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Synthesis of Indolo[3,2-*b*]carbazole based boron complexes with tunable photophysical and electrochemical properties

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Abstract: New synthetic strategies were developed for the synthesis of indolo-pyridine boron difluoride (IPBD) dyes and anti-ladder-type π -conjugated dyes based on the pyridine/pyrazine-indolocarbazole (ICZ) structures. The photophysical and electrochemical properties of the dyes were measured in solution, solid state and thin films, and rationalized by theoretical calculations. Interestingly, these properties of the dyes can be tuned in a wide range using the developed chemical route. For example, the absorption range and fluorescence colour of the dyes in solution and solid state, and the HOMO-LUMO energy gaps were tuned by structure modulations. The absorption properties of those new boron-complexes cover most of the UV-visible-NIR spectrum. Therefore, this appealing tunability feature makes these new types of dyes very promising candidates for their further use in functional material development.

Introduction:

Organic conjugated frameworks containing boron atom are very promising for the development of new functional materials with outstanding photophysical and electronic properties.¹⁻⁸ The boron atom improves the performance of organic electronics by acting as a conduit for the π -conjugated skeleton and substantially decreasing the energy of the lowest unoccupied molecular orbital (LUMO). This immense potential motivated the search for new π -conjugated bidentate ligands to provide boron complexes with promising electronic and optical properties. BODIPY dyes are classical examples of such type of compounds.⁹⁻¹⁰ It is well established that the small organic molecules based on BODIPYs are very efficient components of the active layer of organic optoelectronic devices, such as organic photovoltaic cells (OPV),^{8, 11-15} or organic lasers.¹⁶⁻¹⁷ Anilido-pyridine boron difluorides (APBDs) are another class of highly promising compounds, which exhibit high emission quantum yields and large Stokes shifts but very few reports are available to date.¹⁸⁻²⁰

Indolo[3,2-*b*]carbazoles (ICZs)²¹ are widely studied because of their many interesting properties which made them useful for a large range of applications such as sensing,²² biological studies²³⁻²⁵ and specially in organic electronics. Indeed, high charge carrier mobilities, electronic levels tuning, good stability towards atmospheric conditions makes them ideal components for use in organic field effect transistors (OFETs),²⁶⁻²⁸ organic light emitting diodes (OLEDs),²⁹⁻³¹ Dye Sensitised Solar Cells (DSSCs)³² and even in OPVs.³³⁻³⁶ Thus, it was anticipated that the incorporation of the boron atom in the ICZ moiety may further improve its interest for organic electronics. Despite of recent advances, examples of the incorporation of boron atoms into ICZs molecular frame are rare.³⁷

5,11-dihydroindolo[3,2-*b*]carbazole (**A**, Chart 1), having two inbuilt indolo functions, are nice platforms to synthesize indolo-pyridine boron difluoride (IPBD) dyes similar to APBD dyes. Development of synthetic strategies to insert pyridine moiety at the C4, C10 and C12 positions of **A** enable the synthesis of different bidentate ligands based on indolo-pyridine skeletons *viz.* **B** and **C** (Chart 1). Using similar chemical strategies, a more sophisticated ladder-type ligand can also be synthesized by linking one pyrazine molecule with two ICZ, **A** through their C12 positions. Further, boron coordination with these ligands will allow effective π -delocalization of the ICZs moiety and reinforce the compounds interest for material science. Till now, only one report on ICZs based APBD dye is available in the literature.³⁷ Herein we report, three different types of

APBD dyes based on the pyridine-ICZ structures and three anti-ladder-type π -conjugated dyes based on the pyrazine-ICZ structures. Their detailed photophysical and electrochemical properties were evaluated and discussed for their further use in functional materials developments.

Chart 1. Chemical structure of ICZ (A) and indolo-pyridine type ligands (B, C) based on ICZ.

Results and Discussion:

Synthesis. The synthesis started with ICZ, 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**) which was synthesized according to the reported method.³⁸⁻³⁹ At first, functionalization at the C12 position of **1** was attempted to synthesize **B**-type ligands. Controlled bromination of **1** using FeBr₃ furnished 6-Bromo-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**2**) in a very good yield.³⁹ Then borylation of **2** with pinacolborane provided 6-Boryl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**3**). The Suzuki–Miyaura coupling reaction of **3** with bromopyridine afforded **B** type ligand **4**. Finally, treatment of **4** with excess BF₃·OEt₂ and B(Ph)₃ separately furnished the corresponding dyes **5a** and **5b**, respectively (Scheme 1).

Scheme 1. Synthesis of dye **5a-b**. a) FeBr_3 (3 equiv.), THF:H₂O (5:2), 25 °C, 20 h. b) Pinacolborane, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 1,4-Dioxane, 100 °C, 12 h. c) 2-Bromo-5-methylpyridine, $\text{Pd}(\text{PPh}_3)_4$, Cs_2CO_3 , CsF, Toluene/DMF (2:1), 90 °C, 12 h. d) Et_3N , $\text{BF}_3\cdot\text{OEt}_2$, DCE, 80 °C, 12 h (for **5a**); $\text{B}(\text{Ph})_3$, Toluene, 90 °C, 12 h (for **5b**).

Dye **5a** was characterized by NMR spectroscopy giving well-defined spectra in $(\text{CD}_3)_2\text{CO}$. For example, ^1H NMR spectrum (Figure S8) showed signals for all aromatic protons along with a singlet at 10.84 ppm for the N-H proton. The benzylic methylene and terminal methyl groups of the pentyl lateral chain resonates as triplets at 3.67 and 0.92 ppm, respectively. Other three internal methylene groups signal of pentyl lateral chain were found as three different multiplets centred at 2.00, 1.67 and 1.46 ppm with the expected two protons integration for each signal. Another diagnostic signal is provided by the benzylic methyl group of the pyridine moiety at 3.16 ppm which appeared as a triplet ($J = 3.2$ Hz) due to coupling with F atom of the BF_2 group. The carbon spectra presented the expected six signals for the alkyl atoms and the expected 23 signals for aromatic atoms (Figure S9).

Figure 1. Two orthogonal Ortep views of the crystal structure of compound **5a**.

Moreover, the structure of **5a** was confirmed by X-ray crystallography data (Figure 1). It is important to mention that the indolocarbazole moiety lost its planarity after the chelation of the boron atom (the rms deviation for fifteen atoms of the framework is 0.069 Å when the tail represented by C7, C8 and C9 atoms is lifted out of the plane by max. 0.56 Å). The pyridyl ring is also twisted out of the hypothetical plane containing the ICZ aromatic core (torsion angle C17/C6/C6'/C5' of -18.79°). This is probably due to the van der Waals interactions of the protons at C7 and C5' carbon atoms of ICZ and pyridyl moieties, respectively. This has for consequence to bring a slight conformational helicity to the molecule that becomes *de facto* a chiral object. At the opposite side, the pentyl unit counterbalances the twist making a dihedral angle (C13/C12/C21/C22) with the ICZ moiety of 95.9°, and the all-*trans* configured butyl chain ((C21/C22/C23/C24) adopting a *gauche* conformation (72.0°)) nearly lies in a plane parallel to that of the aromatic system.

As observed elsewhere³⁷ for a similar structure, the B–N bond is sensibly longer for the pyridine (1.618 (3) Å) than for the indolocarbazole (1.504 (3) Å). If the B–F distances look more similar, the H-bond interaction from the amine group of a vicinal molecule in $\frac{1}{2}-x, y, \frac{1}{2}+z$ position with F1 (d N11 – H11 ... F1, 2.11 (3) Å) extended the relevant bond to 1.407 (3) Å in the *c*

direction. The boron atom presents as usual for *F*-BODIPY analogues a slight distorted tetrahedral environment with bond angles ranging from 107.82 to 111.51° and typical values of 108.15(17)° for N–B–N and 109.23(18)° for F–B–F. The double bond localization seems to encompass the N5–C16, N1'–C6', N1'–C2' bonds (average distances of 1.38 Å) in contrast with the 1.40 Å and more distances observed for N5–C15, C16–C6, C6'–C6, and C6'–C5' in particular.

The overall conformation of the molecules looks planar and therefore it is not surprising to see them assembled parallel to the plane (0 0 1) making infinite layers with 3.95 Å interplanar distances (Figure 2, *left*). Along the orthogonal direction coinciding with the chirality axis, the molecules pile up in columnar way with shortest centroid-centroid distances (3.9616 (14) Å) involving the central indole groups. However, the alternation of the enantiomeric helices related by the glide mirror *a* prevents from the formation of super-helical assembly inside the crystal.

