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Isocyanate-, Isothiocyanate-, Urea-, and Thiourea-Substituted Boron Dipyrromethene Dyes as Fluorescent Probes

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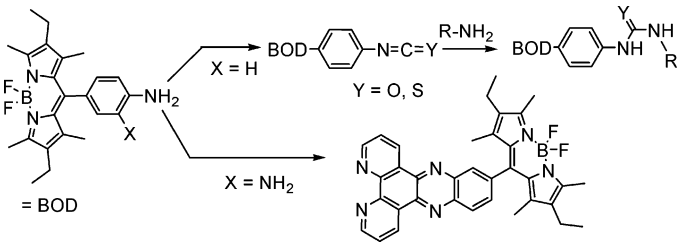

Boron dipyrromethene dyes (Bodipy) bearing a *meso*-phenyl substituent carrying a variety of functional groups can be prepared under mild conditions. A single-crystal X-ray structure determination for the 3,5-dinitrophenyl compound shows the phenyl ring to be almost orthogonal (dihedral angle 84°) to the plane of the Bodipy core, with one nitro group almost coplanar with the ring and the other tilted by ∼21°. Nitro substituents at the 3-, 4-, and 5- positions of the phenyl group are readily reduced to the corresponding amino groups and then converted to isocyanato, isothiocyanato, urea, thiourea, and some polyimine derivatives, the last providing additional functionality (phenazine and pyridylindole units) suitable for chelation of metal ions. All compounds are redox active, the electron-transfer processes being assigned on the basis of comparisons with model compounds. Their fluorescence properties are sensitive to the phenyl group substituents. The Bodipy unit excited state appears to be a strong reductant ($E° \sim -1.4$ V) and a modest oxidant ($E° \sim +1.0$ V). Quenching processes in the nitro and phenazine derivatives appear to involve intramolecular photoinduced electron transfer.

Introduction

The utility of fluorescence for biological and medical analyses stimulates considerable research to improve both the sensitivity and selectivity of appropriate fluorophores. Mapping of both the spatial and temporal distribution of calcium within biological systems is a typical challenge.[1] We and others have previously argued the case that rational modification of known molecules is a field that still retains great promise.[2,3] Binding of the target analyte to a synthetic fluorophore (sensor) can result in either amplification or quenching of the fluorescence but a common instance is that in which photoinduced electron transfer (PET) quenches the luminescence in the absence of the analyte. Analyte binding may then lead to the "switching on" of the emission by inhibition of PET, either because of a direct interaction of the analyte with redox active centers of the sensor or because the binding induces a conformational change which places these centers remote from the emissive site.[4,5] Aromatic amines are good reductants and for this reason have been widely used to provide PET quenching by covalent binding to various fluorophores such as acridine, acridinium,[6] anthracene,[7] phenanthrene,[8]

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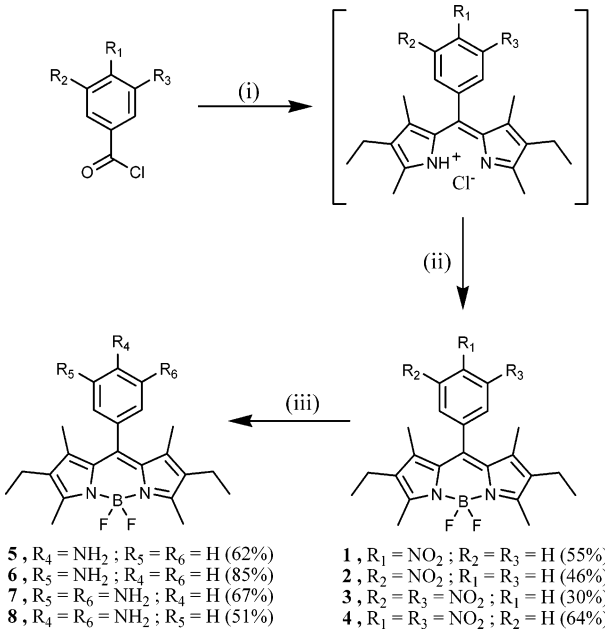
pyrene,[9] and Bodipy dyes.[10,11] These are fluorophores where, in some cases, charge transfer (CT) occurs upon excitation of the fluorophore, leading to emission from a highly polarized CT state in the weak energy domain.[12] In other cases, twisted intramolecular charge transfer (TICT) takes place, leading to unusually long lifetimes of the charge-separated species.[13]

Photoinduced electron-transfer reactions are, of course, at the core of fundamental biochemical processes such as photosynthesis. In Nature, the positioning of the reactants must be such that the electron transfer is unidirectional, facilitated by rigid structures. Many modifications of artificial molecular sensing systems have been engineered, but the simultaneous implementation of urea or thiourea fragments and very efficient fluorophores has not been exploited to a great extent.[14] Recently, preorganized (thio)urea receptors have been designed to complex anions in which the recognition event is driven by multiintramolecular hydrogen bonding.[15]

