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Tuning the Emission Color of Indolo[3,2-*b*]carbazole based Boron Complexes and their Application in OFET and Bioimaging

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Abstract: Synthetic strategies were developed for the indolo-imine boron difluoride (IIBD) dyes based on the Indolo[3,2-*b*]carbazole structures. Four new IIBD dyes were synthesized which were converted to the corresponding -BPh₂-BOR₂ and N-*t*-Boc/N-benzoyl derivatives. The photophysical properties of all the dyes were determined in both solution and solid media. All these dyes absorb in the UV-Vis region, show negative solvatochromism, and are fluorescent in both the media. The absorbance and fluorescence properties of the dyes can be tuned over a wide range by synthetic modifications. These findings are rationalized by theoretical calculations that restore quite nicely the experimental shifts, explain the negative solvatochromism, and allow to quantify the charge transfer (CT). Similarly, the HOMO-LUMO energies measured by CV are in good agreement with the theoretically calculated values. Interestingly, the energy gaps of the dyes can also be tuned by structure modulations using the developed chemical route. Charge transport properties of the dyes were checked and showed that the N-benzoyl derivative has the highest hole mobility which is useful for OFETs applications. Also, easy cellular uptake of the dyes, their low toxicity and high stability inside the cells associated with bright fluorescence in the cytoplasm will be useful for their future applications as cellular imaging agents. All these aspects highlight the interest of this new class of dyes.

Introduction

Organo-boron frameworks with delocalized π -electron systems are known to have outstanding photophysical and electronic properties which are very useful for developing new functional materials.^[1] A common strategy to obtain these systems is the

complexation of boron difluoride (BF₂) units by large π -conjugated bidentate ligands. In these complexes, the boron atom improves the ligand electronic performances by i) rigidifying the ligand backbone, ii) acting as a conduit for the delocalized π -electron systems and iii) creating a cyanine-like electronic structure, substantially decreasing the energy of the lowest unoccupied molecular orbital (LUMO),^[2] so that the dye core acts as an electron acceptor, allowing to create strong push-pull systems when donating groups are located at the periphery of the compounds. Most of these dyes are derived from dipyrin (BODIPYs),^[3] aza-dipyrin (aza-BODIPYs),^[3] bispyrrole (BOPHYs),^[4] anilidopyridine,^[6] indigo-N,N'-di-arylimine^[7] and formazanate^[8] ligands. Despite of recent advances, examples of the incorporation of boron atoms into 5,11-dihydroindolo[3,2-*b*]carbazole (ICZs, **A**, Chart 1) molecular frame remain rare.^[9]

ICZs^[10] have found widespread use in a large array of applications such as sensing,^[11] biological applications,^[12] organic field effect transistors (OFETs),^[13] organic light emitting diodes (OLEDs),^[14] Dye Sensitized Solar Cells (DSSCs)^[15] and even in Organic Photovoltaics (OPVs).^[16] The high charge carrier mobilities, the possibility to easily tune their electronic levels and their good stability towards atmospheric conditions make them ideal components for use in organic electronics. To improve the electronic and photophysical properties of ICZ moiety, we developed previously indolo-pyridine boron difluoride (IPBD) dyes by incorporating the boron atom in the pyridine-indolo[3,2-*b*]carbazole structures (**B**, Chart 1).^[17] Different bidentate ligands were prepared by incorporating pyridine moiety/ies at the C4, C10 and C12 positions of ICZ (**A**, Chart 1) with simultaneous coupling with BF₃ to obtain the dyes. The indolocarbazole moiety in **B** lost its planarity. Indeed, the tail represented by C7, C8 and C9 atoms is lifted out of the plane and the pyridyl ring is also twisted out of

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Chart 1. Chemical structure of ICZ (A), indolo-pyridine boron difluoride (IPBD) (B) and its crystal structure (C),^[17] and indolo-imine boron difluoride (IIBD) (D) based on ICZ.

Scheme 1. Synthesis of dyes 3, 4 and 5. a) Aryl amine (1.2 equiv), PTS (cat. Amount), Na₂SO₄ DCE, 70 °C, 12 h. b) Et₃N, BF₃·OEt₂, DCE, 70 °C, 12 h. c) (Boc)₂O, DMAP, THF, 25 °C, 2 h (for 4a-1 and 4b); PhCOCl, Et₃N, 50 °C, 72 h (for 4a-2). d) BBr₃, DCM, 0 °C to 25 °C, 12 h.

the hypothetical plane containing the ICZ aromatic core (C, Chart 1 and Figure S1). This is clearly due to the steric hindrance between the protons at C7 and the carbon atoms at C5' of ICZ and the pyridyl moieties, respectively (B, Chart 1 and Figure S1). Due to this twisted structure, some of the photophysical and electronic properties of IPBD were compromised which was observed by a relatively low delocalization of the HOMO and LUMO surfaces, rather small longest wavelength absorption maximum (λ_{max}), low fluorescence quantum yield, and low charge transport properties. To circumvent these issues, we designed indolo-imine boron difluoride (IIBD) dyes, by incorporating the imine part at the C4 position of the indolo[3,2-*b*]carbazole to avoid the steric clash as observed in B (D, Chart 1). It was anticipated that the molecules will be more planar which should improve the photophysical and electronic properties as compared to B. Here we discuss below their synthesis, characterization and, photophysical, electronic and biological properties for their further use in functional materials developments. Detailed theoretical studies were also carried out to explain the experimental analyses.

Results and Discussion

Synthesis. The synthesis of the IIBD dyes started with 12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole-6-carbaldehyde (1) which was synthesized according to the literature.^[18] The acid catalysed reaction of 1 with different aromatic amines afforded corresponding imines 2a-d. Finally, treatment of 2a-d with excess BF₃·OEt₂ furnished the corresponding dyes 3a-d (Scheme 1).

Dyes 3a-d can be viewed as *all-in-one* push-pull (D-A) type molecules in which the free nitrogen of the pyrrole ring of ICZ moiety acts as an electron donor and the electron-deficient BF₂-centre on the other side acts as the electron acceptor. The push-pull effect strength in these dyes was tuned by synthesizing: (i) B(OR)₂/B(Ph)₂ analogues (dye 5 and 6) of dye 3a to make the B-centre more electron deficient than in BF₂.^[19] and (ii) N-protected dyes (4a-1, 4a-2, 4b, 7) with electron withdrawing groups to reduce the electron donating effect of the free nitrogen.

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Dyes **3a-b** were reacted with $(\text{Boc})_2\text{O}$ to furnish N-Boc protected dye, **4a-1** and **4b** respectively. Further, **3a** was reacted with benzoyl chloride to furnish N-Benzoyl protected dye, **4a-2**. Finally, dye **3a** was treated with BBr_3 to synthesize B-substituted dye **5**^[20] which is a chiral molecule with a stereogenic boron centre.^[21] Dye **6** was synthesized by treatment of **2a** with excess $\text{B}(\text{Ph})_3$. Further dye **6** was reacted with $(\text{Boc})_2\text{O}$ to furnish N-Boc protected dye, **7** (Scheme 2).

Scheme 2. Synthesis of dyes **6** and **7**. a) $\text{B}(\text{Ph})_3$, Toluene, 90 °C, 12 h. b) $(\text{Boc})_2\text{O}$, DMAP, THF, 25 °C, 2 h.

The structure of dye **3a** was confirmed by analysing its NMR spectra in $(\text{CD}_3)_2\text{SO}$. The ^1H NMR spectrum (Figure S48) shows signals for all twelve aromatic protons along with two characteristic singlets for the N-H and imine protons at 11.83 and 9.68 ppm, respectively. Another diagnostic singlet for the three methyl protons of the methoxy group appears at 3.78 ppm. The benzylic methylene and terminal methyl groups of the pentyl lateral chain resonates as triplets at 3.66 and 0.88 ppm, respectively. Other three internal methylene groups signal of pentyl lateral chain are found as three different multiplets centred at 1.89, 1.58 and 1.38 ppm with the expected two protons integration for each signal. The carbon spectrum shows five signals for the alkyl atoms of pentyl chains, the expected 25 signals for aromatic atoms and one diagnostic signal for methoxy group (Figure S49).