Figure 2. (*Left*) A packing diagram for **5a** viewed along the *b* axis, showing the layer formation parallel to the plane. (*Right*) View down the *c* axis showing the columns through π - π stacking involving the adjacent central indole moieties (in light blue and grey).

Next, we aimed to synthesize anti-ladder type complexes starting from 6-Boryl-ICZ (**3**). The Suzuki–Miyaura coupling reaction of 2,5-dibromopyrazine with two molecules of **3** afforded the ligand **6** with two chelating sites. Then, controlled reaction of **6** with $\text{BF}_3 \cdot \text{OEt}_2$ furnished mono- BF_2 complex **7a** (with 1 eq. $\text{BF}_3 \cdot \text{OEt}_2$) and bis- BF_2 complex **8** (with excess $\text{BF}_3 \cdot \text{OEt}_2$) (Scheme 2). Unfortunately, only mono-BPh₂ complex, **7b** was obtained even after prolonged heating of **6** with excess B(Ph)_3 . Steric bulkiness and twisting of the molecules probably hindered the complexation of the 2nd -BPh₂ moiety with **7b**.

Scheme 2. Synthesis of dyes **7a-b** and **8**. a) 2,5-Dibromopyrrazine, Pd(PPh₃)₄, Cs₂CO₃, CsF, Toluene/DMF (2:1), 90 °C, 12 h. b) Et₃N, BF₃.OEt₂, DCE, 80 °C, 12 h (for **7a**)/48 h (for **8**); B(Ph)₃, Toluene, 90 °C, 48 h (for **7b**).

All the complexes, **7a-b** and **8** were fully characterized by NMR and mass spectroscopy. For example, compound **7a** was identified by the diagnostic 5 singlets in ¹H NMR at 9.13, 10.53, 11.07, 11.35, 11.95 ppm corresponding to three N-H and two pyrazine C-H protons (Figure S15 and S20). Due to the dissymmetry of the structure, all these peaks appeared as well separated singlets. Other diagnostic signals to confirm the **7a** structure were given by the benzylic methylene groups of the pentyl chains which resonated at 3.62 and 3.72 ppm as two separate triplets for two protons each. In contrast, the symmetry of the compound **8** was observed nicely in ¹H NMR spectrum. For example, two pyrrazine C-H and two indole N-H protons resonates at 10.17 and 12.03 ppm, respectively as singlets. Two benzylic methylene groups of the pentyl chains also appeared as a triplet for 4 protons at 3.70 ppm (Figure S19 and S20).

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6 Lastly, we aimed to functionalize the ICZ through C-4 and C-10 positions which are less
7 reactive in nucleophilic substitutions as compared to C-2, C-8 and C-12 positions for the synthesis
8 of C-type ligand.³⁸ Thus, first hurdle was to block these later positions with alkyl groups. The
9 synthesis was started with 2,8-dibromo-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**9**) which
10 was synthesized using a reported method.³⁹ Selective bromination using FeBr₃ furnished tribromo
11 ICZ (**10**) in excellent yield (Scheme 3). Then, **10** was subjected to Sonogashira coupling with
12 trimethylsilylacetylene to furnish acetylene substituted ICZ, **11**. The silyl groups were knocked off
13 by K₂CO₃ mediated reaction and the acetylene group was reduced to ethyl by metal induced
14 hydrogenation reaction to furnish 2,8,12-triethyl substituted ICZ, **13**. Bromination of **13** with Br₂
15 in AcOH furnished 4,10-dibromo ICZ, **14** in excellent yield. Then borylation of **14** with
16 pinacolborane provided 4,10-diboryl-2,8,12-triethyl-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole
17 (**15**). The Suzuki-Miyaura coupling reaction of **15** with 2-Bromo-5-methylpyridine afforded the
18 ligand, which was simultaneously treated (two-fold reaction) with excess BF₃·OEt₂ to furnish the
19 corresponding dye **16**. The dye was characterized by NMR and mass spectrometry.
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Scheme 3. Synthesis of dye **16**. a) FeBr_3 (3 equiv.), $\text{THF}:\text{H}_2\text{O}$ (5:2), 25 °C, 20 h. b) Trimethylsilylacetylene, $\text{Pd}(\text{dppf})_2\text{Cl}_2 \cdot \text{DCM}$, CuI , Diisopropyl amine, Toluene, 110 °C, 12 h. c) K_2CO_3 , DCM/MeOH (1:1), 25 °C, 14 h. d) H_2 , Pd/C , DCM/EtOH (1:1), 50 °C, 12 h. e) Br_2 , AcOH , 100 °C, 2 h. f) Pinacolborane, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 1,4-Dioxane, 100 °C, 12 h. g) 2-Bromo-5-methylpyridine, $\text{Pd}(\text{PPh}_3)_4$, Cs_2CO_3 , CsF , Toluene/DMF (2:1), 90 °C, 12 h. h) Et_3N , $\text{BF}_3 \cdot \text{OEt}_2$, DCE, 80 °C, 12 h.

Photophysical properties. The photophysical properties of the dyes **5a-b**, **7a-b**, **8** and **16** in DCM, solid states and thin films were evaluated at room temperature (25 °C). The measured photophysical parameters (absorption maximum (λ_{abs}), emission maximum (λ_{em}), maximum molar absorptivity (ϵ_{max}) and fluorescence quantum yield (Φ_{fl}) and the calculated Stokes shift (ν) of the dyes in DCM and thin films are presented in Table 1. The absorption, emission and excitation spectra of dyes **5a** and **5b** in DCM are shown in Figure S36 and S37. Absorption spectra of both the dyes showed multiple peaks with the longest wavelength absorption maximum (λ_{max}) ($S_0 \rightarrow S_1$ absorption band) at 493 nm and 516 nm for **5a** and **5b**, respectively. In thin films, due to intermolecular π -stacking, the absorption bands of both the dyes **5a** and **5b** are red shifted with λ_{max} at 508 and 529 nm, respectively (Figure S36 and S37). Both dyes were weakly fluorescent with λ_{em} at 562 nm and 578 nm for **5a** and **5b**, respectively i.e. the Stokes shifts of both the dyes were high. It was noticed that both λ_{max} in solution as well as in film and λ_{em} of **5b** were red shifted by 21-23 nm as compared to those of **5a**. These features clearly revealed that the substitution of the F-groups at the B-atom with the phenyl had significant bathochromic effect on the optical properties of the ICZ-based dye as seen in BODIPY dyes previously.¹⁴

Table 1. Photophysical properties of dyes **5a-b**, **7a-b**, **8** and **16** in DCM and thin films.

Dye	λ_{abs} [nm]	λ_{abs} [nm]-film	ϵ_{max} [M ⁻¹ cm ⁻¹]	λ_{em} [nm]	ν [cm ⁻¹]	$\Phi_{\text{f}}^{\text{[a]}}$	ΔE_{gopt} (eV)
5a	268		36000	562	2500	0.01	
	314	319	18400				2.2
	404	414	14400				
	493	508	16600				
5b	270		70300	578	2100	0.003	
	321	327	32300				2.1
	389	406	23000				
	516	529	18600				
7a	309		29800	-	-	-	
	443	459	12200				1.7
	587	614	21600				
7b	256		69200	-	-	-	
	443	463	14900				1.6
	613	641	22500				
8	317		34700	-	-	-	
	523	540	21000				1.03
	767	809	20100				
	845	910	15700				
16	260		57700	617	3600	0.01	
	317		36700				2.2
	336	343	39300				
	506	517	28600				

^aDetermined using $\Phi_{\text{f}} = 0.88$ for Rhodamine 6G in ethanol as the reference.⁴⁰

The absorption spectra of dyes **7a-b** and **8** in DCM are shown in Figure S38. Both the dyes **7a** and **7b** showed several absorption peaks with λ_{max} ($S_0 \rightarrow S_1$ absorption band) at 587 and 613 nm, respectively (Table 1). It is important to mention that the λ_{max} of **7a** and **7b** are red shifted by 94 and 97 nm respectively with respect to the λ_{max} of **5a** and **5b**. The substitution effect of the F-groups at the B-atom with the phenyl (as seen in case of **5a** and **5b**) is also clearly visible in **7b** as its λ_{max} is red shifted by 26 nm compared to that of **7a**. The absorption spectrum of **8** is further red shifted due to its more planar structure and the presence of the two B-atoms. More importantly the absorption spectrum of **8** extends over the whole UV-visible and near infra-red region. The λ_{max} (845 nm) of dye **8** is red shifted by 352 nm and 254 nm with respect to the λ_{max} of **5a** and **7a**, respectively. In thin films, the absorption bands of the dyes **7a**, **7b** and **8** are red shifted as compared to their solution absorption bands with λ_{max} at 614, 641 and 910 nm, respectively (Figure S38). Compound **8** in solid-state exhibits an impressive bathochromic shift with an absorption onset up to 1200 nm and a broad absorption band covering partly the infrared region. All the dyes **7a-b** and **8** were completely non-fluorescent. These compounds possess an extended π -system lowering the LUMO level, flexible fatty chains attached to the aromatic core and free carbazole amines, which probably offer supplementary non-radiative deactivation pathway compared to compounds **5a-b**.