Difluoroboradiaza-*s*-indacenes, commonly named boron dipyrromethene dyes (*F-Bodipy*),[16] are effective fluorescent probes/sensors and modification of the structure provides new opportunities to vary properties and provide recognition sites for a variety of analytes. These dyes have properties which combine high molar extinction coefficients and high fluorescence quantum yields, strong chemical and photochemical stability in solution and in the solid state, and remarkable electron-transfer properties. Furthermore, the optical properties are sensitive to modifications of the pyrrole core,[17] the central meso position,[18] and the boron substituents.[19] Their current uses include those as chromogenic probes,[20] fluorescent switches,[21] electro-chemiluminescent materials,[22,23] laser dyes,[24] fluorescent labels for biomolecules,[19] drug delivery agents,[25] and as electron-transfer probes for radical ion pairs generated by local electric fields.[26]

SCHEME 1 [a]



5 , $R_4 = NH_2$; $R_5 = R_6 = H$ (62%)
6 , $R_5 = NH_2$; $R_4 = R_6 = H$ (85%)
7 , $R_5 = R_6 = NH_2$; $R_4 = H$ (67%)
8 , $R_4 = R_6 = NH_2$; $R_5 = H$ (51%)

1 , $R_1 = NO_2$; $R_2 = R_3 = H$ (55%)
2 , $R_2 = NO_2$; $R_1 = R_3 = H$ (46%)
3 , $R_2 = R_3 = NO_2$; $R_1 = H$ (30%)
4 , $R_1 = R_3 = NO_2$; $R_2 = H$ (64%)

[a] Key: (i) 2,4-dimethyl-3-ethylpyrrole (2 equiv), CH_2Cl_2, rt, 3 days; (ii) $BF_3{\cdot}Et_2O$ (8 equiv), TEA (6 equiv), rt, 1 day; (iii) H_2 (1 atm), Pd/C 5%, $EtOH/CH_2Cl_2$, rt, 1 day.

Results and Discussion

In the present account, we describe the relatively facile syntheses of nitro- and dinitrophenyl derivatives of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene which can be reduced to the corresponding amines and then converted to a range of new isocyanate, isothiocyanate, urea, thiourea, indole, and dipyrido-[3,2-*a*:2′,3′-*c*]phenazine (dppz) derivatives. "Kryptopyrrole" (2,4-dimethyl-3-ethylpyrrole) was used as the starting material for the three-step synthesis of the desired amino compounds outlined in Scheme 1 because of the known high quantum yield of the resulting Bodipy core.[27] The condensation of kryptopy-

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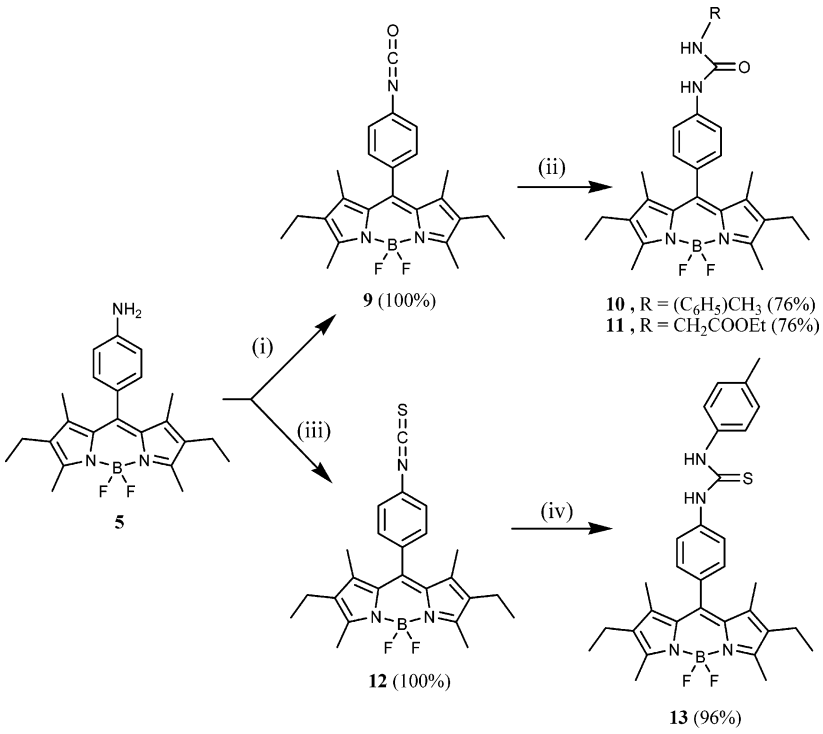
SCHEME 2 [a]



[a] Key: (i) trichloromethyl chloroformate (0.5 equiv), THF, 60 °C, quant; (ii) amine (1 equiv), THF, reflux, 12 h (76%); (iii) thiophosgene, CH_2Cl_2, rt; (iv) tolylamine (1 equiv).

rrole with an acid chloride is straightforward,[28] and the relatively stable dipyrromethene salt can be isolated or directly converted to the desired F-Bodipy core without extensive purification. The second step requires treatment with boron trifluoride etherate in the presence of triethylamine. The nitro substituents were readily reduced to the desired amino groups by catalytic hydrogenation.

