emission spectra measured for compound **18**, in various solvents at room temperature.

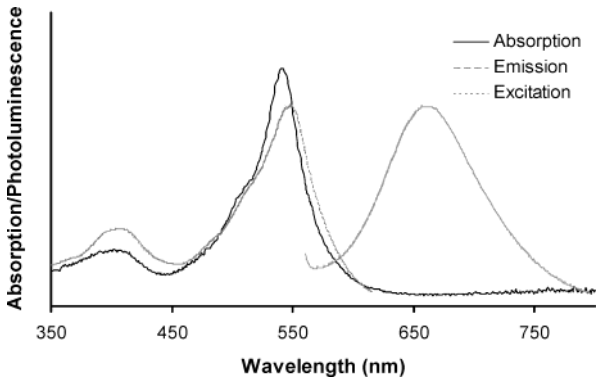

FIGURE 5. Absorption, emission, and excitation spectra measured for compound **18**, in CH_2Cl_2 at room temperature.

less intense and beneath the emission band of the singlet. The fluorescence excitation spectra of **19** recorded at the short and long wavelengths also perfectly match its absorption spectra. These data seem to indicate that the long wavelength emission for **18** originates from a species formed after the excitation of the bodipy chromophoric fragment and the solvatochromism is in keeping with its highly dipolar nature. In light of literature data for amino-substituted borondipyrromethene dyes,[53] this red emission can safely be attributed to a species having pronounced charge-transfer character. Usually this CT state is formed by a fast reaction (picosecond time scale) in the excited state as found in *p*-anthracenyldimethylaniline and related derivatives.[54] At this stage of our investigation we do not have any evidence for the formation of this CT from an intermediate locally excited (LE) state formed from the excitation of the single ground-state species as postulated in donor−acceptor systems. No effect of molecular oxygen has been observed on the properties of this CT state. Interestingly, the lifetime decay and fluorescence quantum yield for the CT state are both diminished compared to these properties for the singlet excited state of the neutral dyes described above.

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Concluding Remarks

Highly fluorescent and soluble probes have been synthesized by following three main strategies that combine the advantages of the ready availability of the starting materials and the synthetic efficiency of C−C bond formation promoted by palladium(0) catalysts. A straightforward route involving ultrasonic activation allows the coupling of the dye with the alkyne-substituted ligands in the time scale of minutes at room temperature. The cross coupling of ethynylphenyl-grafted bodipy with bromo-substituted oligopyridines is feasible but a very effective oxidative homocoupling process hampers the efficiency. When the stability of the ethynyl-linked oligopyridines is not satisfactory, a third protocol, based on a biphasic process, can be employed. This process consists of in situ deprotection of the fragile alkyne-substituted phenanthroline and terpyridine derivatives and cross coupling with a iodo-grafted bodipy. A strong electronic transition located at about 520 nm, which contains long axis polarized electronic transition dipoles, is responsible for the very efficient fluorescence emission reaching 89% in the best case. For the neutral dyes the Stokes' shift is modest (600 cm^{-1}), but much higher when the pyridine fragment is alkylated (3300 cm^{-1}). A charge transfer state is invoked in the pyridinium cases to explain the bathochromic shift of the emission and the solvatochromism.

Furthermore, the remarkable stability, the weak dependence on solvent polarity (for the neutral molecules), the chemical accessibility, the strong absorption, and the luminescence properties of these probes make them highly suitable and attractive for investigating the influence of incoming cations as well as for use as light-emitting materials. Due to their reversible redox properties, these new neutral materials exhibit bipolar character and might behave as exciton carriers in optoelectronic devices. We are currently involved in a research program aimed at the use of these molecules as exciton acceptors from more standard emitting materials in light-emitting diodes and as dopants in plastic solar cells.

Experimental Section

General Methods. The 200.1- (^{1}H), 300.1- (^{1}H), 400- (^{1}H), 50.3- (^{13}C), 75.46- (^{13}C), and 100.3- (^{13}C) MHz NMR spectra were recorded at room temperature with perdeuterated solvents, with residual protiated solvent signals providing internal references. The 128.4- (^{11}B) MHz NMR spectra were recorded at room temperature with glass residual B_2O_3 as reference. A fast-atom bombardment ZAB-HF-VB-analytical apparatus in positive mode was used with *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. FT-IR spectra were recorded on the neat liquids or as thin films, prepared with a drop of dichloromethane and evaporated to dryness on KBr pellets. Melting points were obtained on a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification was conducted with standard aluminum oxide 90. Thin-layer chromatography (TLC) was performed on aluminum oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio.

Materials. CH_2Cl_2 was distilled from P_2O_5. Kryptopyrrole, 4-bromopyridinium hydrochloride, trimethylsilylacetylene, KF, methyl iodide, $(^iPr)_2NH$, DDQ, $BF_3{\cdot}Et_2O$, TFA, *p*-TsOH, 4-formylpyridine, Et_3N, and $BF_3{\cdot}Et_2O$ were used as purchased. $[Pd(PPh_3)_2Cl_2]$,[55] $[Pd(PPh_3)_4]$,[56] 5-formyl-5′-methyl-2,2′-bipyridine,[57] 5,5′-bis(carbonyl chloride)-2,2′-bipyridine,[58] compound **5**,[16] 5-ethynyl-2,2′-bipyridine,[33] 4′-ethynyl-2′:2″;6″:2‴terpyridine,[59] 5,5′-bis-ethynyl-2,2′-bipyridine,[60] 5,5′-bis-ethynyl-2,2′-bipyrimidine,[38] 6,6′-bis-ethynyl-2,2′-bipyridine,[61] 6,6′-dibromo-2:2′;6′:2″-terpyridine,[62] 6,6′-bis-ethynyl-2:2′;6′:2″-terpyridine,[63] 3,8-dibromo-1,10-phenanthroline,[64] 3,8-bis-2-isopropanolsilylethynyl-1,10-phenanthroline,[62] 3,8-bistrimethylsilylethynyl-1,10-phenanthroline,[65] 5,5′-bis-ethynyl-2:2′;6′:2″-terpyridine,[66] and 5,5′-bistrimethylsilylethynyl-2:2′;6′:2″-terpyridine[66] were prepared and purified according to literature procedures. All reactions were carried out under dry argon by using Schlenk-tube techniques and $[Pd(PPh_3)_2Cl_2]$ was recrystallized from hot DMSO.