In case of dye **5**, the ^1H NMR spectrum is similar to that of dye **3a** with all the diagnostic signals. As expected the signal for the methyl protons of the methoxy group is absent in the spectrum of **5** with instead a singlet appearing at 4.42 ppm with one proton integration for the proton of the hydroxyl group attached at B-centre (Figure S62). In the carbon NMR spectrum also, no signal for the methoxy group is obtained and the expected five signals for the alkyl atoms of pentyl chains as well as 25 signals for aromatic atoms are found (Figure S63). Further the structures of **3a** and **5** are confirmed by X-ray crystallography (*vide infra*).

X-ray Crystallography. Structures of **3a** (Figure 1a), **3b** (Figure 1b) and **5** (Figure 3) could be confirmed by X-ray crystallography data. The indolocarbazole moiety in **3a** is planar, i.e., the boron atom and the imine part are all in the same plane as anticipated from our design, which hence significantly contrasts with the previously reported derivative **B** (Chart 1C).^[17] The methoxy-bearing phenyl ring is almost perpendicular (torsion angle C19/N3/C20/C21 of 97°) to the core ICZ plane (Figure 1a). This high torsion angle in **3a** is due to the steric hindrance of the methoxy group at *ortho*-position with the atoms in the ICZ plane.

Figure 1. Two orthogonal Ortep views of the crystal structures of dyes **3a** (a) and **3b** (b).

Figure 2. Packing diagrams for **3a** (a) and **3b** (b) showing the layer formation through π - π stacking.

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The boron atom in **3a** presents a slightly distorted tetrahedral environment with bond angles ranging from 106.54 to 112.4° and typical values of 106.54 (15)° for N–B–N and 108.92 (17)° for F–B–F. The B–N bond is sensibly longer for the imine (1.583(3) Å) than for the indolocarbazole (1.514(3) Å). These are usual observations for indolocarbazole based boron complexes.^[9, 17] The overall conformation of the molecules is planar and they assembled parallelly to the plane (0 0 1) with a slight angle of 7.412° making infinite layers with 3.584 Å interplanar distances (Figure 2a).

The X-ray crystallographic structure of **3b** (Figure 1b) also shows that the core of the compound remains planar, *i.e.*, the indolocarbazole moiety, the boron atom and the imine part are all in the same plane as in **3a**. The phenyl ring is twisted out of ICZ plane (torsion angle C19/N1/C20/C25 of -47°) but as expected, the torsion angle is reduced as compared **3a** due to lower steric hindrance of the *p*-methoxy group. The general trends of other crystal parameters are like **3a** and the molecules are assembled parallelly to the plane (0 0 1) with a reduced interplanar angle of 2.339° and interplanar distances of 3.498 Å instead of 3.584 Å in **3a** (Figure 2b).

In compound **5**, the phenyl ring rotates to bring the oxygen atom attached to its *ortho*- position closer to the boron atom allowing the formation of a B–O bond, and in doing so the phenyl ring partly aligns itself with the core ICZ plane (with a torsion angle C7/N1/C6/C5 of -23°) (Figure 3). Nevertheless, the compound does not become fully planar, as expected in such complexes. Indeed, the tetrahedral boron atom sticks out of the planes containing the phenyl ring and the core ICZ group, resulting in the chirality of compound **5**.

Figure 3. Two orthogonal Ortep views of the crystal structure of compound **5**.

The boron atom in **5** becomes more distorted as compared to **3a** with tetrahedral bond angles ranging from 102.9 to 116.0° and typical values of 104.4(5)° for N–B–N and 106.8(5)° for O–B–O. As in the previous dyes, the B–N bond is slightly longer in the imine (1.572(11) Å) than in the indolocarbazole (1.537(10) Å). The OH- group makes two H-bond interactions, the first with the N–H of the pyrrole group of vicinal molecule (d O2...H–N3, 2.054 Å) the second with an acetonitrile molecule (d O2–H...N=C–CH₃, 2.056 Å), as this solvent was used during crystallization (see Figure 3, *right*). Due to this H bonding interaction, molecules are assembled parallelly to make columns and all the columns are arranged in zig-zag manner (Figure 4).

Figure 4. Packing diagram for dye **5**.

Photophysical properties and its theoretical rationalization.

Photophysical properties in solution. The photophysical properties were evaluated for the dyes **3a–d**, **4a–1**, **4a–2**, **4b**, **5**, **6** and **7** in CH₂Cl₂ at room temperature (25 °C). The measured photophysical parameters and calculated Stokes shift (ν) of these dyes in CH₂Cl₂ are listed in Table 1, together with the values determined in solid state that are discussed in a separate Section below. The absorption, excitation, and emission spectra in CH₂Cl₂ can be found in Figures 5, 6, and S2–S8 in the SI. The absorption spectrum of **3a** shows multiple peaks with a (λ_{max} at 516 nm which is redshifted by 23 nm as compared to its ICZ-pyridine counterpart (**B**).^[17] This confirms the higher electronic delocalization in **3a** due to its improved planarity with respect to **B**. At higher energy, one broad band centred at ca. 429 nm also appears. Dyes **3b–d** show absorption spectra similar to the **3a** spectrum for both the absorption bands illustrating the weak influence of the aryl rings attached to imine N-atom. This is likely due to the out of plane configuration of these aryl rings as compared to the ICZ moieties as revealed from the X-ray (Figure 1) and confirmed by theoretical calculations discussed *vide infra*. Substitution of the N–H group of **3a** with electron withdrawing moieties induces a hypsochromic effect in the absorption spectra by reducing the electron donating effect of the nitrogen atom. This effect is slightly more pronounced in **4a–1** (λ_{max} = 494 nm) with *t*-Boc protection than in the benzoyl protected **4a–2** (λ_{max} = 500 nm) (Figure 5, Table 1) as N-*t*-Boc has more electron withdrawing character than N-benzoyl.

Figure 5. Absorption spectra of dyes **3a–d**, **4a–1**, **4a–2**, **4b**, **5**, **6** and **7** in CH₂Cl₂ (1.0 X 10⁻⁵ M) at 25 °C.

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B-substituted dye **5** displays a redshifted absorption spectrum as compared to its parent dye **3a** (Figure 5, Table 1). This is related to the extension of conjugation in the imino-phenyl ring attached to B-centre that is almost in the same plane as the rest of the dye which was not the case for **3a**. This is observed by X-ray crystallographic data (Figure 3 and 4) and also seen in the theoretical calculations discussed *vide infra*.

Interestingly, dye **6** shows highly redshifted absorbance as compared to its -BF₂ analogue **3a**. Indeed, the λ_{max} of **6** (574 nm)

is 58 nm bathochromically shifted as compared to dye **3a** (Figure 5, Table 1). This unusually large shift in λ_{max} due to the substitution of F atoms by the phenyl groups is in-line with the results of *ab initio* calculations (*vide infra*). Substitution of the N-H group in **6** with electron withdrawing group *t*-Boc (dye **7**) induces similar variations as the BF₂ in dye **4a-1**, but the hypsochromic effect (30 nm) in the absorption band of **7** (λ_{max} = 544 nm) is more pronounced than in **4a-1**.

Table 1. Photophysical properties of dyes **B**, **3a-d**, **4a-1**, **4a-2**, **4b** and **5-7** in CH₂Cl₂ and solid states.