The advantages of these procedures lie in the relatively good yields of each step, the use of inexpensive reagents, and the short reaction times required. Highly reactive intermediates causing side reactions appear not to be involved. The overall yields of the amines **5** to **8** lie in the 32−39% range. Similar nitro-functionalized Bodipy dyes derived from knorrpyrrole (2,4-dimethylpyrrole) have been prepared from the corresponding aldehydes, and reduction to the amino group was performed either under acidic conditions with $SnCl_2 \cdot 2H_2O$[29] or with Pd (10%) on charcoal and hydrazine hydrate[30a] or using molecular hydrogen under atmospheric pressure with a palladium-supported catalyst.[30b]

Our initial approach toward the synthesis of urea and thiourea derivatives was based upon reactions of the amines **5**−**8**. Conventional procedures[31,32] (Scheme 2) provided satisfactory yields of the isocyanate **9** and the isothiocyanate **12** from **5**, the IR spectra exhibiting strong $\nu_{N=C=O}$ and $\nu_{N=C=S}$ stretching vibrations at 2256 and 2095 cm^{-1}, respectively.[33a] Test reactions of these materials with primary amines provided urea compounds **10** and **11** and the thiourea **13** in good yields. For **11**, glycinethylester hydrochloride was used and the neutral amino acid was produced in situ by addition of 2 equiv of TEA. These urea and thiourea derivatives show characteristic carbonyl stretching vibrations near 1660 and 1540 cm^{-1}, respectively. The stability of the Bodipy unit under these reaction conditions was demonstrated by the lack of any evidence for displacement of the possibly sensitive BF_2 fragment.

In contrast, all attempts to convert the diamino compound **7** to its diisocyanate failed, and even IR spectroscopy on the reaction mixture in solution provided no evidence for its presence. Addition of primary amines in the hope of trapping the possibly transient diisocyanate provided only intractable mixtures, with some components being highly polar. A simple and effective way of obtaining the desired bis(urea) and bis(thiourea) compounds, however, proved to be the conduct of the reaction in the reverse sense, viz., by reacting the diamine with commercially available isocyanates and isothiocyanates, a procedure which also worked well with the monoamine. Thus, reactions with phenyl isocyanate and phenyl isothiocyanate (Scheme 3) proceed smoothly and in good yield in anhydrous dichloromethane. As expected, all these single and doubly substituted F-Bodipy (thio)urea derivatives are fairly stable in common solvents, even in the light.

Further investigations of the reactivity of the diamine **8** involved its reactions with 1,10-phenanthroline-5,6-dione[34] and

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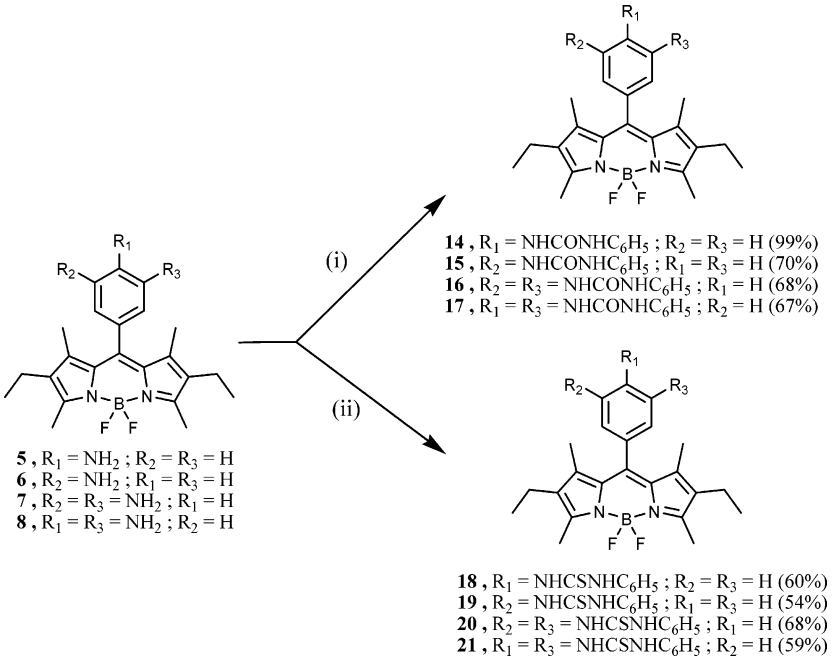
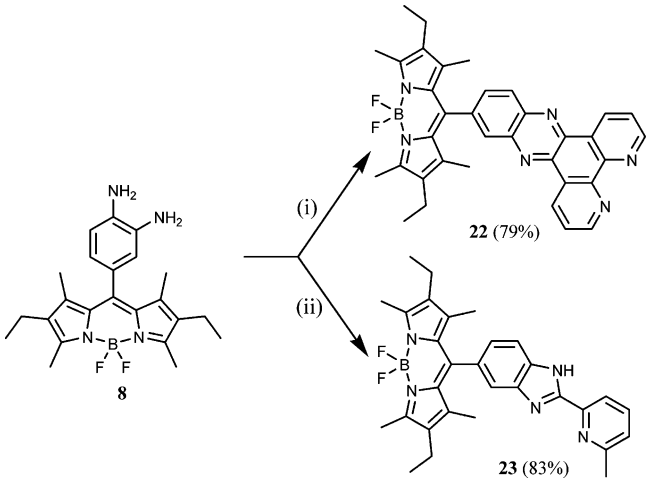
SCHEME 3 [a]