Spectroscopic Measurements. Absorption spectra were recorded on a UVIKON 933 absorption spectrometer. The steady-state fluorescence emission and excitation spectra were obtained by using a LS50B Perkin-Elmer instrument. All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{exp}) was calculated from eq 1.[67]

$$\Phi_{exp} = \Phi_{ref}\frac{F\{1 - \exp(-A_{ref}\ln 10)\}n^2}{F_{ref}\{1 - \exp(-A\ln 10)\}n_{ref}^2} \quad (1)$$

Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium. The reference systems used were rhodamine 6G ($\Phi_{ref} = 0.78$, $\lambda_{exc} = 488$ nm)[44] and $[Ru(bpy)_3]Cl_2$ in air-equilibrated water ($\Phi_{ref} = 0.028$, $\lambda_{exc} = 452$ nm).[45] Luminescence lifetime were measured on a PTI QuantaMaster spectrofluorimeter, using TimeMaster software with Time-Correlated Single Photon Mode coupled to a Stroboscopic system. The excitation source was a thyratron-gated flash lamp filled with nitrogen gas. No filter was used for the excitation. An interference filter centered at 550 nm selected the emission wavelengths. The instrument response function was determined by using a light-scattering solution (LUDOX).

Electrochemical Measurements. Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyzer equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counterelectrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SSCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electroactive substrate in deoxygenated and anhydrous dichloromethane or acetonitrile containing doubly recrystallized tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible within ≈20 mV.

4,4-Difluoro-8-(4′-pyridinyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (2). Kryptopyrrole (760 μL, 5.6 mmol) was stirred with 4-formylpyridine (270 μL, 2.8 mmol) in CH_2Cl_2 at room temperature over 1 day in the presence of *p*-toluenesulfonic acid (20 mg). The solution turned

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deep red. DDQ (0.6 g, 2.8 mmol) was then added to the solution and the stirring continued for 4 h. The dipyrromethene solution was deprotonated with triethylamine (1.5 mL), and trifluoroboride etherate was then added (1.2 mL, 7.5 mmol) in 3 portions during 4 h, and the solution stirred at rt overnight. The resulting dark mixture was washed with a saturated aqueous $NaHCO_3$ solution and dried over $MgSO_4$, and the solvent was removed. Column chromatography on Alumina (Act IV, hexane/dichloromethane, with a gradient from 8:2 to 5:5) afforded the fluorescent desired compound as a red powder (0.065 g, 13%). Mp 168−9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, 6H, ^3J = 7.6 Hz), 1.32 (s, 6H), 2.31 (q, 4H, ^3J = 7.6 Hz), 2.55 (s, 6H), 7.31 (dd, 2H, ^3J = 4.3 Hz, ^4J = 1.5 Hz), 8.78 (dd, 2H, ^3J = 4.5 Hz, ^4J = 1.7 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 12.3 (CH_3), 13.0 (CH_3), 15.0 (CH_3), 17.5 (CH_2), 124.1 (CH), 130.1 (Cq), 133.8 (Cq), 136.6 (Cq), 138.2 (Cq), 144.8 (Cq), 151.0 (CH), 155.2 (Cq). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.79 (t, $^1J_{B-F}$ = 32.8 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 235 (14 800), 382 (6300), 501 (sh, 21 000), 528 (59 000). IR (KBr) 1638 (s, $\nu_{C=N}$), 1414, 1118 cm^{-1}. MS (FAB^+, *m*-NBA) *m*/*z* (%) 382.2 (30) [M + H^+], 381.2 (100) [M], 362.3 (20) [M − F]$^+$. Anal. Calcd for $C_{22}H_{26}BF_2N_3$: C, 69.30; H, 6.87; N, 11.02. Found: C, 69.10; H, 6.61; N, 10.82.

4,4-Difluoro-8-(5″-methyl-2′,2″-bipyridin-5′-yl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (3). A solution of 5-formyl-5′-methyl-2,2′-bipyridine (0.27 g, 1.3 mmol), Kryptopyrrole (0.37 mL, 2.7 mmol), and a catalytic amount of TFA in anhydrous dichloromethane (100 mL) was stirred for 1 week at room temperature. DDQ (0.3 g, 1.3 mmol) was then added and the solution stirred over 2 h. The solution was washed with a saturated aqueous solution of $NaHCO_3$, the organic layers were dried over $MgSO_4$, and the solvent was removed. The dark residue was dissolved in toluene (100 mL), triethylamine (0.2 mL) and $BF_3{\cdot}Et_2O$ (0.25 mL) were added, and the solution was stirred 1 day at rt. The solution was then washed with water, the organic fraction dried over $MgSO_4$, and the solvent removed. Chromatography on alumina (CH_2Cl_2/hexane, 2:8 to 5:5) gave the desired compound as a red powder (0.053 g, 9%). Mp >300 °C dec. ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 0.98 (t, 6H, ^3J = 7.6 Hz, *CH*$_3$), 1.36 (s, 6H, *CH*$_3$), 2.31 (q, 4H, ^3J = 7.5 Hz, *CH*$_2$), 2.43 (s, 3H, *CH*$_3$), 2.54(s, 6H, *CH*$_3$), 7.67 (m, 1H), 7.75 (dd, 1H, ^3J = 8.0 Hz, ^4J = 2.2 Hz), 8.37 (d, 1H, ^3J = 8.4 Hz), 8.52−8.58 (m, 3H). ^{13}C{^{1}H} Dept NMR (100.6 MHz, $CDCl_3$) δ 12.8, 14.9, 17.4, 18.7, 29.9, 120.9, 121.2, 131.9, 133.6, 134.4, 136.4, 137.5, 137.9, 138.4, 148.4, 150.1, 153.1, 154.9, 156.8. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, $^1J_{B-F}$ = 33.26). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 245 (25 400), 289 (26 400), 500 sh (28 500), 529 (83 000). IR (KBr) 2917, 1539 (s, $\nu_{C=N}$), 1464, 1117 cm^{-1}. MS (FAB^+, *m*NBA) *m*/*z* (%) 473.1 (100) [M + $H]^+$, 453 (20) [M − F]$^+$. Anal. Calcd for $C_{28}H_{31}BF_2N_4$: C, 71.19; H, 6.61; N, 11.89. Found C, 70.89; H, 6.43; N, 11.67.