The absorption, emission and excitation spectra of dye **16** in DCM are shown in Figure 39. The absorption spectrum is quite similar to that of **5a** with a 13 nm red shift in λ_{max} (Table 1). This clearly indicates that the whole molecule may not be completely conjugated. In thin film the absorption band of dye **16** is slightly red shifted with λ_{max} at 517 nm (Figure S39). This small red shift in the solid-state highlights probably a poor solid-state π -stacking ability of this bidentate dye as compare to previous molecules. Interestingly, the λ_{em} was highly red shifted (55 nm) as compared to **5a** with large Stokes shift (3600 cm^{-1}). The dye **16** showed orange fluorescence, albeit with a low Φ_{fl} .

In general, these new indolo-pyridine boron difluoride (IPBD) dyes have different properties than the APPD dyes. One drawback of APPD dyes is their low molar absorption coefficients ($\sim 10000 \text{ M}^{-1} \text{ cm}^{-1}$) (given in ref 18). But in the present IPBD dyes the molar absorption coefficient was significantly increased. For instance, dye **16** has an almost 3 times higher molar absorptivity than the carbazole based APPD dyes. Due to extended conjugation in IPBD dyes, the absorption maxima are also highly red-shifted as compared to carbazole APPD dyes. Red-Shifts

in emission maxima are less pronounced. This resulted into low Stokes shifts in case of IPBD dyes as compared to carbazole-based APPD dyes, although the Stokes shift is still high as compared to BODIPY dyes.

Compared to structurally similar carbazole-indole BODIPY dyes published before, these simple ICZ-based boron complexes **5a-5b** exhibit really close absorption features with a significant bathochromic shift in absorption and emission.⁴¹⁻⁴⁴ The previously published carbazole-based BODIPYs were more emissive. The supplementary fused indole moiety induces a nice red-shift concomitantly with a rise of the non-radiative deactivation pathway which makes the dyes **5a-5b** low fluorescent dyes.

Solid state fluorescence. The solid state fluorescence of the dyes embedded in KBr matrix (10^{-6} M microcrystalline dispersed in KBr pellet by grinding) was investigated. Only three dyes (**5a**, **5b** and **16**) exhibited weak but significant emission. The non-radiative deactivation pathways i.e. molecular motion/rotations are inhibited in the solid state. This probably enhances the quantum yield in the solid state. The corresponding normalized emission spectra are compiled in Figure 3a and the photographic images of the powdered dyes under UV-light are shown in Figure 3b. A trend similar to the solution emission was also observed in the solid state emission for dyes **5a** and **5b**. Emission of **5b** was red-shifted as compared to **5a** with λ_{em} of 624 and 586 nm respectively i.e. red-shift of 1300 cm^{-1} and 730 cm^{-1} in solid state. Interestingly, the fluorescence quantum yields ($\Phi_f = 3.2$ and 1.4% for **5a** and **5b**, respectively as recorded with integration sphere as KBr pellets) are higher than the one recorded in solution. In case of dye **16**, slight red-shift in the emission ($\lambda_{em} = 602\text{ nm}$) as compared to dye **5a** was observed confirming the poor delocalization over the whole molecule. But **16** was more fluorescent in the solid state ($\Phi_f = 4\%$) than both **5a** and **5b**.

Figure 3. (a) Solid state spectra of dyes **5a** (red), **5b** (blue) and **16** (green), embedded in KBr matrix, 10^{-6} M solid solution. (b) Photographic images of the powdered dyes **5a**, **5b** and **16** under UV light ($\lambda = 365$ nm).

Cyclic voltammetry (CV). Cyclic voltammetry of **4**, **5a-b**, **7a-b**, **8** and **16** were carried out in DCM solutions to investigate their oxidation and reduction processes as well as to determine the energies of their highest occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) levels. All the redox potentials were calibrated with respect to ferrocene (Fc), assuming that $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.38$ V referred to SCE (see experimental details).

At first, monodentate ligand **4** and its corresponding boronated dyes, **5a-b** were characterized (Table 2, Figures S40 and S41). The pure ligand **4** displayed two reversible oxidation

waves at +0.6 V and +0.8 V which could be assigned to ICZ radical cation and di-cation, respectively. No reduction wave was observed in the electrochemical window accessible from DCM solution. The dye **5a** exhibited two oxidation waves at +0.8 V and +1.15 V which were shifted towards higher anodic potential with respect to that of **4**. As expected, the oxidation processes became more difficult after coordination of the BF₂ unit with **4**. Also, a single and non-reversible reduction wave was observed at -1.4 V for **5a**. Interestingly, replacement of the Fluorine atoms by phenyl groups on the boron atoms of dye **5a** allowed to tune its electrochemical properties. Thus, in case of dye **5b**, only the first reversible oxidation wave was observed at +0.65 V, while the non-reversible reduction wave was measured at -1.6 V. Both the oxidation and reduction potentials were decreased by approximately 0.15 V as compared to the BF₂ derivative **5a**. Such behaviour is well known with the BODIPY dyes.⁴⁵

Table 2. Electrochemical properties of **4**, **5a-b**, **7a-b**, **8** and **16** in DCM.^a

Compound	E _{ox} ^o /V	E _{red} ^o /V	HOMO (eV) ^b	LUMO (eV) ^b	Band Gap (eV)
4	+0.6 V; +0.8 V	-	-5.00	-	-
5a	+0.8 V; +1.15 V	-1.4 V irr	-5.20	-3.00	2.2
5b	+0.65 V	-1.6 V irr	-5.05	-2.80	2.25
7a	+0.8 V; +0.9 V	-0.95 V	-5.20	-3.45	1.75
7b	+0.7 V; +0.75 V	-1.1 V	-5.10	-3.30	1.8
8	+0.8 V; +1.1 V (quasi-reversible)	-0.5 V	-5.20	-3.90	1.3
16	0.7 V	-1.55 V	-5.10	-2.85	2.25

^aCyclic voltammetry was done in deoxygenated DCM containing TBAPF₆ (0.1 M), and a solute concentration of $1-5 \times 10^{-3}$ M, at 25 °C. The error in half-wave potentials is ± 10 mV. ^busing the formula (HOMO = E_{ox} + 4.4 eV) and (LUMO = E_{red} + 4.4 eV) where the onset potentials are in volts (vs SCE) and HOMO and LUMO are in electron volts.⁴⁶

Similar trend was also observed in the anti-ladder type complex series (Table 2, Figures S42 and S43). Indeed, a potential decrease of around 0.1-0.2 V was measured while going from the BF₂ complex **7a** to the BPh₂ complex **7b**. Both the compounds exhibited two reversible oxidation waves at +0.7 V and +0.75 V for **7b** against +0.8 V and +0.9 V for **7a**. In the cathodic

region, a reversible wave for both compounds was recorded at -1.1 V and -0.95 V for **7b** and **7a**, respectively. Due to the electron-poor nature of the two BF₂ complexes, the symmetrical compound **8** exhibited a particular behaviour with two oxidation waves taking place at higher potentials, +0.8 V (reversible) and +1.1 V (quasi-reversible). The reversible reduction process of **8** was observed at a very low potential of -0.5 V, highlighting the strong electron affinity of this bis-BF₂ complex.

Finally, the bis-BF₂ dye **16**, was compared with the mono-BF₂ **5a** complex (Table 2, Figures S44 and S45). In agreement with optical data, their electrochemical properties were also similar, highlighting the low conjugation extension of this symmetrical molecule. However, in cathodic region, a bi-electronic non-reversible reduction wave was observed which indicated that two independent radical anions were formed at a potential of approximately -1.55 V. A reversible oxidation wave was also recorded at +0.7 V. It obviously corresponds also to a bi-electronic oxidation process.