[a] Key: (i) phenyl isocyanate (1 equiv per amino group), CH_2Cl_2, reflux; (ii) phenyl isothiocyanate (1 equiv per amino group), CH_2Cl_2, reflux.

SCHEME 4 [a]



[a] Key: (i) 1,10-phenanthroline-5,6-dione (1 equiv), EtOH, reflux, 15 h; (ii) 6-methylpyridine-2-carboxaldehyde (1 equiv), EtOH, *p*-TsOH (cat.), air, reflux.

6-formyl-2-methylpyridine[35] to give the potential metal chelates[36] **22** and **23**. Good yields were obtained by condensation in hot ethanol (Scheme 4). Reaction with the phenanthroline derivative is relatively slow (15 h reaction time) compared to that with the formylpyridine (<1 h), although isolated yields of the products were acceptable (79% for **22**; 83% for **23**). The reactions are analogous to a recently reported method for the formation of a triazole Bodipy derivative by reaction with nitric oxide, the enhanced fluorescence of the product making the reaction useful for the detection of trace amounts of NO.[37]

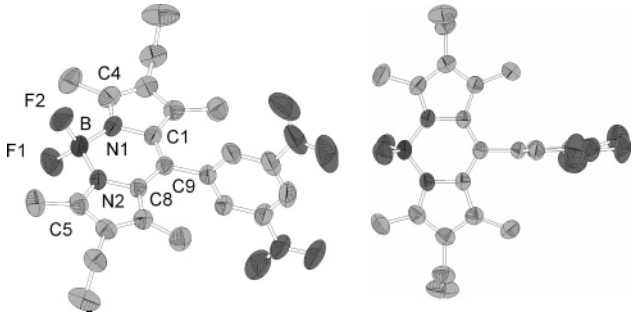


FIGURE 1. Molecular structure of compound **3** with the atom-labeling scheme. Thermal ellipsoids are plotted at the 30% level.

X-ray Structure of Compound 3. The X-ray crystal structure of the dinitro compound **3** has been solved (Figure 1). The molecule adopts approximate but not exact 2-fold rotational symmetry. The central six-membered ring lies coplanar with the adjacent five-membered ring [the maximum deviation from the least-squares mean plane for the 12 atoms of the Bodipy group being −0.041(2) Å]. The Bodipy core including the two pyrrole rings, the four methyl groups and the two methylene carbons is planar [the maximum deviation from the least-squares mean plane for the 19 atoms of the Bodipy group (B, N1, N2, C1A > C1C, C1 > C14) being −0.033(2) Å], while the dinitrobenzene subunit is almost orthogonal, with a dihedral angle of 83.6°. Moreover, the phenyl ring containing the functional reactive amino groups is deviated from planarity of the dipyrromethene core engender the loss of extended conjugation in the synthesized structures. The average B−N and B−F bond lengths are, respectively, around 1.542(3) and 1.384(3)

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TABLE 1. Solution Electrochemical Properties of the Bodipy-Grafted Nitro-, Amino-, Urea-, Thiourea-, and Dipyridinophenazine and Indole Compounds[a]