Dye	λ_{abs} [nm] - CH ₂ Cl ₂	λ_{abs} [nm] solid	ϵ_{max} [M ⁻¹ cm ⁻¹] - CH ₂ Cl ₂	λ_{em} [nm] - CH ₂ Cl ₂	λ_{em} [nm] -solid	ν [cm ⁻¹] - CH ₂ Cl ₂	Φ_{fl} [%] ^[a] - CH ₂ Cl ₂	Φ_{fl} [%] solid	τ (ns) ^[b] - CH ₂ Cl ₂	k_r (10 ⁸ s ⁻¹) ^[c] - CH ₂ Cl ₂	k_{nr} (10 ⁸ s ⁻¹) ^[c] - CH ₂ Cl ₂	ΔE_{opt} (eV)
B	493.0	508.0	16600	562.0	586.0	2500	0.01	-	-	-	-	2.20
	404.0	414.0	14400									
3a	516.0	534.0	19900	548.0	568.0	1130	17.0	2.7	2.78	0.6	3.0	2.11
	429.0	444.0	20700									
3b	522.0	533.0	21600	565.0	-	1460	13.0	-	2.63	0.5	3.3	2.08
	434.0	446.0	21200									
3c	518.0	530.0	16000	550.0	-	1120	15.0	-	2.78	0.5	3.1	2.15
	433.0	445.0	15900									
3d	523.0	540.0	20100	562.0	-	1330	12.0	-	2.43	0.5	3.6	2.11
	436.0	458.0	17600									
4a-1	494.0	507.0	13500	539.0	559.0	1690	18.0	13.0	2.40	0.8	3.4	2.21
	422.0	432.0	14500									
4a-2	500.0	502.0	11200	542.0	575.0	1550	17.0	4.4	2.61	0.7	3.2	2.25
	423.0	427.0	12100									
4b	495.0	507.0	15800	553.0	568.0	2120	15.0	7.1	2.37	0.6	3.6	2.23
	430.0	406.0	16100									
5	549.0	563.0	16000	590.0	-	1270	1.0	-	2.48	0.04	4.0	1.96
	449.0	438.0	16300									
6	574.0	584.0	9500	606.0	626.0	920	18.0	2.6	12.18	0.2	0.7	1.97
	429.0	450.0	15800									
7	544.0	575.0	10700	596.0	607.0	1600	16.0	4.6	7.55	0.2	1.1	1.98
	423.0	462.0	15600									

[a] Determined using $\Phi_{\text{fl}} = 0.88$ for Rhodamine 6G in ethanol as the reference.^[22] [b] Fluorescence lifetime. [c] Radiative (k_r) and non-radiative (k_{nr}) rates were calculated using the following equations: $k_r = \Phi_{\text{fl}}/\tau$, $k_{nr} = (1 - \Phi_{\text{fl}})/\tau$, assuming that the emitting state is produced with unit quantum efficiency.

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In CH_2Cl_2 , dyes **3a-d** show emission maximum in the 548–565 nm range with yellow fluorescence (Figure 6, Table 1). More importantly, the fluorescence quantum yields (12–17%) are significantly increased compared to the earlier-reported **B** ($\Phi_f = 0.01$).^[17] This demonstrates the superior photophysical properties of the new ICZ-Imine dyes as compared to the previously reported ICZ-pyridine dyes, one of the primary motivation of the present work. N-substitutions of the dye **3a** with *t*-Boc (**4a-1**) and benzoyl (**4a-2**) blueshifts their emission maximum as compared to **3a** with greenish yellow fluorescence (Figure 6, Table 1).

Dye **5** shows a redshifted emission compared to the parent dyes with orange fluorescence peaking at 590 nm. The -BPh_2 dye, **6** is even more bathochromically shifted with λ_{em} at 606 nm which is 58 nm redshifted as compared to **3a**. The N-*t*-Boc dye **7** displays an intermediate emission, between the one of **5** and **6** (596 nm) and, shows an orange fluorescence (Figure 6). A similar trend was seen in case of -BF_2 dye series as discussed earlier. This clearly revealed that the substitution of the F-groups at the B-atom with the phenyl has significant bathochromic effect on the optical properties of the ICZ-based dye as seen in BODIPY dyes^[19] and indolo-pyridine boron difluoride dyes (IPBD)^[17] previously.

Figure 6. Emission spectra of dyes **3a** (black), **4a-1** (green), **4a-2** (blue), **5** (red), **6** (magenta) and **7** (orange) in CH_2Cl_2 (1.0×10^{-6} M) at 25 °C.

Solvent effect on photophysical properties. The photophysical properties of dyes **3a** and **6** in solvents of different polarities have been checked to assess solvatochromism. It turns out that the photophysical properties of both dyes slightly depend on the dielectric constant of the solvent (Table 2). Interestingly, both dyes show negative solvatochromism, i.e., hypsochromic shift of the absorption maxima with increasing dielectric constant. In case of dye **3a**, λ_{max} in cyclohexane is 525 nm which is blueshifted by 521 cm^{-1} in acetonitrile ($\lambda_{\text{max}} = 511$ nm) (Figure S9). The effect is slightly more pronounced for dye **6** than for dye **3a**: the λ_{max} in acetonitrile (566 nm) is blueshifted by 661 cm^{-1} as compared to that of in cyclohexane (588 nm), see Figure 7 and Table 2. All these properties indicate that the dipole moments of the dyes decrease in the excited state as compared to in ground state which is observed in ab initio calculations (*vide infra*). Interestingly the solvent polarizabilities have no major effect on the fluorescence properties of the dyes (Figures S10-11, Table 2).

Table 2. Effect of the solvent dielectric constant on the photophysical properties of dyes **3a** and **6** as recorded at room temperature.

Solvent	ϵ_s	Dye 3a			Dye 6		
		λ_{max} (nm)	λ_{em} (nm)	ν (cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	ν (cm^{-1})
Cyclohexane	2.02	525.0	551.0	899	588.0	610.0	613
Toluene	2.43	523.0	550.0	939	585.0	610.0	701
Diethyl ether	4.33	522.0	549.0	942	582.0	608.0	735
THF	7.58	519.0	552.0	1152	579.0	609.0	851
DCM	9.02	517.0	549.0	1127	574.0	607.0	947
DCE	10.4	516.0	549.0	1165	572.0	606.0	981
Acetone	21.4	515.0	551.0	1269	571.0	608.0	1066
Acetonitrile	37.5	511.0	551.0	1421	566.0	607.0	1193

Figure 7. Absorption spectra of dye **6** in different polar solvents (1.0×10^{-5} M) at 25 °C.

Photophysical properties in solid state. Solid state absorptions of dyes **3a-d**, **4a-1**, **4a-2**, **5**, **6** and **7** have been recorded in thin films. Due to intermolecular π -stacking, the absorption bands of all dyes are redshifted as compared to CH_2Cl_2 (Table 1, Figure S12-S13). Solid state absorptions of most of the dyes spread over the whole UV-Vis region. Similar trends as the ones previously discussed in solution, can be seen in solid-state, with a bathochromic shift of the BPh_2 dyes with respect to BF_2 dyes and a hypsochromic shift of N-substituted dyes as compared to NH-dyes.

The solid-state fluorescence of the dyes embedded in a KBr matrix [microcrystalline dyes (10^{-6} M) dispersed in KBr pellet by grinding] was investigated as all. Among all, dyes **3a**, **4a-1**, **4a-2**, **4b**, **6** and **7** exhibit the most significant emissions. Some of the non-radiative deactivation pathways, i.e., molecular motion/rotations are inhibited in the solid state, and this could lead to increase the quantum yield in the solid state, whereas other

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non-radiative routes such as excitons or electron-transfer, can, in contrast be detrimental for the emission yields, so that it is hard to *a priori* determine whether the emission yield of a dye will increase or decrease in going from solution to a more static condensed phase. The measured normalized emission spectra and the photographic images of the powdered dyes under UV-light are shown in Figure 8. When one compares the different dyes, a trend alike the one of solution emission is observed in the solid-state although the yields of fluorescence are significantly modified. Dye **3a** shows very weak orange fluorescence ($\lambda_{\text{em}} = 568$ nm; $\Phi = 2.7\%$). N-*t*-Boc protected dye **4a-1** displays slightly blueshifted yellow fluorescence ($\lambda_{\text{em}} = 559$ nm) as compared to **3a**. Interestingly, fluorescence intensity of **4a-1** is enhanced ~ 5 fold as compared to **3a** ($\Phi = 13.0\%$). We explain this as being due to the larger π -plane in dye **3a** which might allow for stronger intermolecular interactions detrimental for fluorescence, whereas in **4a-1** the bulky *t*-Boc groups may hinder the intermolecular interactions which is favourable to obtain brighter emissions.^[23] Dye **4b** also shows yellow fluorescence ($\lambda_{\text{em}} = 568$ nm; $\Phi = 7.1\%$). The fluorescence maxima of **4a-2** is redshifted ($\lambda_{\text{em}} = 575$ nm; $\Phi = 4.4\%$) in the solid state as compared to **3a**. Tentatively, one could suggest that the benzoyl group takes a nearly coplanar arrangement with the ICZ-BF₂ plane which causes the redshift in the solid state. The larger π -plane could cause strong intermolecular interactions and thus reduce the fluorescence of **4a-2**. The fluorescence spectra of BPh₂ dye **6** is strongly redshifted in the solid state with $\lambda_{\text{em}} = 626$ nm; $\Phi = 2.6\%$. The corresponding N-*t*-Boc protected dye **7** has an increase in fluorescence quantum yield with a slight blueshift in λ_{em} (607 nm; $\Phi = 4.6\%$).