(2′,2″-Bipyridin-5′,5″-yl)bis[4,4-difluoro-8-(1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene)] (4). A solution of 5,5′-bis(carbonyl chloride)-2,2′-bipyridine (0.5 g, 1.9 mmol) and Kryptopyrrole (960 μL, 7.12 mmol) in anhydrous dichloromethane (200 mL) was stirred for 1 week at room temperature. Triethylamine (3 mL, 27.8 mmol) was then added to the solution, followed 5 min later by $BF_3{\cdot}Et_2O$ (3.8 mL, 30.4 mmol). After 3 h of stirring, the organic solution was washed with water and dried over $MgSO_4$, and the solvent was removed. Column chromatography on alumina (CH_2Cl_2/hexane, gradient from 2:8 to 8:2) afforded the title compound as a crystalline red powder (0.11 g, 8%). Mp >300 °C dec. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.00 (t, 12H, ^3J = 7.5 Hz, *CH*$_3$), 1.41 (s, 12H), 2.33 (q, 8H, ^3J = 7.5 Hz), 2.56 (s, 12H), 7.83 (dd, 2H, ^3J = 7.95 Hz, ^4J = 2.2 Hz), 8.63−8.66 (m, 4H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 13.1, 15.0, 17.5, 30.1, 121.5, 131.3, 133.1, 133.8, 136.1, 137.9, 138.4, 148.9, 155.2, 155.9. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.85 (t, J_{B-F} = 32.5 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 246 (33 500), 293 (28 300), 501 (sh, 55 200), 528 (141 000). IR (KBr) 3437, 2918, 1589 (s, $\nu_{C=N}$), 1416, 1116 cm^{-1}. MS (FAB^+, *m*NBA) *m*/*z* (%) 760.2 (100) [M]$^+$, 741.2 (30) [M − F]$^+$, 722.2 (30) [M − 2F]$^+$. Anal. Calcd for $C_{44}H_{50}B_2F_4N_6$: C, 69.49; H, 6.63; N, 11.05. Found: C, 69.33; H, 6.52; N, 10.89.

General Procedure for the Ethynyl-Linked Structures. Method A: A Schlenk flask was charged with ethynyl oligopyridine derivatives (1 equiv), bodipy-phenyliodo **5** (1.1 equiv by acetylenic group), $Pd(PPh_3)_2Cl_2$ (3−6 mol % per acetylenic group), THF, and (^{i}Pr)$_2$NH. The yellow slurry was exhaustively degassed with argon. Copper iodide (5−10 mol % per acetylenic group) was then added, and the mixture was sonicated 30 min. After one night of stirring at room temperature, the solvent was removed under vacuum. The residue was purified by chromatography on alumina. No aqueous treatment was required.

Method B: Ethynyl phenyl bodipy (1 equiv by bromide group), oligopyridine bromide (1.1 equiv), $Pd(PPh_3)_2Cl_2$ (3−6% mol by acetylenic group), THF, and (^{i}Pr)$_2$NH were mixed in a Schlenk flask. The pink slurry was exhaustively degassed with argon. Copper iodide (5−10 mol % per acetylenic group) was then added, and the mixture was sonicated for 30 min. After one night of stirring at room temperature, the solvent was removed under vacuum. The residue was purified by chromatography on alumina. No aqueous treatment was required.

Method C: A benzene/water biphasic mixture containing trimethylsilylacetylene or propargylic oligopyridine derivatives (1 equiv), phenyl iodide **5** (1.1 equiv by acetylenic group), sodium hydroxide (10 equiv), and Et_3BzNCl (6 mol %) was exhaustively degassed with argon. $Pd(PPh_3)_4$ (3−6 mol % per acetylenic group) and copper iodide (6−12 mol %) was then added and the reaction mixture was heated under argon at 60 °C for 1 day. The benzene was then removed, water was added, and the compound was extracted with dichloromethane. The organic fractions were dried over $MgSO_4$, and chromatography on alumina afforded the pure compounds.

4,4-Difluoro-8-(pyridine-4′-ethynylphenyl-)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (6). Method B: 13a (0.054 g, 0.134 mmol), 4-bromopyridinium hydrochloride (0.039 g, 0.2 mmol), $Pd(PPh_3)Cl_2$ (0.005 g, 0.07 mmol), THF (3 mL), (^{i}Pr)$_2$NH (1 mL), and CuI (0.003 g, 0.01 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 3:7) gave **6** (0.052 g, 80%). Mp 273 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 6H, ^3J = 7.5 Hz), 1.32 (s, 6H), 2.30 (q, 4H, ^3J = 7.5 Hz), 2.53 (s, 6H), 7.41 (dd, 2H, ^3J = 4.5 Hz, ^4J = 1.5 Hz), 7.51 (AB sys, 4H, J_{AB}= 8.5 Hz, $\nu_0\delta$ = 106.3 Hz), 8.63 (dd, 2H, ^3J = 4.5 Hz, ^4J = 1.5 Hz). ^{13}C{^{1}H} NMR (75.46 MHz, $CDCl_3$) δ 11.9, 12.5, 14.6, 17.1, 87.8, 93.1, 122.7, 125.5, 128.7, 130.5, 131.0, 132.5, 133.0, 136.9, 138.1, 138.8, 149.9, 154.2. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.84 (t, $^1J_{B-F}$ = 33.7 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 239 (29 500), 286 (43 000), 497 (sh, 33 200), 527 (100 200). IR (KBr) 3437, 2920, 1542 (s, $\nu_{C=N}$), 1474, 1119 cm^{-1}. MS (FAB^+, *m*NBA) *m*/*z* (%) 482.1 (50) [M + H^+], 481.2 (100) [M]$^+$, 462.2 (30) [M − F]$^+$. Anal. Calcd for $C_{30}H_{30}BF_2N_3$: C, 74.85; H, 6.28; N, 8.73. Found: C, 74.63; H, 5.98; N, 8.52.