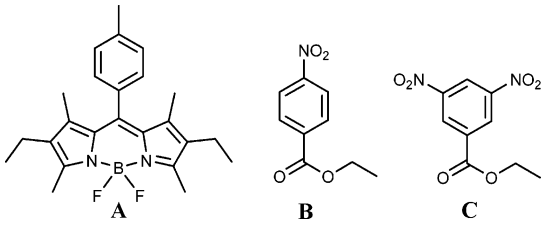
compd	E'°_{ox}, V (ΔE, mV)	E'°_{red}, V (ΔE, mV)
A	+1.11 (60)	−1.26 (70)
1	+1.05 (60)	−1.09 (110); −1.33 (60)
2	+1.05 (60)	−1.10 (110); −1.43 (80)
3	+1.13 (80)	−0.85 (90); −1.27 (90); −1.49 (90)
4	+1.10 (60)	−0.77 (90); −1.16 (90)
B		−1.02 (90); −1.60 (irrev)
C		−0.93 (110); −1.44 (irrev)
5	+0.95 (60)	−1.44 (80)
6	+0.96 (60)	−1.41 (70)
7	+0.98 (irrev.)	−1.42 (70)
8	+0.99 (90)	−1.45 (60)
10	+0.94 (60)	−1.40 (60)
11	+0.93 (60)	−1.41 (60)
13	+0.99 (60)	−1.32 (70)
14	+0.94 (60)	−1.36 (60)
15	+0.94 (60)	−1.35 (60)
16	+0.93 (60)	−1.36 (60)
17	+0.93 (60)	−1.37 (60)
18	+0.99 (60)	−1.31 (60)
19	+0.99 (70)	−1.30 (60)
20	+0.97 (60)	−1.32 (60)
21	+0.98 (60)	−1.31 (60)
22[b]	+1.04 (60)	−1.16 (60); −1.31 (irrev)*
22[c]	+1.04 (60)	−0.94 (60); −1.18 (60)
23[b]	+1.02 (60)	−1.32 (60)

[a] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solutions, containing 0.1 M $TBAPF_6$, at a solute concentration of 1.5×10^{-3} M, at 20 °C. Potentials were standardized using ferrocene (Fc) as internal reference and converted to SCE assuming that $E_{1/2}$ (Fc/Fc^+) = +0.38 V (ΔE_p = 70 mV) vs SCE. Error in half-wave potentials is ±10 mV. Scan rate 100−200 mV/s. When the redox process is irreversible, the peak potentials (E_{ap} or E_{cp}) are quoted. All waves are monoelectronic unless otherwise specified. *This process corresponds to the exchange of about two electrons. [b] Measured in a mixture of anhydrous CH_3CN and CH_2Cl_2 (1/1, v/v). [c] Obtained after addition of 1 equiv of anhydrous $Zn(CF_3SO_3)_2$ as an acetonitrile solution under argon.

Å, and the N1−B−N2, F1−B−F2, N1−B−F2, and N2−B−F1 angles are, respectively, 107.4(2), 110.0(2), 109.8(2), and 109.9(2)°. These observations are in line with previous molecular structures.[38] A point of interest is the pronounced double-bond character for the C4−N1 and C5−N2 bonds [1.349(3) Å], which contrasts with the longer C1−N1 and C8−N2 bond lengths [1.398(2) Å]. Such an observation has also been previously made for similar compounds.[39] One of the two nitro groups is basically coplanar with the phenyl ring (the dihedral angle between the mean planes of the phenyl ring and the nitro group O1−N1A−O2 is 0.91°) whereas the second one is slightly twisted versus the phenyl ring (with a dihedral angle of 20.86°). The lattice shows no significant intermolecular contacts below 4 Å except for short nitro oxygen interactions with carbons (≤2.88 Å).

Electrochemical Properties. The electrochemical properties of the new molecules were determined by cyclic voltammetry in dichloromethane solution. Table 1 lists the potentials (relative to the SCE reference electrode) for the waves that were observed in the +1.6 to −2.0 V window. First, for all of the compounds (except **7**), a single reversible anodic wave was observed in the region between +1.11 and +0.93 V that is due to the (Bodipy/$Bodipy^{+\cdot}$) couple. Note that this wave is less anodic in the amino-, urea-, and thiourea-substituted Bodipy's than in the toluyl reference compound **A** or the dipyridinophenazine **22** or indole **23** derivatives. This probably reflects the fact that the amino-, urea-, thiourea substituents are better electron-donating groups compared to the nitro or the other derivatives. The oxidation of the Bodipy is facilitated by 60 mV in the urea compounds **14**−**17** compared to the thiourea compounds **18**−**21**. There is no indication of oxidation to the ($Bodipy^{2+}$) dication within the given electrochemical window as previously observed for pyridine linked Bodipy's.[11]

CHART 1



A **B** **C**

Without nitro substituents, the reduction of the Bodipy fragment to the radical anion ($Bodipy^{\bullet-}$) was in all cases reversible and more cathodic compared to the toluyl compound **A** (Chart 1). For the amino derivatives **5**−**8**, this reduction is more difficult by at least 140 mV, by 100 mV for the urea, and 50 mV for the thiourea compounds compared to **A**. For compounds **5**−**8** protonation of the amino group obtained by progressive addition of trifluoroacetic acid to the solution does not significantly perturb the redox potentials of the Bodipy fragments. Given the well-known redox activity of nitro groups,[40] it was anticipated that the reduction of the Bodipy to the radical anion would be significantly perturbed. For compounds **1**−**4**, the first reduction is assigned to the nitro group reduction (Figure 2).