Figure 8. (a) Photographic images of the powdered dyes **3a**, **4a-1**, **4a-2**, **4b**, **6** and **7** under UV light ($\lambda = 365$ nm) (top). (b) Solid state spectra of dyes **3a**, **4a-1**, **4a-2**, **4b**, **6** and **7**, embedded in KBr matrix, 10^{-6} M solid solution (bottom).

Theoretical analysis of the photophysical properties. To gain more insights into the photophysical properties of the synthesized dyes, we have performed first principles calculations on all new compounds.^[24] For all derivatives, DFT foresees a nearly planar core for the dye, in line with the available X-Ray data measurements. The N-attached aromatic rings are, in contrast, significantly twisted with dihedral angles in the 42–50° range for **3a**, **3b**, **4a-1**, **4a-2** and **4b**, but significantly larger values in the 65–77° range for **3c**, **3d**, **6** and **7**, which is an obvious consequence of the higher steric hindrance caused by the use of large aromatics (**3c** and **3d**) or the B-attached phenyl rings (**6** and **7**). Eventually, in **5**, the dihedral angle amounts to 19° only, indicating that this dye is much flatter, as expected from its Lewis structure displayed in Scheme 1 and available X-Ray data measurements (Figure 3).

Although comparisons between experimental λ_{abs} and vertical transition energies imply many approximations,^[25] our best estimate for the experimental wavelength (498 nm) of **3a** is in very reasonable agreement with the actual measurements of 516 nm (Table S4). As in the experiment going to **3b**, **3c**, and **3d** only induces trifling changes with estimated absorption wavelengths of 508, 497, and 504 nm, respectively. In contrast, theory returns significant blue shifts for **4a-1**, **4a-2**, and **4b** with vertical wavelengths at 455, 467, and 470 nm, respectively, which is perfectly in line with the experimental trend. Eventually, for **5**, **6**, and **7**, theory returns 532, 567, and 536 nm, respectively, values shifted by +34 nm (**5**) to +69 (**6**) nm, as compared to **3a**, which again compared very favorably with the experimental trends measured in the same solvent (+33 nm for **4** and +58 nm for **5**). This illustrates that the selected protocol is adequate for the investigated compounds. The interested reader will find in the SI, comparisons for emission wavelengths, as well, as for 0-0 energies (Table S4).

The density difference plots obtained for six selected dyes are displayed in Figure 9, the corresponding representation for all systems can be found in Figure S18 in the SI. As can be seen all dyes show excited-state with a π - π^* character, the amino group of the ICZ acting as a donor group (in blue) and the N-aryl atom vicinal to the boron atom has the acceptor group. All dyes are characterized by a quite moderate dipolar CT. Using the well-known Le Bahers' model,^[26] we quantify a CT of 0.5–0.6 e over ca. 1.0–1.5 Å, rather small values. In going from **3a** to **4a-1** or **4a-2**, it is clear in Figure 9, that the donating character of the N atom of the ICZ core decreases, but in the same time, the leftmost phenyl rings of the ICZ moiety starts to play the role of an auxiliary donor group (blue lobes), so that the overall CT effects are similar in all these structures. Note that in **3a**, **4a-1**, and **4a-2**, the *o*-OMe-Ph ring is not directly involved in the transition. In **6** and **7**, the added phenyl rings have no direct impact on the nature of the electronic transition (as expected), and only the reduction of inductive effect as compared to the fluorine atoms is at play. Eventually in the more planar **5**, the “bottom” phenyl ring starts to be partially involved in the transition, although this effect remains moderate, hence explaining the small redshift as compared to **3a**.

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Figure 9. Electron density difference plots (EDD) between the lowest excited state and the ground state. The red (blue) zones indicate increase (decrease) of density upon electronic transition. A contour threshold of 0.001 au was used for all compounds.

For **6**, the experimental evidences show a significant blueshift in increasing the solvent dipolarity (*vide supra*), hinting at a significant decrease of dipole moment between the ground and excited-state upon absorption. We indeed computed μ_{S0} and μ_{S1} of 6.9 and 5.0 D, respectively for the Franck-Condon geometry for dye **6** in DCM, consistent with experimental observations.

Determination of HOMO-LUMO energies by Cyclic voltammetry (CV) and Theoretical Calculations. The oxidation and reduction processes of the dyes **3a-d**, **4a-1**, **4a-2**, **4b**, **5**, **6** and **7** were investigated in CH_2Cl_2 solutions by Cyclic voltammetry (CV). Then the energies of their highest occupied molecular

orbital (HOMO) and lower unoccupied molecular orbital (LUMO) levels were estimated as the measured redox potentials. These potentials were calibrated with respect to ferrocene (Fc), assuming that $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.38 \text{ V}$ referred to SCE (see the SI for experimental details).

At first, dyes, **3a-d** were characterized (Table 3, Figures S14, S15 and S17). The dye **3a** displays two reversible oxidation waves at +0.86 V and +1.34 V which could be assigned to ICZ radical cation and di-cation, respectively. Also, a single reversible reduction wave is observed at -1.51 V for **3a**. In the series **3a-d**, not much change is observed in oxidation and reduction potentials. *t*-Boc protected dyes **4a-1** (Figure S14 and S16) and **4b** (Figure S17) exhibit one oxidation wave each at +1.15 V which is shifted towards higher anodic potential by approximately 0.3 V with respect to that of **3a** and **3b**, respectively. In contrast, they become easily reducible as compared to **3a** and **3b** by approximately 0.1 to 0.15 V. Substitution of benzoyl also shows similar results in case of **4a-2** (Figure S14).

Importantly, replacement of the fluorine atoms on the boron atoms of dye **3a** allowed to tune the dye electrochemical properties. For instance, two reversible oxidation waves are observed at +0.97 V and +0.127 V for dye **5**, while a non-reversible reduction wave is measured at -1.47 V. In case of dye **6**, two reversible oxidation waves are observed at +0.59 V and +0.81 V, while the non-reversible reduction wave is measured at -1.68 V. Both the oxidation and reduction potentials are decreased as compared to the BF_2 derivative **3a**. Such behaviour is well known with the BODIPY dyes.^[19] The *t*-Boc protection of the dye, i.e., dye **7** exhibits one oxidation wave at +0.86 V which is shifted towards higher anodic potential by 0.27 V with respect to that of **6** (Figure S16). In addition, it becomes easily reducible as compared to **6** by 0.10 V. A similar trend is also observed with the BF_2 dyes, **3a-b**. Thus, we stress that the chemistry developed for the synthesis of various ICZ based boron complexes allows really the fine-tuning of electrochemical properties of the dyes.

Table 3. Electrochemical properties and calculated HOMO (seventh column) and LUMO (eighth column) energy levels of **3a-d**, **4a-1**, **4a-2**, **5**, **6** and **7** in CH_2Cl_2 .^[a]

Dye	E _{ox} ^o (V) ^[b]	E _{red} ^o (V)	HOMO-CV (eV) ^[c]	LUMO-CV (eV) ^[c]	Band (eV)	Gap-CV	HOMO-DFT (eV)	LUMO-DFT (eV)	Band (eV)	Gap-DFT
3a	+0.86, +1.34	-1.51	-5.26	-2.89	2.37		-5.18	-2.25	2.93	
3b	+0.88	-1.45	-5.28	-2.95	2.33		-5.12	-2.25	2.87	
3c	+0.92, +1.41	-1.48	-5.32	-2.92	2.40		-5.21	-2.30	2.91	
3d	+0.93, +1.37	-1.40	-5.33	-3.00	2.33		-5.21	-2.31	2.90	
4a-1	+1.15	-1.38	-5.55	-3.02	2.53		-5.36	-2.30	3.06	
4a-2	+1.11	-1.41	-5.51	-2.99	2.52		-5.43	-2.39	3.04	
4b	+1.15, +1.49	-1.34	-5.55	-3.06	2.49		-5.30	-2.29	3.01	
5	+0.97, +1.27	-1.47	-5.37	-2.93	2.44		-5.06	-2.28	2.78	
6	+0.59, +0.81	-1.68	-4.99	-2.72	2.27		-4.85	-2.08	2.77	
7	+0.86	-1.58	-5.26	-2.82	2.44		-5.08	-2.22	2.86	

[a] Cyclic voltammetry was done in deoxygenated CH_2Cl_2 containing TBAPF₆ (0.1 M), and a solute concentration of $1.5 \times 10^{-3} \text{ M}$, at 25 °C. The error in half-wave potentials is $\pm 10 \text{ mV}$. [b] all peaks are reversible. [c] using the formula (HOMO (eV) = $-[E_{\text{onsetox}}(\text{vs SCE}) + 4.4]$) and (LUMO (eV) = $-[E_{\text{onsetred}}(\text{vs SCE}) + 4.4]$) where the onset potentials are in volts (vs SCE).^[27]

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DFT calculations using B3LYP at the 6-31G(d) level in vacuum were carried out to calculate the energies and visualize the topologies of the HOMO and LUMOs of the dyes **3a-d**, **4a-1**, **4a-2**, **5**, **6** and **7** which are shown in Table S5. The calculated HOMO and LUMO as well as the difference between calculated and measured frontier orbitals can be found in Table 3.