Interestingly, it can be noted that the electrochemical band-gaps (calculated as the difference between the LUMO and HOMO measured by CV: Table 2), are consistent with optical band-gaps measured from solid-state absorption onsets (Table 1). Further, the symmetrical compound **8** exhibits a significantly lower electrochemical band-gap compared to its mono-complex counterparts **7a-b**.

Thus, it is worth noting that the chemistry developed for the synthesis of various ICZ based boron complexes allows really the fine-tuning of photophysical and electrochemical properties of the dyes.

Theoretical calculations. Energetically favourable configurations of the ligand **4** and dyes **5a**, **5b**, **7a**, **7b**, **8** and **16** were optimized to understand their geometry in the ground state and also to calculate and visualize their HOMO and LUMOs. This was done by density functional theory (DFT) calculations using B3LYP at the 6-31G* level in vacuum. All the pentyl side chains were changed to methyl groups in order to keep a reasonable calculation time and anticipating no influence of the aliphatic chains on the electronic structures of the dyes.

Figure 4. Optimized structure of **4** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The optimized structure of **4** can be found in Figure 4 together with the calculated HOMO and LUMO surfaces. The pyridyl ring is out of the hypothetical plane containing the ICZ aromatic core with a calculated torsion angle of -34° . The torsion angle leads to poorly delocalized HOMO and LUMO of **4** (Figure 4). The HOMO mainly spreads over the ICZ moiety while the LUMO is localized on the pyridyl moiety and centre phenyl ring of the ICZ moiety. The calculated frontier energy levels for the LUMO and HOMO are -1.34 eV and -4.78 eV, respectively. The calculated HOMO is reasonably close to the one measured by CV (-5.0 eV) (Table 3).⁴⁷

Figure 5. Optimized structure of **5a** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The **5a** optimized structure can be found in Figure 5 together with the calculated HOMO and LUMO surfaces. The optimized structure is in good agreement with the crystal structure measured by X-Ray, for instance a twist of the pyridyl ring which is out of the hypothetical plane containing the ICZ aromatic core with a calculated torsion angle C17/C6/C6'/C5' of -19.58° instead of -18.79° as measured by X-Ray (the identification of the C atoms rely on the Ortep view in Figure 1). The torsion angle leads to poorly delocalized HOMO and LUMO of **5a** (Figure 5). The HOMO spreads over the ICZ moiety while the LUMO is mainly centred on the pyridyl moiety. The calculated frontier energy levels for the LUMO and HOMO are -2.02 eV and -4.95 eV, respectively. As usually observed for this type of calculations, the calculated HOMO is reasonably close to the one measured by CV (-4.95 eV by DFT and -5.2 eV by CV) but the calculated LUMO (-2.02 eV) lies almost 1.0 eV above the CV measured one (-3.0 eV).⁴⁷ The calculated HOMO and LUMO as well as the difference between calculated and measured frontier orbitals can be found in Table 3.

Table 3. Calculated HOMO (second column) and LUMO (fourth column) energy levels together with the offset between the measured (by CV) and the calculated (by DFT) HOMO (third column) and LUMO (fifth column) for **4**, **5a**, **5b**, **7a**, **7b**, **8** and **16**.

Dye	HOMO _{DFT} (eV)	Δ_{HOMO} (eV)	LUMO _{DFT} (eV)	Δ_{LUMO} (eV)
4	-4.78	0.22	-1.34	-
5a	-4.95	0.25	-2.02	0.98
5b	-4.74	0.31	-1.94	0.86
7a	-4.87	0.33	-2.44	1.01
7b	-4.75	0.35	-2.38	0.92
8	-4.98	0.22	-3.00	0.9
16	-4.52	0.58	-1.91	0.94

Figure 6. Optimized structure of **5b** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The **5b** optimized structure can be found in Figure 6 together with the calculated HOMO and LUMO surfaces. The torsion angle between the ICZ and pyridyl planes slightly increases (-23°) as compared to **5a**. Delocalization of the HOMO and LUMO remain similar to that of **5a**. The calculated frontier energy levels for the LUMO and HOMO are -1.94 eV and -4.74 eV, respectively. The general trend for the calculated frontier energy levels is in-line with the measured HOMO and LUMO values measured by CV (Table 3) with almost no change for the energy band-gap between **5a** and **5b** and frontier energy levels downshifted by 0.1 to 0.2 eV when fluorine atoms are present on the dye (**5a**).

Figure 7. Optimized structure of **7a** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The **7a** optimized structure can be found in Figure 7 together with the calculated HOMO and LUMO surfaces. The torsion angle between the two planes containing the ICZ moieties (in green in Figure 7) is as high as 50°. Consequently, the extension of the LUMO is very limited as the LUMO is mainly confined to the pyrazine ring. Nevertheless, the LUMO delocalization is slightly more pronounced on the ICZ unit bridged to the pyrazine moiety by the BF₂ group. Surprisingly, the HOMO is far less confined and it extends significantly over the two ICZ moieties. The general trend for the calculated frontier energy levels is in-line with the measured HOMO and LUMO values measured by CV (Table 3) with almost no change for the HOMO level between **5a** and **7a** but a much deeper LUMO level for **7a** compared to **5a**.

Figure 8. Optimized structure of **7b** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The optimized structure of **7b** (Figure 8) shows that the torsion angle between the two planes containing the ICZ moieties (in green in Figure 8) increases (56°) as compared to **7a**. Delocalization of the HOMO and LUMO (Figure 8) remain similar to that of **7a**. The calculated frontier energy levels for the LUMO and HOMO are -2.38 eV and -4.75 eV, respectively (Table 3) *i.e.* the same trend is observed between **7a** and **7b** than between **5a** and **5b** with a downshifting of both frontier energy levels on the F-grafted dye compared to its phenyl-grafted counterpart.

Figure 9. Optimized structure of **8** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The optimized structure of **8** can be found in Figure 9 together with the calculated HOMO and LUMO surfaces. The torsion angle between the two planes containing the ICZ moieties (in green in Figure 9) is less than 38° to be compared with the 50° calculated for **7a**. Consequently, the HOMO and LUMO for **8** are much more extended than for **7a**. The HOMO is far less confined and it extends significantly over the two ICZ moieties. The general trend for the calculated frontier energy levels is in-line with the HOMO and LUMO values measured by CV (Table 3) with almost no change for the HOMO level between **5a**, **7a** and **8** but a significantly deeper LUMO level for **8** compared to **5a** and **7a**. Consequently, the calculated band-gap for **8** (1.98 eV) is almost 1 eV lower than the calculated band-gap for **5a** (2.93 eV). This calculated result is perfectly consistent with the CV measurements with a 0.9 eV higher electrochemical gap for **5a** (2.2 eV) compared to **8** (1.3 eV).

Figure 10. Optimized structure of **16** (left) and calculated LUMO (right-top) and HOMO (right-bottom) surfaces.

The optimized structure of **16** can be found in Figure 10 together with the calculated HOMO and LUMO surfaces. The optimized structure is very planar in the case of **16** and the HOMO and LUMO are nicely delocalized over the dye. This very planar structure is in contradiction with the experimental evidences of a limited conjugation for this dye. The general trend for the calculated LUMO is in-line with the LUMO value measured by CV (Table 3). On the other hand, the calculated HOMO value for **16** is above the one calculated for **5a**, **7a** and **8** and seems too shallow compared to the measured one. Indeed, while the offset between the measured and calculated HOMO values is in the 0.6-0.7 eV range for **5a**, **7a** and **8**, it reaches 1 eV for **16** (Table 3, third column). The weak conjugation of this dye, observed experimentally but not by simulation, impacts mainly the calculated HOMO value.

Conclusion: Thus, new synthetic strategies were developed for the functionalization of the ICZ moiety. Using these strategies three different types of pyridine-ICZ based APBD dyes and three anti-ladder-type π -conjugated dyes based on the pyrazine-ICZ structures were synthesized. Their detailed electrochemical and photophysical properties in solution, solid state and thin films were evaluated by cyclic voltammetry and optical spectroscopy, respectively. Interestingly, due to the high versatility of the developed chemical route, those properties can be tuned in a wide range. For instance, the absorption properties of those new boron-complexes cover most of the UV-visible-NIR spectrum, from 350 to 950 nm even in solution. As a consequence, this appealing tunability feature makes those new types of dyes very promising candidates for their further use in functional material development.