5-{Ethynylphenyl-4″-[4‴,4‴-difluoro-8‴-(1‴,3‴,5‴,7‴-tetramethyl-2‴,6‴-diethyl-4‴-bora-3‴a,4‴a-diaza-*s*-indacene)]}-2,2′-bipyridine (7). Method A: 5-Ethynyl-2,2′-bipyridine (0.057 g, 0.316 mmol), **5** (0.16 g, 0.316 mmol), $Pd(PPh_3)Cl_2$ (0.014 g, 0.019 mmol), THF (10 mL), (^{i}Pr)$_2$NH (5 mL), CuI (0.006 g, 0.03 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 5:5 to 7:3) gave **7** as a deep-pink powder (0.154 g, 87%). Mp >300 °C dec. ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 0.98 (t, 6H, ^3J = 7.4 Hz), 1.33 (s, 6H), 2.29 (q, 4H, ^3J = 7.5 Hz), 2.54 (s, 6H), 7.29−7.32 (m, 1H), 7.51 (ABsys, 4H, J_{AB}= 8.2 Hz, $\nu_0\delta$ = 75.7 Hz), 7.78−7.87 (m, 1H), 7.97 (dd, 1H, ^3J = 8.3 Hz, ^4J = 2.2 Hz), 8.41−8.46 (m, 2H), 8.68−8.70 (m,1H), 8.85 (s, 1H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 12.0, 12.6, 14.7, 17.2, 87.7, 92.9, 120.0, 120.5, 121.5, 123.3, 124.1, 128.8, 130.6, 132.4, 133.1, 136.5, 137.1, 138.2, 139.1, 139.5, 149.4, 151.8, 154.2, 155.2, 155.4. IR (KBr) 2919, 1635 (s, $\nu_{C=N}$), 1115 (m, $\nu_{B=F}$) cm^{-1}. UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ,

M^{-1} cm^{-1}) 354 (40 700), 499 (sh, 23 700), 527 (67 000). MS (FAB$^+$, *m*NBA):*m*/*z* (%) 559.1 (10) [M + H]$^+$, 558.1 (100) [M]$^+$, 539.2 (20) [M − F]$^+$. Anal. Calcd for $C_{35}H_{33}BF_2N_4$: C, 75.27; H, 5.96; N, 10.03. Found: C, 75.05; H, 5.70; N, 9.84.

4′-{Ethynylphenyl-4‴-[4⁗,4⁗-difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2:2′;6′:2″terpyridine (8). Method A: 4′-Ethynyl-2:2′;6′:2″-terpyridine (0.224 g, 0.896 mmol), **5** (0.4 g, 0.79 mmol), Pd(PPh_3)Cl_2 (0.033 g, 0.047 mmol), THF (15 mL), (^{i}Pr)$_2$NH (5 mL), and CuI (0.015 g, 0.078 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 3:7) gave **8** as red crystals (0.46 g, 83%). Mp 256−7 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 0.99 (t, 6H, ^3J = 7.5 Hz), 1.34 (s, 6H), 2.31 (q, 4H, ^3J = 7.5 Hz), 2.54 (s, 6H), 7.32−7.38 (m, 4H), 7.70 (d, 2H, ^3J = 7.5 Hz), 7.88 (td, 2H, ^3J = 7.7 Hz, ^4J = 1.8 Hz), 8.62−8.65 (m, 4H), 8.71−8.73 (m, 2H). ^{13}C{^{1}H} DEPT NMR (75.4 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.5 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 88.7, 92.9, 121.2 (CH), 122.8 (CH), 123.1, 124.1 (CH), 128.7 (CH), 130.5, 132.5 (CH), 133.0, 136.7, 136.9 (CH), 138.2, 139.1, 149.2 (CH), 154.1, 155.6, 155.7. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 33.08 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 243 (62 700), 298 (81 500), 498 sh (41 300), 526 (123 000). IR (KBr) 3436, 2921, 1620 (br, $\nu_{C=N}$), 1581, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 635.2 (100) [M $^+$]. Anal. Calcd for $C_{40}H_{36}N_5BF_2$: C, 75.59; H, 5.71; N, 11.02. Found: C, 75.33; H, 5.49; N, 10.98.

5,5′-Bis{ethynylphenyl-4‴-[4⁗,4⁗-difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2,2′-bipyridine (9). Method A: 5,5′-Bis-ethynyl-2,2′-bipyridine (0.050 g, 0.245 mmol), **5** (0.254 g, 0.502 mmol), Pd(PPh_3)Cl_2 (0.02 g, 0.028 mmol), THF (15 mL), (^{i}Pr)$_2$NH (5 mL), and CuI (0.01 g, 0.05 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 7:3) gave **9** as a deep-pink powder (0.16 g, 68%). Mp >300 °C dec. ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 0.99 (t, 12H, ^3J = 7.5 Hz), 1.34 (s, 12H), 2.32 (q, 8H, ^3J = 7.4 Hz), 2.54 (s, 12H), 7.53 (ABsys, 8H, J_{AB}= 8.3 Hz, $\nu_0\delta$ = 75.1 Hz), 7.99 (dd, 2H, ^3J = 8.3 Hz, ^4J = 2.1 Hz), 8.48 (d, 2H, ^3J = 8.3 Hz), 8.85−8.86 (m, 2H). ^{13}C{^{1}H} JMOD NMR (100.6 MHz, $CDCl_3$) δ 12.3 (CH_3), 12.9 (CH_3), 15.0 (CH_3), 17.5 (CH_2), 87.9, 93.6, 120.6, 121.1 (CH), 123.6, 129.1 (CH), 130.9, 132.7 (CH), 133.4, 136.9, 138.5, 139.4, 139.8 (CH), 152.2 (CH), 154.6, 154.8. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 33.40 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 354 (126 000), 498 (sh, 73 000), 527 (194 000). IR (KBr) 3437, 2919, 1620 (br, $\nu_{C=N}$), 1594, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 960.4 (100) [M]$^+$, 941.2 (15) [M − F]$^+$. Anal. Calcd for $C_{60}H_{58}B_2F_4N_6$: C, 75.01; H, 6.08; N, 8.75. Found: C, 74.80; H, 5.90; N, 8.53.