In case of **3a** and **3b**, the HOMOs are highly delocalized and spread over the planar ICZ moiety while the LUMOs are shifted towards the B-centre, consistent with the density difference plots described above. The torsion angle between the ICZ moiety and the methoxy-bearing phenyl ring as discussed earlier leads to almost no delocalization of HOMOs and LUMOs on the methoxy-bearing phenyl rings (Table S5). The calculated frontier energy levels of **3a** for the LUMO and HOMO are -2.25 eV and -5.18 eV, respectively with a calculated band-gap of 2.93 eV. The calculated HOMO is similar to the one measured by CV (-5.18 eV by DFT and -5.20 eV by CV) but the calculated LUMO (-2.25 eV) lies almost 0.75 eV above the CV measured one (-2.98 eV). This is consistent with the previous observations for this type of calculations.^[28] The calculated HOMO and LUMO levels of **3b** are similar to that of **3a**, in-line with the HOMO and LUMO levels measured by CV. Unlike **3a** and **3b**, there are no more extension of the frontier energy surfaces on the bottom side of the molecule, neither in **3c** nor in **3d** due to out of the plane aromatic rings.

Insertion of the *t*-Boc group in **3a** and **3b** leads to deeper HOMO and LUMO levels. For both **4a-1** and **4b**, the calculated HOMOs are decreased by 0.18 eV and the calculated LUMOs are deeper by ca. 0.05 eV with respect to their parent dyes. The influence of the *t*-Boc on the HOMO delocalization is clearly seen in the Table S5 which shows that the HOMO does not extend on the right part of the indolo[3,2-*b*]carbazole based boron complex (circled part) when *t*-Boc is present in both **4a-1** and **4b**. The influence of *t*-Boc on the LUMO extension is rather limited (Table S5). The same qualitative effect was also found for **4a-2** in which the benzoyl group replaces *t*-Boc but the changes are more pronounced than in **4a-1** (Table 3).

In case of dye **6**, the ICZ moiety is perfectly planar while the three phenyl groups are almost perpendicular to the ICZ plane making **6** a 3D molecule. This impacts the HOMO and LUMO delocalization that are now almost delocalized on the ICZ and neighbouring ring only. The HOMO remains significantly delocalized and spreads over the planar ICZ moiety with a slight delocalization on the benzene rings linked to B-centre (Table S5) while the LUMO is shifted towards the B-centre with a slight delocalization on the methoxy-bearing benzene ring. The calculated frontier energy levels for the LUMO and HOMO are -2.08 eV and -4.85 eV, respectively with a calculated band-gap of 2.77 eV *i.e.* the HOMO and LUMO levels are deeper in **3a** bearing a BF₂ moiety on the backbone than in **6** with a BPh₂ group. Thus, adding highly electronegative F in the backbone decreases both frontier energy levels. The HOMO is decreased by 0.33 eV and the LUMO by 0.17 eV from **6** to **3a**. In the CV measurements, the substitution of F with phenyls impacts both the HOMO (+0.3 eV) and LUMO (+0.18 eV) in close agreement with DFT calculations (Table 3).

Insertion of the *t*-Boc group leads to a deeper calculated HOMO and LUMO levels. Thus in **7**, the calculated HOMO is deeper by 0.23 eV compared to **6** and the calculated LUMO is deeper by 0.04 eV as compared to **6** (Table 3). This is also in good agreement with the CV measurements with a HOMO downshifted by 0.3 eV and a LUMO deeper by 0.1 eV from **6** to **7**.

Similar conclusions can be reached when comparing **3a** and **4a-1** or **3b** and **4b**.

Charge transport properties.

The charge-carrier mobility in dyes **3a-b**, **4a-1**, **4a-2**, **4b**, **6** and **7** in were calculated from the transfer characteristics of bottom-gate bottom contacts organic field-effect transistors (OFETs) (Table S6). The details of the elaboration procedure can be found in the Supporting Informations. Dyes **3a** and **3b** shows only hole conduction with a hole mobility in the linear regime of $(6 \pm 1) \times 10^{-8} \text{ cm}^2/\text{V.s}$ for the neat dyes. After a 100°C thermal annealing for 10 minutes, the hole-mobility in the linear regime reaches $(2.0 \pm 0.5) \times 10^{-7} \text{ cm}^2/\text{V.s}$ (*i.e.* multiplied by more than 3) before it degrades after a thermal annealing at 120 °C for 10 minutes (Figure S19, S20, S28 and S29).

Insertion of the *t*-Boc group (from **3a** to **4a-1** or from **3b** to **4b**) hardly changes the hole mobilities that remains in the same order of magnitude. Moreover, the hole-mobility increases after annealing at 100°C and then decreases after annealing at 120°C, which was also observed for **4a-1** and **4b** (Table S6, Figure S23, S25, S32 and S34).

Replacing the F atoms by phenyl groups (from **3a** to **6** and from **4a-1** to **7**) has a stronger impact on the charge-transport properties (Table S6, Figure S26, S27, S35 and S36). No transistor characteristics could be measured when dye **7** was used as the OFET channel before a thermal annealing at 150°C for 10 minutes. After such high-temperature treatment, a very small hole-mobility of $(1.0 \pm 0.2) \times 10^{-8} \text{ cm}^2/\text{V.s}$ could be determined from an OFET transfer characteristic (Table S6, Figure S27 and S36). In contrast, dye **6** hole mobility in the linear regime increases from $(5.4 \pm 0.6) \times 10^{-7} \text{ cm}^2/\text{V.s}$ in as-deposited devices to $(6.6 \pm 0.8) \times 10^{-7} \text{ cm}^2/\text{V.s}$ after a (10 minutes, 100°C) thermal treatment and even $(2.0 \pm 0.2) \times 10^{-6} \text{ cm}^2/\text{V.s}$ after an isochronal 120°C thermal annealing (Table S6, Figure S26 and S35). This value remains quite low for an OFET hole mobility.

The highest hole-mobility was measured in dye **4a-2** transistors, *i.e.*, when a benzoyl group replaces *t*-Boc (compared to **4a-1**). Even with a strong contact resistance that tends to underestimate the charge-carrier mobility, a hole mobility in the saturation regime of $(1.6 \pm 0.4) \times 10^{-5} \text{ cm}^2/\text{V.s}$ was measured for dye **4a-2** after thermal annealing at 100°C for 10 minutes (Table S6, Figure S24 and S33). This value remains low for OPV applications but is rather acceptable for OFETs applications highlighting the interest of the dyes synthesized in the present study.

Biological studies.

Potential applications of the new synthesized dyes as cellular imaging agents were investigated. For this, the cellular uptake, subcellular localization, bio-compatibility, and stability of the dyes after internalization into cells were all checked as these are prerequisites for any dyes to be used to cellular imaging.^[29] The toxicity of the dyes (**3a**, **3b**, **3d**, **4a-2**, **5** and **6**) towards cells were checked by viability assays (MTT assay) using Human breast cancer MCF 7 cells. The MTT assay revealed that among all the dyes, **3d** and **4a-2** were non-toxic to cells even at higher concentrations (for **3d**: ~96% viability at 20 µM and for **4a-2**: ~80% viability at 20 µM) (Figure S37). Other dyes showed moderate toxicity towards the MCF 7 cells (~56-77% viability at 20 µM) (Figure S37). Thus, based on this initial results, dyes **3d** and **4a-2** were chosen for further studies.