Experimental Section:

Experimental Details. All reactions were performed under argon atmosphere using standard Schlenk tube techniques. All the chemicals were used as received from commercial sources unless stated otherwise. DCM, THF and DMF were distilled from P₂O₅, sodium and benzophenone, and KOH respectively under an argon atmosphere. Chromatographic purifications were performed using silica gel (40-63 μ m). TLC was performed on silica gel plates coated with fluorescent indicator. The ¹H and ¹³C spectra were recorded at room temperature with a 300 MHz or 400 MHz spectrometer, using perdeuterated solvents as the internal standards. The ¹H and ¹³C chemical shifts are given in ppm relative to the residual protiated solvent or the solvent, respectively. The

FT-IR spectra were recorded as thin solid layers using an apparatus equipped with an ATR "diamond" apparatus. Absorption spectra were recorded on a Shimadzu UV-2600 absorption spectrometer. Absorption in the solid state was done on thin film of neat compound prepared by spin-coating. The steady-state emission and excitation spectra were recorded with a spectrofluorimeter (Fluoromax-4 Horiba Jobin Yvon). All fluorescence spectra were corrected. The following equation was used to determine the relative fluorescence quantum yield:

$$\phi(X) = (A_S/A_X)(F_X/F_S)(n_X/n_S)^2\phi(S)$$

Where A is the absorbance at the excitation wavelength (in the range 0.01-0.1 A.U.), F is the area under the corrected emission curve, n is the refractive index of the solvents (at 25°C) used in measurements, and the subscripts S and X represent standard and unknown, respectively. Fluorescence quantum yields (Φ_f) were determined using Rhodamine 6G in ethanol ($\Phi_f = 0.88$) as the reference.⁴⁰ Solid state fluorescence spectra were recorded with KBr pellets of desired compound at 10^{-6} M concentration. KBr pellets were made after proper grinding of the desired compounds with the dry KBr. The quantum yields were determined with an integration sphere using the KBr pellets.

Oxidation and reduction potentials were determined by cyclic voltammetry with a conventional 3-electrode system using a voltammetric analyzer equipped with a platinum micro disk (2 mm²) working electrode and a platinum wire counter electrode. The reference electrode is constituted of a non-aqueous silver electrode including the following electrolyte solution: 0.01 M silver nitrate + 0.1 M Tetrabutylammonium perchlorate in Acetonitrile. Potentials were calibrated versus the saturated calomel electrode (SCE), using the ferrocene/ferrocinium (Fc/Fc^+) couple as an internal reference and a conventional scan rate of 150 mV/s. Recrystallized tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the supporting electrolyte (0.1 M) in distilled and anhydrous DCM. All potentials are referred to the SCE electrode that was calibrated at 0.38 V vs Fc/Fc^+ system. Following the work of Jenekhe *et al.*,⁴⁶ we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO and HOMO levels were calculated from the following equations, using the oxidation and reduction onset potentials: LUMO (eV) = $-[E_{onsetred} \text{ (vs SCE)} + 4.4]$ and HOMO (eV) = $-[E_{onsetox} \text{ (vs SCE)} + 4.4]$, based on an SCE energy level of 4.4 eV relative to the vacuum.

Synthetic Details.

General Procedure for the Synthesis of 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazoles (**1/9**):

To a mixture of indole (for **1**)/5-bromoindole (for **9**) (9.2 mmol) and hexanal (0.56 mL, 4.6 mmol) in CH₃CN (15 mL), I₂ (233.0 mg, 0.92 mmol) was added, and the reaction mixture was allowed to stir at 25 °C for 14 h. The reaction was quenched with saturated aq. Na₂SO₃ (50 mL) and the solution was extracted with EtOAc (30 mL X 3). The organic layer was washed with H₂O (50 mL X 3) and dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the crude product dissolved in MeOH (6 mL). Then triethyl orthoformate (0.76 mL, 4.6 mmol) and methanesulfonic acid (60.0 μL, 0.92 mmol) were added to it, and the reaction mixture was stirred overnight at 25 °C. The precipitate formed was filtered off, washed with MeOH and dried under vacuum to get yellowish compounds **1/9**.

Compound 1³⁸. Yield: 1.26 g (42%); ¹H NMR (400 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.38-1.48 (m, 2H), 1.59-1.67 (m, 2H), 1.91-1.98 (m, 2H), 3.58 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.34-7.39 (m, 2H), 7.47-7.52 (m, 2H), 8.03 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 10.15 (s, 1H), 10.19 (s, 1H); ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆, 25 °C, TMS): δ 13.9, 22.3, 28.3, 28.7, 31.6, 97.9, 110.3, 110.6, 117.5, 117.7, 118.2, 120.1, 120.2, 121.7, 122.2, 122.5, 122.8, 124.7, 125.3, 134.0, 135.6, 141.2.

Compound 9³⁸. Yield: 978 mg (22%); ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C, TMS): δ 0.90 (t, *J* = 7.3 Hz, 3H), 1.37-1.46 (m, 2H), 1.52-1.59 (m, 2H), 1.76-1.84 (m, 2H), 3.43 (t, *J* = 7.8 Hz, 2H), 7.44-7.53 (m, 4H), 8.07 (s, 1H), 8.19 (d, *J* = 1.6 Hz, 1H), 8.45 (d, *J* = 1.9 Hz, 1H), 11.17 (s, 1H), 11.37 (s, 1H); ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆, 25 °C, TMS): δ 13.9, 22.0, 28.1, 28.3, 31.5, 98.8, 109.5, 109.6, 112.3, 112.5, 118.6, 119.6, 121.9, 122.9, 124.0, 124.1, 124.7, 127.3, 127.9, 134.4, 136.0, 139.9, 140.0. MS (*m/z*): 405.0 [M+H]⁺; Anal. calcd. for C₂₃H₂₀Br₂N₂: C, 57.05; H, 4.16; N, 5.79%. Found: C, 57.38; H, 4.38; N, 5.57%.

Compound 2³⁸. To a solution of **1** (400 mg, 1.23 mmol) in THF/H₂O (5:2, 28 mL), anhydrous FeBr₃ (1.09 g, 3.68 mmol) was added and the mixture was stirred at 25 °C for 20 h. H₂O (20 mL) was added to it and the solution was extracted with EtOAc (30 mL X 3). The organic layer was washed with H₂O (50 mL X 3) and dried over anhydrous Na₂SO₄. After removal of solvents under vacuum, the crude product was purified by column chromatography (silica gel, EtOAc/petroleum

ether, 25:75) to furnish **2** (427 mg, 86%) as a white solid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.88 (t, J = 7.2 Hz, 3H), 1.33-1.42 (m, 2H), 1.52-1.59 (m, 2H), 1.77-1.85 (m, 2H), 3.49 (t, J = 7.6 Hz, 2H), 7.18-7.23 (m, 2H), 7.41-7.48 (m, 2H), 7.55-7.61 (m, 2H), 8.12 (d, J = 8.0 Hz, 1H), 8.67 (d, J = 7.8 Hz, 1H), 11.13 (s, 1H), 11.25 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6 , 25 °C, TMS): δ 14.4, 22.6, 28.4, 29.1, 31.9, 93.2, 111.2, 111.6, 118.1, 118.3, 119.0, 119.8, 121.1, 121.9, 122.5, 123.1, 125.8, 126.3, 134.4, 135.0, 141.6. MS (m/z): 405.0 $[\text{M}+\text{H}]^+$; Anal. calcd. for $\text{C}_{23}\text{H}_{21}\text{BrN}_2$: C, 68.15; H, 5.22; N, 6.91%. Found: C, 68.06; H, 5.26; N, 6.73%.

Compound 3: A solution of **2** (330.0 mg, 0.81 mmol) in 1,4-dioxane (15 mL) in a Schlenk flask was purged with argon and then charged with pinacolborane (0.6 mL, 4.1 mmol), Et_3N (1.23 mL) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (57.0 mg, 0.08 mmol) respectively. The mixture was stirred at reflux for 12 h under argon. After removal of solvents under vacuum, the crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 25:75) to furnish **3** (250 mg, 80%) as a yellowish solid. ^1H NMR (300 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.88 (t, J = 7.2 Hz, 3H), 1.32-1.44 (m, 2H), 1.53-1.62 (m, 14H), 1.76-1.87 (m, 2H), 3.54 (t, J = 7.5 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.35-7.43 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 9.05 (d, J = 8.1 Hz, 1H), 10.14 (s, 1H), 11.07 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6 , 25 °C, TMS): δ 14.0, 22.3, 24.8, 28.4, 28.6, 31.6, 83.7, 110.4, 111.1, 117.3, 118.2, 119.1, 121.7, 121.8, 122.9, 123.5, 124.2, 124.9, 125.4, 126.0, 133.9, 140.6, 141.4, 142.3; MS (m/z): 452.2 $[\text{M}]^+$; Anal. calcd. for $\text{C}_{29}\text{H}_{33}\text{BN}_2\text{O}_2$: C, 76.99; H, 7.35; N, 6.19%. Found: C, 76.67; H, 7.28; N, 6.10%.