5,5′-Bis{ethynylphenyl-4‴-[4⁗,4⁗-difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2,2′-bipyrimidine (10). Method A: 5,5′-Bis-ethynyl-2,2′-bipyrimidine (0.044 g, 0.213 mmol), **5** (0.227 g, 0.448 mmol), Pd(PPh_3)Cl_2 (0.01 g, 0.014 mmol), THF (10 mL), (^{i}Pr)$_2$NH (3 mL), and CuI (0.004 g, 0.02 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 3:7) gave **10** as a pinkish powder (0.185 g, 90%). Mp >300 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 0.99 (t, 12H, ^3J = 7.5 Hz), 1.33 (s, 12H), 2.31 (q, 8H, ^3J = 7.5 Hz), 2.54 (s, 12H), 7.55 (AB sys, 8H, J_{AB}= 8.1 Hz, $\nu_0\delta$ = 111.6 Hz), 9.17 (s, 4H). ^{13}C{^{1}H} JMOD NMR (75.4 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.5 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 83.8, 97.7, 119.8 (Cq), 122.2 (Cq), 128.9 (CH), 130.4 (Cq), 132.5 (CH), 133.1 (Cq), 137.4 (Cq), 138.0 (Cq), 138.7 (Cq), 154.3 (Cq), 159.8 (CH). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.84 (t, $^1J_{B-F}$ = 33.808). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 349 (69 500), 498 (47 000), 527 (140 000). IR (KBr): 3436, 1636, 1570 (br, $\nu_{C=N}$), 1122 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 963.2 (300) [M + H$^+$], 962.3 (100) [M$^+$]. Anal. Calcd for $C_{58}H_{56}B_2F_4N_8$: C, 72.36; H, 5.86; N, 11.64. Found: C, 72.00; H, 5.64; N, 11.41.

6,6′-Bis{ethynylphenyl-4‴-[4⁗,4⁗-difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2,2′-bipyridine (11). Method A: 6,6′-Bis-ethynyl-2,2′-bipyridine (0.050 g, 0.245 mmol), **5** (0.250 g, 0.494 mmol), Pd(PPh_3)Cl_2 (0.02 g, 0.028 mmol), THF (15 mL), (^{i}Pr)$_2$NH (5 mL), and CuI (0.01 g, 0.05 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 2:8 to 7:3) gave **11** as a pinkish powder (0.216 g, 86%). Mp >300 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 0.99 (t, 12H, ^3J = 7.5 Hz), 1.33 (s, 12H), 2.31 (q, 8H, ^3J = 7.5 Hz), 2.54 (s, 12H), 7.55 (ABsys, 8H, J_{AB}= 8.3 Hz, $\nu_0\delta$ = 129.7 Hz), 7.62 (dd, 2H, ^3J = 7.7 Hz, ^4J = 1.1 Hz), 7.87 (t, 2H, ^3J = 7.8 Hz), 8.52 (dd, 2H, ^3J = 8.5 Hz, ^4J = 1.0 Hz). ^{13}C{^{1}H} Dept NMR (75.4 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.5 (CH_3), 15.6 (CH_3), 17.0 (CH_2), 88.7, 90.3, 121.4, 123.4, 128.0, 129.1, 130.9, 133.1, 133.4, 137.1, 137.6, 138.6, 139.4, 142.9, 154.5, 156.4. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 32.86 Hz). IR (KBr) 3435, 2922, 1647 (br, $\nu_{C=N}$), 1577, 1122 cm^{-1}. UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) = 287 (60 000), 315 (52 400), 499sh (53 400), 527 (160 000). MS (FAB$^+$, *m*NBA) *m*/*z* (%) 960.4 (100) [M]$^+$, 922.2 (49) [M − 2F]$^+$. Anal. Calcd for $C_{60}H_{58}B_2F_4N_6$: C, 75.01; H, 6.08; N, 8.75. Found: C, 74.73; H, 5.90; N, 8.56.

6,6″-Bis{ethynylphenyl-4‴-[4⁗,4⁗-difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2:2′;6′:2″-terpyridine (12). Method A: 6,6′-Bis-ethynyl-2:2′;6′:2″-terpyridine (0.060 g, 0.213 mmol), **5** (0.230 g, 0.454 mmol), Pd(PPh_3)Cl_2 (0.01 g, 0.014 mmol), THF (20 mL), (^{i}Pr)$_2$NH (5 mL), and CuI (0.004 g, 0.02 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 5:5 to 6:4) gave **12** as a pinkish powder (0.200 g, 90%).