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Following up with the short term viability assay, long term toxicity of the dyes **3d** and **4a-2** were checked by clonogenic assay which tests the reproductive ability of cells over a longer time period.^[30] For this, reason MCF 7 cells were treated with the dyes **3d** and **4a-2** (10 μ M and 25 μ M) for a period of 12 days and were then analysed for their viability by quantifying the number of colonies formed. If the treatments meted out to the cells are toxic, it would lead to the formation of lesser number of viable colonies in the treated samples as compared to untreated. Interestingly, it was found that both the dyes were non-toxic to cells and there was no significant difference in the number of colonies even after treatment with dyes at 25 μ M (for **3d**: ~90% viable, **4a-2**: ~83% viable w.r.t. untreated samples) (Figure S38). Thus, it was confirmed that both the dyes **3d** and **4a-2** are non-toxic to cells and qualify as dyes for imaging cells.

Next, fluorescence microscopic studies were carried out to investigate the cellular uptake and localization of the two key dyes, **3d** and **4a-2**.^[31] Fluorescence microscopy images obtained showed that the cellular uptake of both the dyes, **3d** and **4a-2** inside the cell was rapid and robust, i.e., within a very short span of time (30 min). Both the dyes exhibited cytoplasmic localization in the cells as revealed from the red fluorescence (Figure 10 and S39, 2nd panel). The images of the cells, stained with the nucleus specific dye, Hoechst 33342 are shown in the 1st panel of the same figures. The merged images (Figure 10 and S39, 3rd panel) clearly revealed that the intra-cellular accumulation of both the dyes were outside the nucleus.

Figure 10. MCF 7 cells were treated with vehicle or dyes, **3d** and **4a-2** (10 μ M) for different time periods (2 h, 4 h, 8 h), stained with Hoechst 33342 and observed under a LSM 780 microscope (Zeiss) under 63X objective. The nucleus appears as blue, whereas the dyes (**3d** and **4a-2**) appeared as red inside the cells. Representative images are shown.

Finally, the time kinetics of the dyes (**3d** and **4a-2**) that is, the leaching out/drop in fluorescence was checked by visualising the retention of dyes after specific time intervals (2 h, 4 h, and 8 h) by fluorescence microscopy (Figure 10). Interestingly, even after 8 h, the dyes were retained in high amounts inside the cells with considerable amounts of residual fluorescence (Figure 10). These confirmed that the dyes are highly stable (low decay rate/degradation) inside the cells with high retention time. Thus,

all these properties are very promising for the dyes to be used as potential cellular imaging agents.

Conclusion

Thus, new chemical methods were developed to synthesize indolo-imine boron difluoride (IIBD) dyes and their corresponding -BPh₂-BOR₂ and N-Boc/N-benzoyl derivatives. Also, a boron substituted asymmetric dye was synthesized from a IIBD dye by BBr₃ mediated reaction. Photophysical and electrochemical properties of the dyes were evaluated which were rationalized by theoretical calculations. The theory restores quite nicely the experimental observations, and explains the negative solvatochromism with small or moderate dipolar charge transfer (CT). Also, the HOMO-LUMO energies measured by CV are in good agreement with the theoretically calculated values. Importantly, their absorbance and fluorescence properties, HOMO-LUMO energies and energy gaps can be tuned over a wide range by structure modulations using the developed chemical route. Finally, charge transport properties of all the dyes were checked which highlighted their usefulness in OFETs applications. Also, cellular studies indicate their potential applications as cellular imaging agents. All these are highlighting the interest of this new class of dyes synthesized in the present study.

Experimental Section

General Procedure for the Synthesis of ICZ-Schiff bases (2a-d). Corresponding aryl amines (1.2 mmol), PTS (cat. Amount) and anhydrous Na₂SO₄ (100 mg) were added to a solution of 12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole-6-carbaldehyde (**1**) (1.0 mmol) in dry DCE (20 mL), and the mixture was stirred at 70 °C for 12 h. The reaction mixture was filtered, concentrated under vacuum, and the residue was subjected to column chromatography (basic alumina, hexane/EtOAc) to furnish the desired Schiff bases **2a-d**.

2a: Schiff base **2a** was prepared by reaction of *o*-anisidine (42 mg, 0.339 mmol) and **1** (100 mg, 0.282 mmol) in 20 mL DCE according to the general procedure. Crude product was purified by column chromatography (basic alumina, hexane/EtOAc, 80:20) to furnish pure **2a** (96 mg, 74%) as red solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.40-1.48 (m, 2H), 1.62-1.68 (m, 2H), 1.95-2.00 (m, 2H), 3.68 (t, *J* = 8.1 Hz, 2H), 4.07 (s, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.21-7.24 (m, 2H), 7.28 (q, *J* = 7.7 Hz, 2H), 7.43-7.49 (m, 2H), 7.58-7.61 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 10.16 (s, 1H), 10.62 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.4, 23.5, 29.9, 32.9, 56.4, 110.7, 112.1, 112.2, 112.9, 119.8, 120.0, 120.7, 120.8, 122.0, 122.4, 123.2, 123.5, 124.5, 125.3, 126.3, 126.7, 127.1, 127.7, 142.7, 158.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₃₁H₂₉N₃O: 460.2389; Found: 460.2343.

2b: Schiff base **2b** was prepared by reaction of *p*-anisidine (42 mg, 0.339 mmol) and **1** (100 mg, 0.282 mmol) in 20 mL DCE according to the general procedure. Crude product was purified by column chromatography (basic alumina, hexane/EtOAc, 80:20) to furnish pure **2b** (92 mg, 71%) as red solid. ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.36-1.43 (m, 2H), 1.56-1.62 (m, 2H), 1.83-1.89 (m, 2H), 3.59 (t, *J* = 7.8 Hz, 2H), 3.84 (s, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.44-7.47 (m, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 9.92 (s, 1H), 11.36 (s, 1H), 11.77 (s, 1H); ¹³C{¹H} NMR

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(125 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.9, 22.2, 28.5, 28.6, 31.5, 55.3, 109.2, 111.2, 111.8, 114.5, 118.5, 119.0, 120.2, 120.7, 121.6, 121.7, 121.8, 122.6, 123.6, 123.9, 125.2, 125.7, 134.0, 134.7, 140.9, 141.5, 144.9, 155.4, 157.8. MS (m/z): 460.2 [M + H]⁺; Anal. calcd. for C₃₁H₂₉N₃O: C, 81.02; H, 6.36; N, 9.14%. Found: C, 80.13; H, 6.50; N, 8.85%.

2c: Schiff base **2c** was prepared by reaction of 1-naphthylamine (49 mg, 0.339 mmol) and **1** (100 mg, 0.282 mmol) in 20 mL DCE according to the general procedure. Crude product was purified by column chromatography (basic alumina, hexane/EtOAc, 80:20) to furnish pure **2c** (55 mg, 41%) as yellow solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.93 (t, J = 7.5 Hz, 3H), 1.45-1.46 (m, 2H), 1.67-1.69 (m, 2H), 2.00-2.02 (m, 2H), 3.71 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.43-7.49 (m, 3H), 7.60-7.66 (m, 4H), 7.83-7.87 (m, 2H), 8.00 (d, J = 7.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 7.0 Hz, 1H), 10.09 (s, 1H), 10.65 (s, 1H), 11.94 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.4, 23.5, 29.5, 29.9, 33.0, 110.6, 112.2, 112.6, 112.7, 114.7, 119.8, 120.2, 120.3, 121.8, 121.9, 123.1, 124.6, 125.1, 126.3, 126.4, 126.7, 126.8, 127.3, 127.5, 128.6, 129.7, 135.1, 136.7, 136.9, 142.3, 142.4, 142.8, 151.4, 159.8. MS (m/z): 480.2 [M + H]⁺; Anal. calcd. for C₃₄H₂₉N₃: C, 85.14; H, 6.09; N, 8.76%. Found: C, 84.95; H, 6.00; N, 8.80%.