General Procedure for the Ligand Synthesis by Suzuki–Miyaura Coupling Reaction: A mixture of **3/15**, corresponding 2-bromopyridine/2,5-dibromopyrrazine, $\text{Pd}(\text{PPh}_3)_4$, Cs_2CO_3 and CsF and, dry toluene and DMF (2/1, v/v) in a Schlenk flask was degassed thoroughly and then stirred at 90 °C for 12 h under argon. The reaction was quenched with water, and the mixture was extracted with DCM. The organic layer was dried over anhydrous sodium sulfate. After removal of solvents under vacuum, the crude product was purified by column chromatography to afford the desired product.

Compound 4. Ligand **4** was prepared by the Suzuki–Miyaura coupling reaction of **3** (200 mg, 0.5 mmol) with 2-bromo-5-methylpyridine (27.0 mg, 1.6 mmol) in presence of Pd(PPh₃)₄ (15 mg, 0.01 mmol), Cs₂CO₃ (102 mg, 0.3 mmol) and CsF (48 mg, 0.3 mmol) in 6 mL toluene and DMF (2/1, v/v) according to the general procedure. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure **4** (175 mg, 80%) as a yellow solid. Mp: 190.2 °C; IR (neat, cm⁻¹): 3414, 2924, 2863, 1688, 1571, 1531, 1455, 1313, 740; ¹H NMR (400 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.41-1.50 (m, 2H), 1.63-1.70 (m, 2H), 1.95-2.01 (m, 2H), 2.69 (s, 3H), 3.64 (t, *J* = 8.0 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.30-7.39 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 10.21 (s, 1H) 10.35 (s, 1H); ¹³C{¹H} NMR (75 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.5, 23.5, 24.8, 33.0, 111.5, 111.6, 115.4, 118.3, 119.1, 120.0, 120.4, 121.8, 122.3, 123.0, 123.1, 123.5, 123.7, 123.9, 125.9, 126.2, 135.6, 135.8, 137.7, 142.6, 142.7, 157.3, 159.6; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₂₉H₂₇N₃: 418.5640; Found: 418.5254; Anal. calcd. for C₂₉H₂₇N₃: C, 83.42; H, 6.52; N, 10.06%. Found: C, 83.13; H, 6.45; N, 9.79%.

Compound 6. Ligand **6** was prepared by the Suzuki–Miyaura coupling reaction of **3** (140 mg, 0.31 mmol) with 2,5-dibromopyrazine (33.0 mg, 0.45 mmol) in presence of Pd(PPh₃)₄ (36 mg, 0.03 mmol), Cs₂CO₃ (326 mg, 0.74 mmol) and CsF (113 mg, 0.74 mmol) in 12 mL toluene and DMF (2/1, v/v) according to the general procedure. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish pure **6** (70 mg, 69%) as a yellow solid. Mp: 294.3 °C; IR (neat, cm⁻¹): 3457, 2860, 1607, 1530, 1463, 1318, 741; ¹H NMR (400 MHz, DMSO-d₆, 25 °C, TMS): δ 0.94 (t, *J* = 7.2 Hz, 6H), 1.41-1.50 (m, 4H), 1.62-1.70 (m, 4H), 1.90-1.97 (m, 4H), 3.63 (t, *J* = 7.6 Hz, 4H), 6.95-6.99 (m, 2H), 7.22-7.26 (m, 2H), 7.38-7.45 (m, 4H), 7.59 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 9.42 (s, 2H), 10.97 (s, 1H), 11.30 (s, 2H); ¹³C{¹H} NMR (75 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.5, 23.6, 29.1, 33.1, 111.4, 111.8, 112.0, 118.8, 119.6, 120.6, 121.8, 122.2, 123.1, 123.2, 123.5, 123.9, 126.3, 126.7, 135.9, 136.4, 142.7, 142.8, 146.8, 151.4; HRMS (ESI-TOF) *m/z*: [M]⁺ Calcd. for C₅₀H₄₄N₆: 728.3627; Found: 728.3573. Anal. calcd. for C₅₀H₄₄N₆: C, 82.39; H, 6.08; N, 11.53%. Found: C, 82.07; H, 6.24; N, 11.37%.

General Procedure for the Synthesis of BF₂-complexes (5a/7a/8). In a solution of the ligand (4/6) in DCE was added trimethylamine (Et₃N) and the mixture was stirred at 25 °C for 15 min. BF₃·OEt₂ was added dropwise into it and the reaction mixture was stirred at 80 °C for 12 h (for 5a and 7a)/48 h (for 8) under argon and then cooled to room temperature. The reaction was quenched with aq. NaHCO₃, extracted with DCM. The organic layer was washed with H₂O (50 mL X 3) and dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel to afford the desired product.

Compound 5a. Dye 5a was prepared by reaction of 4 (230 mg, 0.55 mmol), Et₃N (0.23 mL, 1.65 mmol) and BF₃·OEt₂ (0.21 mL, 1.65 mmol) in 20 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure 5a (230 mg, 90%) as orange solid. Mp: 207.0 °C; IR (neat, cm⁻¹): 3419, 2952, 1610, 1550, 1516, 1461, 1255, 736; ¹H NMR (400 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.40-1.49 (m, 2H), 1.62-1.70 (m, 14H), 1.96-2.03 (m, 2H), 3.16 (t, *J* = 3.2 Hz, 3H), 3.68 (t, *J* = 8.0 Hz, 2H), 7.13-7.17 (m, 1H), 7.27-7.31 (m, 1H), 7.43-7.51 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.34-8.38 (m, 2H), 8.92 (d, *J* = 8.0 Hz, 1H), 10.84 (s, 1H); ¹³C {¹H} NMR (75 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.4, 23.0, 23.2, 23.5, 27.5, 33.0, 104.8, 112.6, 114.5, 118.2, 118.8, 120.6, 122.1, 122.6, 123.2, 123.6, 124.6, 125.4, 125.7, 126.6, 126.9, 127.5, 136.5, 141.4, 142.5, 145.2, 152.1, 157.2, 158.8; MS (*m/z*): 465.1 [M]⁺; HRMS (ESI-TOF) *m/z*: [M]⁺ Calcd. for C₂₉H₂₆BF₂N₃: 465.2188; Found: 465.2216.

Compound 7a. Dye 7a was prepared by reaction of 6 (150 mg, 0.21 mmol), Et₃N (71 μL, 0.20 mmol) and BF₃·OEt₂ (25 μL, 0.20 mmol) in 15 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure 7a (115 mg, 72%) as blue solid. Mp: 210.0 °C; IR (neat, cm⁻¹): 3431, 2919, 1664, 1578, 1515, 1318, 740; ¹H NMR (400 MHz, DMSO-d₆, 25 °C, TMS): δ 0.90-0.95 (m, 6H), 1.41-1.47 (m, 4H), 1.62-1.67 (m, 4H), 1.91-1.97 (m, 4H), 3.62 (t, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 7.6 Hz, 2H), 6.93 (t, *J* = 9.4 Hz, 1H), 7.24 (t, *J* = 9.2 Hz, 1H), 7.33-7.45 (m, 3H), 7.52-7.61 (m, 4H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 9.13 (s, 1H), 10.53 (s, 1H), 11.07 (s, 1H), 11.35 (s, 1H), 11.95 (s, 1H); ¹³C {¹H} NMR (75 MHz, DMSO-d₆, 25 °C, TMS): δ 14.0, 14.1, 22.3, 22.4,

28.4, 28.5, 28.8, 28.9, 31.6, 31.7, 101.5, 108.6, 110.9, 111.2, 112.3, 113.3, 116.3, 117.8, 118.5, 118.6, 119.1, 120.6, 120.8, 121.1, 121.2, 121.3, 121.5, 121.9, 122.1, 122.2, 122.5, 122.9, 124.4, 125.5, 125.9, 126.4, 126.8, 129.5, 134.4, 135.0, 135.5, 138.4, 140.0, 141.4, 141.5, 141.6, 143.2, 147.9, 149.1; HRMS (ESI-TOF) m/z : $[M]^+$ Calcd. for $C_{50}H_{43}BF_2N_6$: 776.3610; Found: 776.3591.