Method B: 6,6′-Dibromo-2:2′;6′:2″-terpyridine (0.046 g, 0.117 mmol), **13b** (0.095 g, 0.235 mmol), Pd(PPh_3)Cl_2 (0.01 g, 0.007 mmol), THF (10 mL), (^{i}Pr)$_2$NH (2 mL), and CuI (0.005 g, 0.01 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 2:8 to 7:3) afforded the coupled compound as a pinkish powder (0.036 g, 30%). The homocoupled product **16** was isolated (0.04 g, 52%). Mp 221−2 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 0.99 (t, 12H, ^3J = 7.5 Hz), 1.34 (s, 12H), 2.31 (q, 8H, ^3J = 7.5 Hz), 2.54 (s, 12H), 7.56 (ABsys, 8H, J_{AB}= 8.0 Hz, $\nu_0\delta$ = 175.5 Hz), 7.62 (dd, 2H, ^3J = 7.5 Hz, ^4J = 1.0 Hz), 7.90 (t, 2H, ^3J = 7.8 Hz), 7.99 (t, 1H, ^3J = 7.8 H), 8.59 (d, 2H, ^3J = 7.5 Hz), 8.63 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.0 Hz). ^{13}C-{^{1}H} Dept NMR (100.6 MHz, $CDCl_3$) δ 12.3 (CH_3), 12.9 (CH_3), 15.0 (CH_3), 17.5 (CH_2), 88.6, 90.4, 121.1 (CH), 122.2 (CH), 123.4, 127.8 (CH), 129.0 (CH), 130.9, 133.12 (CH), 133.4, 137.0, 137.5 (CH), 138.4 (CH), 138.6, 139.4, 142.9, 154.5, 155.1, 157.132. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 33.44 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 286 (92 000), 314 (90 300), 497 (sh, 70 000), 526 (210 000). IR (KBr) 3436, 2921, 1638 (br, $\nu_{C=N}$), 1121 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 1037.1 (100) [M]$^+$, 1018.2 (20) [M − F]$^+$, 999.1 (10) [M − 2F]$^+$. Anal. Calcd for $C_{65}H_{61}B_2F_4N_7$: C, 75.22; H, 5.92; N, 9.45. Found: C, 75.01; H, 5.72; N, 9.28.

4,4-Difluoro-8-(4′-trimethylsilylethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (13a). Method A: 5 (0.515 g, 1.017 mmol), Pd(PPh_3)Cl_2 (0.043 g, 0.06 mmol), THF (20 mL), (^{i}Pr)$_2$NH (5 mL), CuI (0.002 mg, 0.01 mmol), and trimethylsilylacetylene (0.22 mL, 1.526 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 2:8) gave **13a** (0.45 g, 93%). Mp 245 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 0.98 (t, 6H, ^3J = 7.5 Hz,), 1.30 (s, 6H), 2.30 (q, 4H, ^3J = 7.5 Hz), 2.53 (s, 6H), 7.42 (AB sys, 4H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 106.1 Hz). ^{13}C{^{1}H} NMR (75.46 MHz, $CDCl_3$) δ −0.1 (CH_3), 11.9 (CH_3), 12.5 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 95.6, 104.4, 123.7 (Cq), 128.4 (CH), 130.5 (Cq), 132.6 (CH), 132.9 (Cq), 136.1 (Cq), 138.2 (Cq), 139.2 (Cq), 154.0 (Cq). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.84 (t, $^1J_{B-F}$ = 33.5 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 499 (sh, 23 000), 528 (69 000). IR (KBr) 3436, 2920, 1619 (br, $\nu_{C=N}$), 1591, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 476.2(100) [M]$^+$, 457.3 (10) [M − F]$^+$. Anal. Calcd for $C_{28}H_{35}BF_2N_2Si$: C, 70.58; H, 7.40; N, 5.88. Found: C, 70.38; H, 7.27; N, 5.66.

4,4-Difluoro-8-(4′-ethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (13b). A solution of **13a** (0.4 g, 0.84 mmol) and KF (0.5 g, 8.6 mmol) in a 10%

aqueous methanol/dichloromethane mixture (1:1, 10 mL) was stirred at room temperature for 1 day. The solvents were removed, and chromatography (Al_2O_3, CH_2Cl_2/hexane, 2:8) gave the pure acetylenic compound **13b** (0.245 g, 72%). Mp 250 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, 6H, ^3J = 7.5 Hz), 1.31 (s, 6H), 2.31 (q, 4H, ^3J = 7.6 Hz), 2.54 (s, 6H), 3.19 (s, 1H), 7.45 (AB sys, 4H, J_{AB} = 8.3 Hz, $\nu_o\delta$ = 104.8 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.5 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 78.4, 83.0, 122.7 (Cq), 128.5 (CH), 130.5 (Cq), 132.8 (CH), 133.0 (Cq), 136.5 (Cq), 138.2 (Cq), 139.0 (Cq), 154.1 (Cq). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.84 (t, $^1J_{B-F}$ = 32.9 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 497 (sh, 36 000), 527 (96 000). IR (KBr) 3436, 2917, 1544, 1114 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 404.2 (100) [M]$^+$, 385.2 (15) [M − F]$^+$. Anal. Calcd for $C_{25}H_{27}BF_2N_2$: C, 74.27; H, 6.73; N, 6.93. Found: C, 74.13; H, 6.63; N, 6.59.

3,8-Bis{ethynylphenyl-4′-[4″,4″-difluoro-8″-(1″,3″,5″,7″-tetramethyl-2″,6″-diethyl-4″-bora-3″a,4″a-diaza-*s*-indacene)]}-1,10-phenantroline (14). Method B: 3,8-Dibromo-1,10-phenanthroline (0.043 g, 0.128 mmol), **13b** (0.104 g, 0.257 mmol), $Pd(PPh_3)Cl_2$ (0.01 g, 0.007 mmol), THF (10 mL), (^{i}Pr)$_2$NH (2 mL), and CuI (0.005 g, 0.01 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 2:8 to 7:3) gave **14** as a pinkish powder (0.010 g, 5%). The homocoupled product **16** was isolated (0.052 g), and the monocoupled phenanthroline (0.038 g).

Method C: 3,8-Bis-2-isopropanolsilylethynyl-1,10-phenanthroline (0.033 g, 0.096 mmol), **5** (0.0980 g, 0.192 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.0118 mmol), benzene (10 mL), Et_3BzNCl (0.001 g, 0.006 mmol), NaOH (0.04 g, 0.99 mmol), water (10 mL), and CuI (0.002 g, 0.01 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 5:5) gave **14** as a red powder (0.033 g, 35%).