2d: Schiff base **2d** was prepared by reaction of 1-aminopyrene (74 mg, 0.339 mmol) and **1** (100 mg, 0.282 mmol) in 20 mL DCE according to the general procedure. Crude product was purified by column chromatography (basic alumina, hexane/EtOAc, 80:20) to furnish pure **2d** (117 mg, 71%) as red solid. ¹H NMR (500 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.89 (t, J = 7.0 Hz, 3H), 1.38-1.42 (m, 2H), 1.57-1.63 (m, 2H), 1.87-1.93 (m, 2H), 3.67 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.47 (q, J = 7.9 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 7.7 Hz, 1H), 8.15 (t, J = 6.8 Hz, 2H), 8.21-8.30 (m, 5H), 8.41-8.46 (m, 2H), 8.79 (d, J = 9.2 Hz, 1H), 10.08 (s, 1H), 11.48 (s, 1H), 11.96 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6 , 25 °C, TMS): δ 14.1, 22.4, 28.7, 28.8, 31.6, 109.8, 111.6, 112.3, 117.1, 118.9, 119.5, 120.6, 121.1, 121.8, 121.9, 122.0, 123.5, 123.9, 124.2, 124.3, 124.7, 124.9, 125.1, 125.4, 125.6, 126.1, 126.4, 126.5, 126.6, 127.3, 127.6, 128.9, 131.2, 131.3, 134.3, 135.3, 141.2, 141.7, 147.2, 159.7. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd. for C₄₀H₃₁N₃: 554.2596; Found: 554.2575.

General Procedure for the synthesis of boron complexes of Schiff bases (3a-d). A mixture of corresponding Schiff base (**2a-d**) (1.0 mmol) and Et₃N (0.18 mL) in dry DCE was stirred for 15 min. Then BF₃·Et₂O (0.12 mL, 1.0 mmol) was added to the mixture and the solution stirred overnight at 70 °C. The resulting dark mixture was washed with aqueous saturated NaHCO₃, water, and brine and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, petroleum ether - EtOAc) furnished the boron complexes **3a-d**.

3a: Dye **3a** was prepared by reaction of **2a** (89 mg, 0.194 mmol), Et₃N (116 mg, 1.160 mmol) and BF₃·Et₂O (161 mg, 1.160 mmol) in 10 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether - EtOAc, 80:20) to furnish pure **3a** (58 mg, 60%) as red solid. ¹H NMR (500 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.88 (t, J = 7.3 Hz, 3H), 1.35-1.43 (m, 2H), 1.55-1.61 (m, 2H), 1.86-1.92 (m, 2H), 3.66 (t, J = 7.6 Hz, 2H), 3.78 (s, 3H), 7.18 (q, J = 7.8 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.48-7.53 (m, 3H), 7.66 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 8.52 (d, J = 8.1 Hz, 1H), 9.68 (s, 1H), 11.83 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.8, 22.2, 28.8, 29.1, 31.4, 56.2, 101.7, 112.0, 113.2, 113.8, 119.1, 119.4, 119.8, 120.3, 120.8, 121.1, 122.2, 122.9, 123.8, 126.0, 126.7, 129.3, 132.0, 134.0, 135.2, 139.7, 140.9, 141.1, 143.3, 153.5, 161.8. MS (m/z): 507.2 [M]⁺; Anal. calcd. for C₃₁H₂₈BF₂N₃O: C, 49.06; H, 3.40; N, 4.97%. Found: C, 48.83; H, 3.52; N, 4.72%.

3b: Dye **3b** was prepared by reaction of **2b** (82 mg, 0.178 mmol), Et₃N (109 mg, 1.070 mmol) and BF₃·Et₂O (150 mg, 1.070 mmol) in 10 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether - EtOAc, 80:20) to furnish pure

3b (58 mg, 64%) as red solid. ¹H NMR (500 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.88 (t, J = 7.5 Hz, 3H), 1.35-1.43 (m, 2H), 1.55-1.61 (m, 2H), 1.86-1.92 (m, 2H), 3.65 (t, J = 7.5 Hz, 2H), 3.87 (s, 3H), 7.17 (d, J = 8.9 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.52 (q, J = 7.6 Hz, 2H), 7.67 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 3H), 8.24 (d, J = 7.9 Hz, 1H), 8.50 (d, J = 8.2 Hz, 1H), 9.63 (s, 1H), 11.79 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.8, 22.1, 28.7, 29.0, 31.4, 55.5, 102.5, 111.8, 113.7, 114.4, 119.1, 119.2, 119.6, 120.9, 121.0, 122.2, 123.3, 123.9, 125.8, 125.9, 126.6, 133.9, 134.7, 137.1, 139.5, 141.1, 143.1, 158.1, 159.0. HRMS (ESI-TOF) m/z: [M - H]⁺ Calcd. for C₃₁H₂₈BF₂N₃O: 506.2215; Found: 506.2243.

3c: Dye **3c** was prepared by reaction of **2c** (55 mg, 0.115 mmol), Et₃N (70 mg, 0.690 mmol) and BF₃·Et₂O (98 mg, 0.690 mmol) in 10 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether - EtOAc, 80:20) to furnish pure **3c** (30 mg, 50%) as red solid. ¹H NMR (500 MHz, DMSO- d_6 , 25 °C, TMS): δ 0.90 (t, J = 7.3 Hz, 3H), 1.38-1.45 (m, 2H), 1.58-1.65 (m, 2H), 1.89-1.96 (m, 2H), 3.69 (t, J = 7.7 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.50-7.54 (m, 2H), 7.60-7.65 (m, 2H), 7.72-7.75 (m, 3H), 7.81 (d, J = 8.5 Hz, 1H), 8.11-8.16 (m, 2H), 8.27 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 9.80 (s, 1H), 11.86 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.8, 22.1, 28.8, 29.1, 31.4, 101.8, 111.9, 113.8, 119.1, 119.2, 119.9, 120.7, 121.2, 122.2, 122.9, 123.1, 123.9, 124.1, 125.2, 126.0, 126.4, 126.7, 127.0, 128.0, 128.4, 129.7, 133.8, 134.0, 135.8, 139.5, 140.1, 141.0, 143.3, 161.5. HRMS (ESI-TOF) m/z: [M - H]⁺ Calcd. for C₃₄H₂₈BF₂N₃: 526.2266; Found: 526.2292.

3d: Dye **3d** was prepared by reaction of **2d** (110 mg, 0.200 mmol), Et₃N (121 mg, 1.200 mmol) and BF₃·Et₂O (169 mg, 1.200 mmol) in 10 mL DCE according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether - EtOAc, 80:20) to furnish pure **3d** (55 mg, 46%) as red solid. ¹H NMR (500 MHz, DMSO- d_6 + CDCl₃, 25 °C, TMS): δ 0.92 (t, J = 7.5 Hz, 3H), 1.41-1.48 (m, 2H), 1.61-1.67 (m, 2H), 1.92-1.99 (m, 2H), 3.69 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 6.8 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 9.3 Hz, 1H), 8.11 (t, J = 7.6 Hz, 1H), 8.15-8.19 (m, 2H), 8.25 (d, J = 7.9 Hz, 1H), 8.27-8.30 (m, 4H), 8.38 (d, J = 7.5 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 9.83 (s, 1H), 11.80 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6 , 25 °C, TMS): δ 13.9, 22.3, 28.9, 29.3, 31.5, 102.1, 112.0, 113.9, 114.0, 119.3, 119.4, 120.8, 121.5, 122.1, 122.4, 123.1, 123.7, 124.1, 124.4, 124.8, 124.9, 125.6, 126.0, 126.2, 126.8, 126.9, 127.2, 128.1, 128.7, 130.4, 130.8, 134.2, 136.1, 137.4, 141.2, 161.9. MS (m/z): 601.2 [M]⁺; Anal. calcd. for C₄₀H₃₀BF₂N₃: C, 79.87; H, 5.03; N, 6.99%. Found: C, 80.04; H, 5.12; N, 7.15%.

General Procedure for BOC protection of boron complexes. (4a-1, 4b and 7). A mixture of corresponding dye (**3a-b** and **6**) (1.0 mmol) and DMAP (1.2 mmol) in dry THF was stirred for 15 min. Then Boc-anhydride (3.0 mmol) was added to the mixture and the solution stirred for 3 h at 25 °C. The resulting mixture was extracted in ethyl acetate, washed with water and brine, and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, petroleum ether - EtOAc) furnished the desired compound **4a-1**, **4b** and **7** respectively.