Compound 8. Dye **8** was prepared by reaction of **6** (150 mg, 0.21 mmol), Et_3N (0.43 mL, 1.2 mmol) and $BF_3 \cdot OEt_2$ (0.15 mL, 1.2 mmol) in 15 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure **8** (102 mg, 60%) as blue solid. Mp: $>300.0^\circ C$; IR (neat, cm^{-1}): 3429, 1567, 1509, 1320, 1220, 941, 745; 1H NMR (300 MHz, $DMSO-d_6$, $25^\circ C$, TMS): δ 0.91 (t, $J = 7.2$ Hz, 6H), 1.36-1.47 (m, 4H), 1.58-1.68 (m, 4H), 1.87-1.97 (m, 4H), 3.70 (t, $J = 7.5$ Hz, 4H), 7.31-7.42 (m, 4H), 7.51-7.65 (m, 4H), 7.83 (t, $J = 8.4$ Hz, 4H), 8.26 (d, $J = 8.1$ Hz, 2H), 8.55 (d, $J = 8.4$ Hz, 2H), 10.17 (s, 2H), 12.03 (s, 2H); $^{13}C\{^1H\}$ NMR could not be done due to poor solubility; HRMS (ESI-TOF) m/z : $[M]^+$ Calcd. for $C_{50}H_{42}B_2F_4N_6$: 824.3604; Found: 824.3635. Anal. calcd. for $C_{50}H_{42}B_2F_4N_6$: C, 72.83; H, 5.13; N, 10.19%. Found: C, 72.59; H, 5.32; N, 9.89%.

Compound 5b. A mixture of **4** (150 mg, 0.36 mmol) and triphenylborane (105 mg, 0.43 mmol) in toluene (15 mL) was heated ($90^\circ C$) under inert atmosphere for 12 h. The mixture was allowed to cool down, and the solvent was removed in a rotary evaporator. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish pure **5b** (94 mg, 45%) as orange solid. Mp: $199.0^\circ C$; 1H NMR (300 MHz, $(CD_3)_2CO$, $25^\circ C$, TMS): δ 0.91 (t, $J = 7.2$ Hz, 3H), 1.38-1.46 (m, 2H), 1.59-1.65 (m, 2H), 1.88-1.94 (m, 2H), 2.18 (s, 3H), 3.54 (t, $J = 7.8$ Hz, 2H), 6.50-6.53 (m, 1H), 6.99-7.18 (m, 9H), 7.37-7.46 (m, 6H), 7.55 (d, $J = 8.4$ Hz, 1H), 8.10-8.17 (m, 2H), 8.24 (d, $J = 8.1$ Hz, 1H), 8.71 (d, $J = 8.1$ Hz, 1H), 10.60 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$, $25^\circ C$, TMS): δ 14.4, 23.4, 26.8, 33.1, 107.5, 112.4, 115.2, 118.1, 118.6, 118.8, 122.4, 122.8, 123.4, 123.6, 125.5, 125.7, 126.2, 126.4, 126.5, 126.9, 128.2, 134.4, 136.3, 140.6, 141.4, 142.4, 147.6, 153.2, 159.4; HRMS (ESI-TOF) m/z : $[M]^+$ Calcd. for $C_{41}H_{36}BN_3$: 581.3002; Found: 581.3068. Anal. calcd. for $C_{41}H_{36}BN_3$: C, 84.68; H, 6.24; N, 7.23%. Found: C, 84.41; H, 6.11; N, 6.97%.

Compound 7b. A mixture of **6** (150 mg, 0.21 mmol) and triphenylborane (119 mg, 0.49 mmol) in toluene (10 mL) was heated (90 °C) under inert atmosphere for 48 h. The mixture was allowed to cool down, and the solvent was removed in a rotary evaporator. Crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish pure **7b** (46 mg, 25%) as blue solid. Mp: >300.0 °C; ¹H NMR (400 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.87-0.98 (m, 6H), 1.45-1.50 (m, 4H), 1.67-1.71 (m, 4H), 1.95-2.06 (m, 4H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.74 (t, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.94 (t, *J* = 8.1 Hz, 1H), 7.06-7.23 (m, 9H), 7.34-7.39 (m, 6H), 7.49-7.69 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.29 (t, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.70 (s, 1H), 10.45-10.49 (m, 3H), 10.94 (s, 1H); ¹³C{¹H} NMR (75 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.4, 14.5, 23.5, 33.1, 104.9, 109.9, 111.7, 111.8, 112.8, 115.1, 117.7, 119.0, 119.3, 119.7, 120.3, 122.0, 122.3, 122.8, 122.9, 123.0, 123.1, 123.2, 123.3, 123.7, 123.8, 125.9, 126.0, 126.3, 126.8, 127.2, 127.6, 128.4, 129.3, 135.0, 135.6, 136.2, 136.4, 138.5, 142.4, 142.5, 142.6, 142.8, 143.3, 147.2, 148.0, 150.5; HRMS (ESI-TOF) *m/z*: [M]⁺ Calcd. for C₆₂H₅₃BN₆: 892.4425; Found: 892.4395.

Compound 10. To a solution of **9** (850 mg, 1.76 mmol) in a THF/H₂O (5:2, 60 mL), anhydrous FeBr₃ (1.56 g, 5.27 mmol) was added portion wise under N₂ atmosphere at 25 °C and the mixture was stirred for 20 h. Then, H₂O (30 mL) was added, and the mixture was extracted with EtOAc. The organic layer was washed with brine (25 mL) and dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish pure **10** (930 mg, 94%) as yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C, TMS): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.37-1.46 (m, 2H), 1.51-1.59 (m, 2H), 1.76-1.84 (m, 2H), 3.45 (t, *J* = 7.6 Hz, 2H), 7.54-7.64 (m, 4H), 8.22 (s, 1H), 8.80 (s, 1H), 11.44 (s, 1H), 11.55 (s, 1H); ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆, 25 °C, TMS): δ 13.9, 22.0, 27.8, 28.2, 31.4, 93.2, 109.5, 110.5, 112.8, 113.2, 118.6, 119.0, 120.3, 123.6, 123.7, 124.3, 128.2, 128.6, 134.6, 135.1, 140.0, 140.1. MS (*m/z*): 559.8 [M]⁺; Anal. calcd. for C₂₃H₁₉Br₃N₂: C, 49.06; H, 3.40; N, 4.97%. Found: C, 48.83; H, 3.52; N, 4.72%.

Compound 11. A solution of **10** (900 mg, 1.60 mmol) and diisopropylamine (18 mL) in toluene (18 mL) in a Schlenk flask was purged with argon and then charged with trimethylsilylacetylene (3.3 mL, 24 mmol), Pd(dppf)₂Cl₂.DCM (392 mg, 0.48 mmol) and CuI (91.4 mg, 0.48 mmol)

respectively. The mixture was heated at 110 °C for 12 h under argon. After removal of solvents under vacuum, the crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish **11** (800 mg, 81%) as a yellowish solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 0.28 (s, 9H), 0.30 (s, 9H), 0.48 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H), 1.41-1.51 (m, 2H), 1.57-1.61 (m, 2H), 1.88-1.96 (m, 2H), 3.40 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.56-7.59 (m, 2H), 8.03 (s, 1H), 8.26 (s, 1H), 8.46 (s, 1H), 8.90 (s, 1H); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C, TMS): δ -0.6, -0.5, 13.2, 21.7, 27.7, 28.1, 31.4, 90.5, 90.8, 93.9, 99.5, 103.1, 105.9, 106.1, 109.3, 109.6, 112.5, 112.8, 118.9, 120.1, 121.1, 122.5, 122.6, 125.7, 125.9, 128.6, 128.9, 133.2, 136.9, 139.2, 139.6; MS (*m/z*): 614.3 [M]⁺, 615.4 [M+H]⁺; Anal. calcd. for C₃₈H₄₆N₂Si₃: C, 74.21; H, 7.54; N, 4.55%. Found: C, 74.06; H, 7.69; N, 4.36%.