There are significant differences in the second reduction potentials depending on the substitution position of the nitro group, and the situation is more complicated when two nitro groups are present. The reference compounds **B** and **C** were used to help the potential assignments. They display two quasireversible cathodic waves likely corresponding to the successive reduction of each nitro group (Figure 3). The presence of a Bodipy fragment in place of the ethyl ester facilitates the reduction of the nitro groups, highlighting the electron-withdrawing effect of the Bodipy moiety.

The second reduction likely corresponds to the reduction of the Bodipy unit to the radical anion. The reduction of the second nitro group is only observed in compound **3,** and the potential at −1.49 V is in keeping with the one determined for **C**. Interestingly, the position of the nitro on the phenyl ring has also a major influence on the reduction potential of the Bodipy. In the 4-position (compd **1**), the reduction of the Bodipy is easier by 100 mV than it is when in the 3-position (compd **2**), whereas the nitro group reduction potentials are similar. With two nitro groups, reduction of both the nitro and Bodipy centers is facilitated: 3,4-disubstitution (compound **4**) decreases the reduction potential by 110 mV compared to 3,5-disubstitution (compound **5**), and reduction of one of the nitro groups is easier by 80 mV.

Finally, the urea derivatives **10**, **11**, and **14**−**17** are easier to oxidize ($\Delta E_{ox} \approx 50$ mV) than the thiourea compounds **13** and

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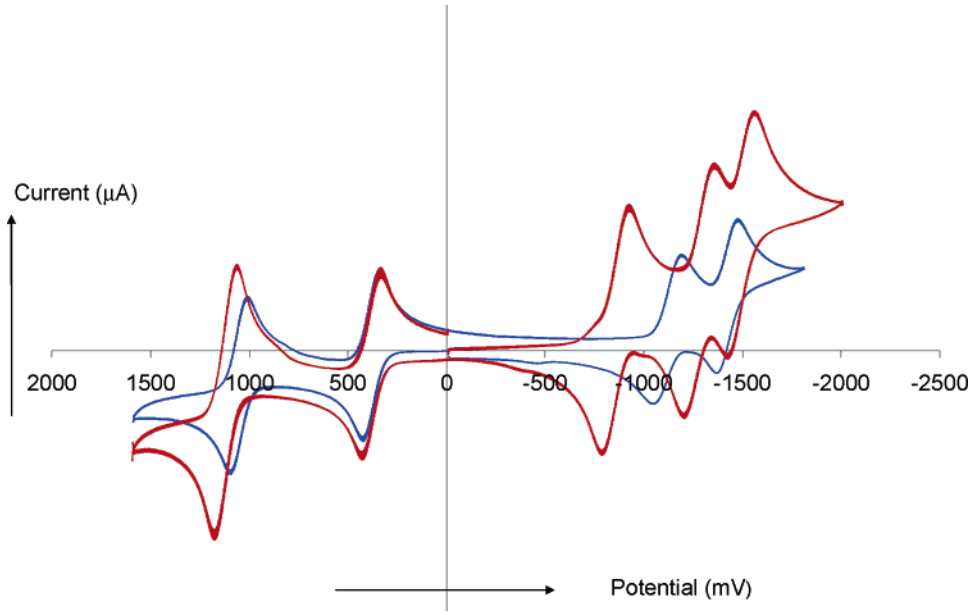

FIGURE 2. Cyclic voltammetry of compounds **2** (blue) and **3** (red) in CH_2Cl_2 at rt using 0.1 M $^nBu_4PF_6$ as supporting electrolyte at a scan rate of 200 mV/s. Ferrocene is used as internal reference at +0.38 V.

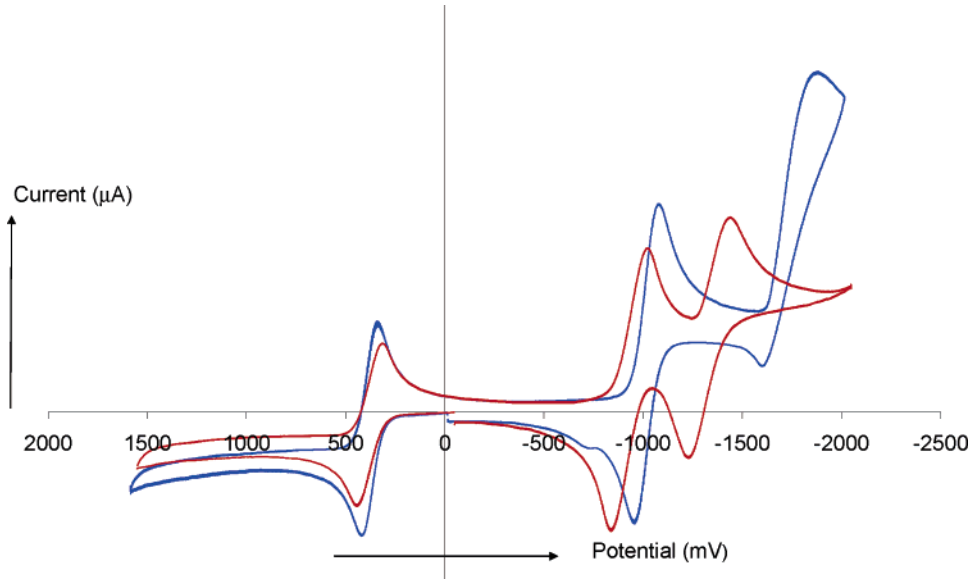

FIGURE 3. Cyclic voltammetry of compounds **B** (blue) and **C** (red) in CH_2Cl_2 at rt using 0.1 M $^nBu_4PF_6$ as supporting electrolyte at a scan rate of 100 mV/s. Ferrocene is used as internal reference at +0.38 V.