Method C: 3,8-Bis-trimethylsilylethynyl-1,10-phenanthroline (0.058 g, 0.155 mmol), **5** (0.165 g, 0.326 mmol), $Pd(PPh_3)_4$ (0.011 g, 0.011 mmol), benzene (20 mL), Et_3BzNCl (0.002 g, 0.012 mmol), NaOH (0.063 g, 1.55 mmol), water (20 mL), and CuI (0.002 g, 0.01 mmol) were added. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 5:5) gave a red powder (0.130 g, 85%). Mp 266 °C dec. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 1.01 (t, 12H, ^3J = 7.5 Hz), 1.37 (s, 12H), 2.33 (q, 8H, ^3J = 7.4 Hz), 2.55 (s, 12H), 7.57 (ABsys, 8H, J_{AB}= 8.1 Hz, $\nu_0\delta$ = 161.2 Hz), 7.85 (s, 2H), 8.45 (d, 2H, ^4J = 1.9 Hz), 9.34 (d, 2H, ^4J = 1.8 Hz). ^{13}C{^{1}H} DEPT NMR (100.6 MHz, $CDCl_3$) δ 12.3 (CH_3), 12.9 (CH_3), 15.0 (CH_3), 17.5 (CH_2), 87.9 (CC), 93.8 (CC), 120.0, 123.4, 127.4 (CH), 128.6, 129.2 (CH), 130.9, 132.8 (CH), 133.4, 137.1, 138.5, 138.6 (CH), 139.3, 145.0, 152.9 (CH), 154.6. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 32.50 Hz). UV−vis (CH_2Cl_2, 23 °C): λ_{max} (ϵ, M^{-1} cm^{-1}) 285 (79 500), 365 (104 000), 498 sh (60 700), 526 (180 000). IR (KBr) 3444, 2924, 1650 (br, $\nu_{C=N}$), 1540, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 984.2 (100) [M]$^+$, 965.2 (10) [M − F]$^+$. Anal. Calcd for $C_{62}H_{58}B_2F_4N_6$: C, 75.62; H, 5.94; N, 8.53. Found: C, 75.48; H, 5.81; N, 8.33.

3-Bromo-8-{ethynylphenyl-4′-[4″,4″-difluoro-8″-(1″,3″,5″,7″-tetramethyl-2″,6″-diethyl-4″-bora-3″a,4″a-diaza-*s*-indacene)]}-1,10-phenantroline (15). Mp 270 °C dec. ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 0.99 (t, 6H, ^3J = 7.5 Hz), 1.35 (s, 6H), 2.32 (q, 4H, ^3J = 7.4 Hz), 2.55 (s, 6H), 7.36 (d, part of AB sys, 2H, ^3J = 8.0 Hz), 7.74−7.84 (m, 5H), 8.42 (dd, 2H, ^3J = 6.3 Hz, ^4J = 2.2 Hz), 9.18 (d, 1H, ^4J = 2.1 Hz). ^{13}C{^{1}H} JMOD NMR (50 MHz, $CDCl_3$) δ 11.9, 12.5, 14.6, 17.1, 87.5, 93.4, 119.6, 120.2, 122.9, 126.8, 127.0, 128.2, 128.8, 129.6, 130.5, 132.4, 133.0, 136.7, 137.6, 138.1, 138.9, 144.2, 144.6, 151.6, 152.5, 154.2. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 32.50 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 284 (37 000), 349 (40 000), 498 (sh, 18 900), 526 (38 000). IR (KBr) 3444, 2917, 1620 (br, $\nu_{C=N}$), 1595, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 660−662 (90−100) [M + H]$^+$, 641−643 (20−30) [M − F]$^+$. Anal. Calcd for $C_{37}H_{32}BBrF_2N_4$: C, 67.19; H, 4.88; N, 8.47. Found: C, 66.84; H, 4.65; N, 8.29.

1,4-Bis{phenyl-4′-[4″,4″-difluoro-8″-(1″,3″,5″,7″-tetramethyl-2′,6′-diethyl-4′-bora-3′a,4′a-diaza-*s*-indacene)]}-butadyine (16). Mp 233−4 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 0.98 (t, 12H, ^3J = 7.5 Hz), 1.31 (s, 12H), 2.31 (q, 8H, ^3J = 7.4 Hz), 2.54 (s, 12H), 7.48 (ABsys, 8H, J_{AB}= 8.4 Hz, $\nu_0\delta$ = 72.9 Hz). ^{13}C{^{1}H} DEPT NMR (100.6 MHz, $CDCl_3$) δ 12.3 (CH_3), 12.9 (CH_3), 14.9 (CH_3), 17.5 (CH_2), 75.3, 81.9, 122.7, 129.1 (CH), 130.8, 133.5, 133.6 (CH), 137.5, 138.5, 139.2, 154.6. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.84 (t, J_{B-F} = 33.8 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 342 (40 500), 499 (sh, 52 600), 529 (150 000). IR (KBr) 3436, 2918, 1544, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 807.1 (20) [M + H$^+$], 806.2 [M]$^+$, 787.2 (30) [M − F]$^+$. Anal. Calcd for $C_{50}H_{52}B_2F_4N_4$: C, 74.45; H, 6.50; N, 6.95. Found: C, 74.22; H, 6.20; N, 6.71.

5,5″-Bis{ethynylphenyl-4‴-[4⁗,4⁗-Difluoro-8⁗-(1⁗,3⁗,5⁗,7⁗-tetramethyl-2⁗,6⁗-diethyl-4⁗-bora-3⁗a,4⁗a-diaza-*s*-indacene)]}-2:2′;6′:2″-terpyridine (17). Method A: 5,5″-Bis-ethynyl-2:2′;6′:2″-terpyridine (0.0540 g, 0.192 mmol), **5** (0.195 g, 0.384 mmol), $Pd(PPh_3)Cl_2$ (0.008 g, 0.011 mmol), THF (15 mL), (^{i}Pr)$_2$NH (3 mL), and CuI (0.004 g, 0.02 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, gradient from 5:5 to 6:4) gave **17** as a pinkish powder (0.024 g, 12%).