Compound 12. A mixture of **11** (460 mg, 0.75 mmol) and K₂CO₃ (3.1 g, 7.50 mmol) in DCM/MeOH (1:1, 30 mL) was stirred for 14 h at 25 °C. The mixture was washed with H₂O (50 mL X 3), extracted with DCM and dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure **12** (280 mg, 94%) as yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.37-1.47 (m, 2H), 1.51-1.59 (m, 2H), 1.85-1.93 (m, 2H), 3.10 (s, 2H), 3.35 (t, *J* = 7.6 Hz, 2H), 3.93 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.57-7.61 (m, 2H), 8.04 (s, 1H), 8.27 (s, 1H), 8.45 (s, 1H), 8.84 (s, 1H); ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆, 25 °C, TMS): 14.0, 22.1, 28.2, 28.4, 31.5, 78.2, 78.3, 79.5, 85.2, 89.4, 93.1, 110.8, 111.3, 111.4, 111.5, 119.5, 120.9, 121.5, 122.1, 122.3, 125.0, 125.7, 129.1, 129.6, 134.2, 138.4, 141.0, 141.1; MS (*m/z*): 398.1 [M]⁺. Anal. calcd. for C₂₉H₂₂N₂: C, 87.41; H, 5.56; N, 7.03%. Found: C, 87.74; H, 5.57; N, 6.73%.

Compound 13. To a stirred, degassed DCM/EtOH (1:1, 40 mL) solution of **12** (280 mg, 0.70 mmol) was added under argon Pd/C 10% (60 mg, 20% mol.). The reaction mixture was stirred at 50 °C under H₂ (atmospheric pressure) for 24 h. After that, the solution was filtered through Celite and the solvent was evaporated. The crude mixture was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish pure **13** (240 mg, 85%) as yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C, TMS): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.28-1.32 (m, 6H), 1.38-1.47 (m, 5H), 1.55-1.63 (m, 2H), 1.76-1.84 (m, 2H), 2.76-2.82 (m, 4H), 3.41-3.51 (m, 4H), 7.22-7.24 (m,

2H), 7.40-7.43 (m, 2H), 7.91 (s, 1H), 7.95 (s, 1H), 10.76 (s, 1H), 10.80 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.8, 14.0, 16.4, 16.7, 21.2, 22.2, 28.1, 28.5, 28.7, 31.7, 110.2, 115.1, 116.4, 119.3, 119.6, 120.4, 122.8, 123.0, 124.8, 132.6, 132.8, 134.1, 134.5, 139.7; MS (m/z): 410.2 $[\text{M}]^+$; Anal. calcd. for $\text{C}_{29}\text{H}_{34}\text{N}_2$: C, 84.83; H, 8.35; N, 6.82%. Found: C, 84.50; H, 8.31; N, 6.79%.

Compound 14. To a solution of **13** (250 mg, 0.61 mmol) in AcOH (5 mL), Br_2 (195 mg, 1.22 mmol) in AcOH (2 mL) was added dropwise at 25 °C during 30 mins. Then the mixture was stirred at 100 °C for 2 h. The reaction was quenched with aq. Na_2SO_3 and extracted with DCM. The organic layer was washed with NaHCO_3 (20 mL X 2) and H_2O (30 mL X 3) and, dried over anhydrous Na_2SO_4 . After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 20:80) to furnish pure **14** (320 mg, 92%) as yellow solid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.90 (t, J = 7.2 Hz, 3H), 1.28-1.32 (m, 6H), 1.36-1.46 (m, 5H), 1.56-1.63 (m, 2H), 1.72-1.79 (m, 2H), 2.78-2.83 (m, 4H), 3.56-3.65 (m, 4H), 7.49 (s, 2H), 7.93 (s, 1H), 8.00 (s, 1H), 10.50 (s, 1H), 10.57 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.8, 14.0, 16.2, 16.5, 20.5, 22.2, 27.4, 27.9, 28.0, 28.6, 31.6, 102.9, 103.0, 117.0, 118.3, 120.0, 120.2, 120.5, 120.7, 124.8, 125.0, 127.6, 127.7, 134.5, 134.9, 135.1, 135.3, 138.0; MS (m/z): 566.2 $[\text{M}]^+$; Anal. calcd. for $\text{C}_{29}\text{H}_{32}\text{Br}_2\text{N}_2$: C, 61.28; H, 5.67; N, 4.93%. Found: C, 61.03; H, 5.59; N, 4.69%.

Compound 15. A solution of **14** (250 mg, 0.44 mmol) in 1,4-dioxane (20 mL) in a Schlenk flask was purged with argon and then charged with pinacolborane (0.64 mL, 4.4 mmol), Et_3N (1.33 mL) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (62.0 mg, 0.09 mmol) respectively. The mixture was stirred at reflux for 12 h under argon. After removal of solvents under vacuum, the crude product was purified by column chromatography (silica gel, DCM/petroleum ether, 40:60) to furnish **15** (204 mg, 70%) as a yellowish solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ 0.96 (t, J = 7.2 Hz, 3H), 1.39 (t, J = 7.5 Hz, 6H), 1.48 (s, 24H), 1.53-1.63 (m, 7H), 1.95-2.04 (m, 2H), 2.88 (q, J = 7.5 Hz, 4H), 3.46-3.56 (m, 4H), 7.72 (s, 2H), 8.15 (s, 1H), 8.17 (s, 1H), 9.19 (s, 1H), 9.23 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ 13.4, 14.2, 16.9, 17.1, 22.1, 22.7, 25.1, 28.8, 29.1, 29.2, 32.3, 83.8, 115.5, 116.7, 119.5, 119.9, 123.1, 123.2, 124.9, 125.0, 131.7, 131.8, 133.6, 133.7, 134.0, 134.6,

145.0, 145.1; MS (m/z): 662.5 [M]⁺; Anal. calcd. for C₄₁H₅₆B₂N₂O₄:C, 74.33; H, 8.52; N, 4.23%. Found: C, 74.24; H, 8.49; N, 4.26%.

Compound 16. 1st step: A mixture of **15** (90 mg, 0.14 mmol), 2-bromo-5-methylpyridine (56.0 mg, 0.33 mmol), Pd(PPh₃)₄ (31 mg, 0.03 mmol), Cs₂CO₃ (213 mg, 0.65 mmol) and CsF (99 mg, 0.3 mmol) in dry toluene/DMF (2/1, v/v, 6mL) in a Schlenk flask was degassed thoroughly and then stirred at 90 °C for 12 h under argon. The reaction was quenched with water, and the mixture was extracted with DCM. The organic layer was dried over anhydrous Na₂SO₄. After removal of solvent under vacuum, the crude product (72 mg) was obtained which was pure enough to use for the next step without further purification.

2nd step: In a solution of the crude obtained from 1st step (72 mg, 0.12 mmol) in DCE (10 mL) was added Et₃N (0.17 mL, 1.18 mmol) and the mixture was stirred at 25 °C for 15 min. BF₃·OEt₂ (0.15 mL, 1.18 mmol) was added dropwise into it and the reaction mixture was stirred at 80 °C for 12 h under argon and then cooled to room temperature. The reaction was quenched with aq. NaHCO₃ (20 mL) and extracted with DCM (30 mL). The organic layer was washed with H₂O (50 mL X 3) and dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 50:50) to furnish pure **16** (67 mg, 72%) as orange solid. Mp: >300.0 °C; IR (neat, cm⁻¹): 1631, 1563, 1515, 1484, 1063, 724; ¹H NMR (400 MHz, C₂D₂Cl₄, 25 °C, TMS): δ 1.09 (t, *J* = 7.6 Hz, 3H), 1.50-1.54 (m, 10H), 1.60-1.69 (m, 5H), 1.83-1.91 (m, 2H), 2.02-2.09 (m, 2H), 2.60 (s, 6H), 3.14-3.21 (m, 2H), 7.91 (s, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.41 (s, 1H), 8.46 (s, 1H), 8.89 (s, 2H). ¹³C{¹H} NMR could not be done due to poor solubility; HRMS (ESI-TOF) m/z: [M]⁺ Calcd. for C₄₁H₄₂B₂F₄N₄: 688.3532; Found: 688.3599. Anal. calcd. for C₄₁H₄₂B₂F₄N₄: C, 71.53; H, 6.15; N, 8.14%. Found: C, 71.34; H, 6.29; N, 8.01%.

Supporting Information: Copies of the ¹H NMR and ¹³C{¹H} NMR spectra of the synthesized compounds, Cyclic voltammograms, X-ray crystallographic and Computational data (PDF). X-ray crystallographic data for **5a** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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