4a-1: Dye **4a-1** was prepared by reaction of **3a** (52 mg, 0.103 mmol), DMAP (15 mg, 0.123 mmol) and Boc-anhydride (67 mg, 0.31 mmol) in 10 mL THF according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether - EtOAc) to furnish pure **4a-1** (57 mg, 92%) as orange solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.87 (t, J = 7.3 Hz, 3H), 1.35-1.41 (m, 2H), 1.40-1.49 (m, 2H), 1.76 (s, 9H), 1.88-1.92 (m, 2H), 3.72 (t, J = 7.9 Hz, 2H), 3.87 (s, 3H), 7.17 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.38-7.42 (m, 2H), 7.48-7.52 (m, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 9.85 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.3, 23.2, 27.5, 28.2, 29.4, 32.9, 56.7, 85.6, 113.8, 115.3, 116.2, 121.3, 122.3, 123.8, 123.9, 124.8, 125.1, 125.6, 126.5,

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127.4, 127.8, 129.3, 130.5, 133.2, 134.2, 141.2, 142.7, 152.6, 154.5, 163.5. MS (m/z): 607.3 [M]⁺; Anal. calcd. for C₃₆H₃₆BF₂N₃O₃: C, 71.18; H, 5.97; N, 6.92%. Found: C, 71.01; H, 6.31; N, 7.16%.

4b: Dye **4b** was prepared by reaction of **3b** (45 mg, 0.089 mmol), DMAP (13 mg, 0.106 mmol) and Boc-anhydride (58 mg, 0.266 mmol) in 10 mL THF according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether-EtOAc) to furnish pure **4b** (40 mg, 75%) as yellow solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.34-1.39 (m, 2H), 1.42-1.46 (m, 2H), 1.75 (s, 9H), 1.87-1.92 (m, 2H), 3.70 (t, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.38-7.45 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 9.77 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.3, 23.2, 28.3, 32.8, 32.9, 56.1, 85.7, 104.1, 115.3, 115.4, 116.1, 122.3, 123.4, 123.9, 124.3, 124.7, 125.4, 125.8, 126.6, 127.0, 127.4, 129.3, 134.3, 138.6, 140.8, 142.2, 142.8, 145.2, 152.8, 159.8, 161.0. HRMS (ESI-TOF) m/z: [M - F]⁺ Calcd. for C₃₆H₃₆BF₂N₃O₃: 588.2834; Found: 588.2866.

7: Dye **7** was prepared by reaction of **6** (103 mg, 0.165 mmol), DMAP (24 mg, 0.198 mmol) and Boc-anhydride (108 mg, 0.495 mmol) in 10 mL THF according to the general procedure. Crude product was purified by column chromatography (silica gel, petroleum ether-EtOAc) to furnish pure **7** (30 mg, 25%) as red solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.39-1.43 (m, 2H), 1.50-1.53 (m, 2H), 1.76 (s, 9H), 1.92-1.93 (m, 2H), 3.25 (s, 3H), 3.64 (t, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.07-7.16 (m, 7H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.48 (s, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 8.39 (d, *J* = 8.0 Hz, 1H), 9.60 (s, 1H); HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd. for C₄₈H₄₆BN₃O₃: 724.3710; Found: 724.3697.

4a-2: A mixture of corresponding dye **3a** (50 mg, 0.099 mmol) and Et₃N (0.02 mL, 0.134 mmol) in 5 mL dry THF was stirred for 15 min. Then Benzoyl chloride (0.03 mL, 0.296 mmol) was added to the mixture and the solution stirred for 72 hr at 50 °C. The resulting mixture was extracted in ethyl acetate washed with water and brine, and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, petroleum ether -EtOAc) furnished the desired compound **4a-2** (28 mg, 50%) as red solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.23-1.28 (m, 2H), 1.33-1.39 (m, 2H), 1.79-1.85 (m, 2H), 3.39 (t, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.33-7.39 (m, 3H), 7.42-7.45 (m, 1H), 7.50-7.56 (m, 2H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 7.9 Hz, 1H), 9.92 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.2, 22.9, 28.7, 32.4, 32.8, 56.7, 113.8, 114.2, 115.3, 121.3, 122.3, 123.8, 124.1, 124.8, 125.0, 125.7, 127.1, 127.4, 127.9, 128.8, 129.1, 129.3, 129.6, 130.3, 130.4, 130.5, 131.5, 133.2, 133.7, 135.4, 135.5, 135.7, 139.4, 142.8, 154.5, 163.4, 172.3. MS (m/z): 611.3 [M]⁺; Anal. calcd. for C₃₈H₃₂BF₂N₃O₂: C, 74.64; H, 5.27; N, 6.87%. Found: C, 74.39; H, 5.43; N, 6.91%.

6: A mixture of corresponding Schiff base **2a** (213 mg, 0.463 mmol) and BPh₃ (225 mg, 0.926 mmol) in 10 mL dry toluene was stirred overnight at 90 °C. The resulting dark mixture was washed with aqueous saturated NaHCO₃, water and brine, and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, petroleum ether -EtOAc) furnished the boron complex **6** (189 mg, 65%) as red solid. ¹H NMR (500 MHz, (CD₃)₂CO, 25 °C, TMS): δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.44-1.48 (m, 2H), 1.67-1.70 (m, 2H), 1.99-2.02 (m, 2H), 3.24 (s, 3H), 3.65 (t, *J* = 8.5 Hz, 2H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 7.02-7.15 (m, 9H), 7.18-7.21 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.49-7.50 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 8.34 (d, *J* = 8.1 Hz, 1H), 9.49 (s, 1H), 10.82 (s, 1H); ¹³C{¹H} NMR (125 MHz, (CD₃)₂CO, 25 °C, TMS): δ 14.4, 23.5, 30.4, 33.1, 56.2, 104.5, 112.5, 112.6, 113.3, 116.2, 119.7, 120.1, 120.3, 120.9, 121.8, 122.6, 122.7, 123.0,

123.6, 125.0, 125.3, 125.4, 126.6, 127.2, 127.3, 127.4, 127.6, 129.6, 133.8, 134.6, 135.2, 136.5, 141.8, 142.5, 146.0, 154.5, 163.3. MS (m/z): 624.1 [M + H]⁺; Anal. calcd. for C₄₃H₃₈BN₃O: C, 82.82; H, 6.14; N, 6.74%. Found: C, 82.80; H, 6.58; N, 6.39%.

5: A corresponding dye **3a** (150 mg, 0.258 mmol) was dissolved in 10 mL of dry DCE and was cooled down to 0 °C. Then BBr₃ (0.12 mL, 1.290 mmol) was added and the solution stirred overnight at 25 °C. The resulting mixture was extracted in DCM, washed with water, and brine and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, petroleum ether-EtOAc) furnished the desired compound **5** (61 mg, 50%) as red solid. ¹H NMR (500 MHz, DMSO-*d*₆, 80 °C, TMS): δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.34-1.42 (m, 2H), 1.55-1.61 (m, 2H), 1.85-1.91 (m, 2H), 3.63 (t, *J* = 6.3 Hz, 2H), 4.42 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.29-7.36 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.79 (d, *J* = 8.1 Hz, 1H), 9.93 (s, 1H), 11.74 (s, 1H); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆, 80 °C, TMS): δ 13.9, 22.2, 29.0, 29.1, 31.5, 105.4, 111.8, 113.5, 114.0, 116.2, 118.7, 118.9, 119.3, 120.6, 120.8, 121.4, 122.3, 123.1, 124.6, 125.8, 126.5, 129.5, 132.0, 132.8, 134.0, 137.9, 141.0, 144.0, 147.0, 155.8. MS (m/z): 471.3 [M]⁺; Anal. calcd. for C₃₀H₂₆BN₃O₂: C, 76.44; H, 5.56; N, 8.91%. Found: C, 76.31; H, 5.50; N, 8.62%.

Computational Methods. The computational details are described in the SI. For the optical properties, we follow a protocol heavily tested for BODIPY derivatives,^[24] in which the structures are modelled with TD-DFT, and more precisely M06-2X/6-31G(d), the total and transition energies determined with SOS-CIS(D), and the solvent effects are accounted for using the polarizable continuum model. The combination is needed as often TD-DFT is not accurate enough for BODIPY derivatives due to a too large differential electron correlation between the ground and excited states.^[24] For the electrochemical properties, we use a more standard protocol based on the computations of MOs at the B3LYP level.

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Indolo[3,2-*b*]carbazole based Boron Complexes with tunable photophysical and electrochemical properties were synthesized for their application in OFET and Bioimaging.