18−**21**, whereas the latter are easier to reduce ($\Delta E_{ox} \approx 60$ mV). Note that the LUMO−HOMO gap (at about 2.30 eV) remains similar in both series, as reflected by the constancy of the emission wavelength (vide infra). Changing the substitution position or increasing the number of urea fragments does not significantly change the redox potentials of the concerned fragments (Figure 4).

These observations reflect the different electronic environments of Bodipy and nitro groups and indicate that significant electronic interaction are effective despite the quasi-orthogonality of the Bodipy and phenyl fragments (see the X-ray structure of compound **3** in Figure 1). These results clearly reflect the combined effects of electron withdrawal and charge delocalization and are in keeping with previous observations on related molecules.[38]

For **22**, the anodic envelope around −1.24 V involves an overlap of two reduction processes, as would be expected from the presence of the two redox-active dipyridinophenazine and Bodipy sites. The overlapping could be fortuitous, but no splitting of the wave is observed using anhydrous DMF or CH_2Cl_2 as solvent. The use of a mixture of acetonitrile and dichloromethane enables partial resolution of both signals (Figure 5). By progressive addition of anhydrous $Zn(CF_3SO_3)_2$ or $[Cu(CH_3CN)_4](PF_6)_2$, a new reversible anodic system at −0.94 V grows at the expense of the redox system appearing as a shoulder at −1.16 V. This new wave is attributed to the dipyridinophenazine fragment complexed to the metal. Significantly, on the addition of either Zn(II) or Cu(I) the color of the solution turned deep-red while the oxidation process remained unaffected. Visual observations of metal ion complexation by

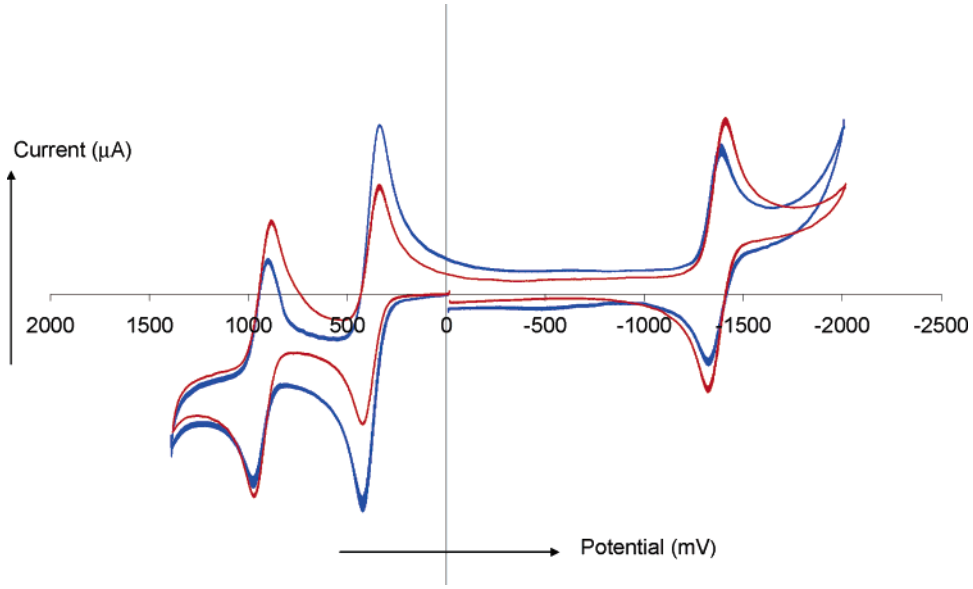

FIGURE 4. Cyclic voltammetry of compounds **15** (blue) and **17** (red) in CH_2Cl_2 at rt using 0.1 M $^nBu_4PF_6$ as supporting electrolyte at a scan rate of 200 mV/s. Ferrocene is used as internal reference at +0.38 V.