Method C: 5,5″-Bis-trimethylsilylethynyl-2:2′;6′:2″-terpyridine (0.042 g, 0.099 mmol), **5** (0.100 g, 0.198 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.0118 mmol), benzene (15 mL), Et_3BzNCl (0.001 g, 0.006 mmol), NaOH (0.04 g, 0.99 mmol), water (10 mL), and CuI (0.0025 g, 0.01 mmol) were used. Chromatography (Al_2O_3, CH_2Cl_2/hexane, 5:5) gave a red powder (0.089 g, 87%). Mp 232−4 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 0.99 (t, 12H, ^3J = 7.5 Hz), 1.35 (s, 12H), 2.31 (q, 8H, ^3J = 7.5 Hz), 2.54 (s, 12H), 7.56 (AB sys, 8H, J_{AB}= 8.2 Hz, $\nu_0\delta$ = 114.5 Hz), 7.96−8.02 (m, 3H), 8.51 (d, 2H, ^3J = 7.9 Hz), 8.66 (d, 2H, ^3J = 8.3 Hz), 8.87 (d, 2H, ^4J = 2.1 Hz). ^{13}C{^{1}H} DEPT NMR (75.4 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.6 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 87.7, 92.9, 120.1, 120.5 (CH), 121.6 (CH), 123.2, 128.4, 128.7 (CH), 129.1, 130.5, 132.4 (CH), 133.0, 136.5, 138.1 (CH), 138.2, 138.6, 139.0, 139.3 (CH), 151.7 (CH), 154.1, 154.8, 155.0. ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.86 (t, J_{B-F} = 33.3 Hz). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 347 (140 000), 497 (sh, 86 000), 526 (225 000). IR (KBr) 3437, 2920, 1620 (br, $\nu_{C=N}$), 1594, 1384, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 1037 (100) [M]$^+$, 1018 (20) [M − F]$^+$. Anal. Calcd for $C_{65}H_{61}B_2F_4N_7$: C, 75.22; H, 5.92; N, 9.45. Found: C, 75.05; H, 5.77; N, 9.22.

4,4-Difluoro-8-(methylpyridium-4′-yl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene Iodide (18). To a solution of **2** (0.035 g, 0.09 mmol) in ethyl acetate (5 mL) was added methyl iodide (60 μL, 0.9 mmol). The mixture was stirred at rt for 3 days. The solvent was removed and chromatography on alumina (Act V, CH_2Cl_2/methanol, with a gradient from 100:0 to 98:2) gave **18** as deep red crystals (0.018 g, 38%). Mp 230 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 6H, ^3J = 7.5 Hz), 1.39 (s, 6H), 2.30 (q, 4H, ^3J = 7.6 Hz), 2.54 (s, 6H), 4.89 (s, 3H), 8.00 (d, 2H, ^3J = 6.6 Hz), 9.49 (d, 2H, ^3J = 6.5 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 12.8 (CH_3), 13.8 (CH_3), 14.5 (CH_3), 17.1 (CH_2), 50.4 (CH_3N^+), 128.9 (CH), 129.1 (Cq), 131.2 (Cq), 135.1 (Cq), 137.4 (Cq), 146.8 (CH), 154.8 (Cq), 157.4 (Cq). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.64 (t, $^1J_{B-F}$ = 32.3). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 238 (22 000), 399 (5800), 509 (sh, 11 600), 541 (26 000). IR (KBr) 2918, 1647 (s, $\nu_{C=N}$), 1384, 1117 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 396 (100) [M]$^+$, 377.2 (25) [M − F]$^+$. Anal. Calcd for $C_{23}H_{29}BF_2IN_3$: C, 52.80; H, 5.59; N, 8.03. Found: C, 52.64; H, 5.47; N, 7.83.

4,4-Difluoro-8-(methylpyridium-4′-ethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene Iodide (19). To **6** (0.032 g, 0.066 mmol) in chloroform (10 mL) was added methyl iodide (0.041 mL, 0.66 mmol), and the solution was stirred for 1 day. Additional methyl iodide (0.04 mL) was then added and the solution was stirred for 2 days more. Solvent was removed, and chromatography (alumina, CH_2Cl_2/MeOH, with a gradient from 99:1 to 90:10) gave

19 as a deep red powder (0.036 g, 87%). Mp 240 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, 6H, ^3J = 7.5 Hz), 1.31 (s, 6H), 2.31 (q, 4H, ^3J = 7.5 Hz), 2.54 (s, 6H), 4.73 (s, 3H), 7.60 (AB sys, 4H, J_{AB}= 8.5 Hz, $\nu_0\delta$ = 142.8 Hz), 8.69 (AB sys, 4H, J_{AB} = 6.5 Hz, $\nu_0\delta$ = 515.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 11.9 (CH_3), 12.6 (CH_3), 14.6 (CH_3), 17.0 (CH_2), 49.3 (CH_3N^+), 85.8, 104.5, 120.6 (Cq), 129.2 (CH), 129.4 (CH), 130.2 (Cq), 133.2 (CH), 137.9 (Cq), 138.0 (Cq), 139.1 (Cq), 140.5 (Cq), 145.4 (CH), 154.5 (Cq). ^{11}B NMR (128.4 MHz, $CDCl_3$) 3.82 (t, $^1J_{B-F}$ = 32.95). UV−vis (CH_2Cl_2, 23 °C) λ_{max} (ϵ, M^{-1} cm^{-1}) 240 (46 300), 352 (45 700), 500 (sh, 28 000), 529 (77 500). IR (KBr) 3436, 2921, 1620 (br, $\nu_{C=N}$), 1584, 1116 cm^{-1}. MS (FAB$^+$, *m*NBA) *m*/*z* (%) 496.2 (100) [M]$^+$, 477.1 (10) [M − F]$^+$. Anal. Calcd for $C_{31}H_{33}BF_2IN_3$: C, 59.73; H, 5.34; N, 6.74. Found: C, 59.51; H, 5.17; N, 6.53.

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