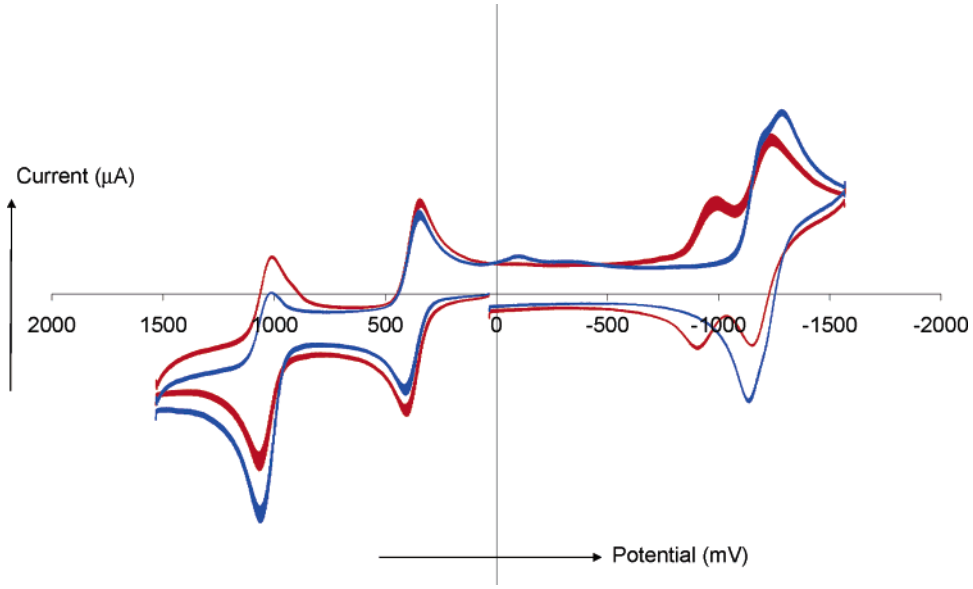

FIGURE 5. Cyclic voltammetry of compounds **22** (blue) and **22/Zn** (red) (stoichiometric amounts) in CH_2Cl_2 at rt using 0.1 M $^nBu_4PF_6$ as supporting electrolyte at a scan rate of 200 mV/s. Ferrocene is used as internal reference at +0.38 V.

similar molecules have been previously applied to the detection of trace environmental levels of transition metals.[18] Another effect of the metal ion binding is to shift the Bodipy reduction wave anodically by 130 mV and render it reversible. Such effects are as expected on the basis of previous observations of polypyridine complexes.[18]

In contrast, for the indole derivative **23** the reversible formation of the Bodipy$^{\bullet+}$ and Bodipy$^{\bullet-}$ are observed at the expected potential range but the addition of metal cations has little effect, indicating that compound **23** is not a good ligand for Zn^{II} or Cu^{I}.

Optical Properties. Spectroscopic data relevant to the present discussion are collected in Table 2. All compounds exhibit absorption patterns that might be considered characteristic of Bodipy fluorophores,[16,17,27,41,42] and prototypical examples are given in Figure S1 (Supporting Information). In solution, the absorption spectrum shows a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition located around 526 nm with extinction coefficients (between 55000 and 87000 M^{-1} cm^{-1}) almost independent of the number and nature of the substituents.

Note that for the nitro compounds **1**−**4**, clear bathochromic shifts in the absorption and emission spectra were observed compared to the other derivatives, likely related to the significant decrease of the LUMO energy level and in line with the electrochemical data. A second weak and broad $S_0 \rightarrow S_2$ ($\pi-$

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TABLE 2. Spectroscopic Data in Dichloromethane Solution at 298 K

compd	λ_{abs} (nm)	ϵ (M^{-1} cm^{-1})	λ_F (nm)	Φ_F[a]	τ_F (ns)	k_r[b] (10^8 s^{-1})	k_{nr}[b] (10^8 s^{-1})	ΔG_{ES}[c] (eV)	$E°$ B*/B•+ [d] (eV)	$E°$ B•−/B* [e] (eV)
1	533	70000	540	0.02	<1					
2	536	72000	544	0.01	<1					
3	536	67000	541	0.01	<1					
4	536	55000	543	0.005	<1					
5	526	71000	536	0.18	9.3	0.19	0.88	2.40	−1.45	0.96
6	524	85000	538	0.42	12.4	0.34	0.47	2.41	−1.45	1.00
7	524	70000	539	0.20	1.1	0.09	9	2.38	−1.40	0.96
8	523	84000	531	0.01	<1					
10	524	87000	540	0.85	4.5	1.80	0.33	2.41	−1.47	1.01
11	524	74000	540	0.83	4.3	1.93	0.39	2.41	−1.48	1.00
13	525	85000	542	0.71	5.6	1.27	0.52	2.38	−1.39	1.06
14	525	88000	541	0.86	6.4	1.34	0.22	2.39	−1.45	1.03
15	525	77000	540	0.86	6.2	1.39	0.22	2.40	−1.46	1.05
16	526	81000	540	0.84	5.5	1.52	0.29	2.40	−1.47	1.04
17	526	78000	541	0.86	7.3	1.18	0.19	2.38	−1.45	1.01
18	526	83000	542	0.73	5.3	1.58	0.51	2.38	−1.39	1.07
19	526	62500	542	0.69	11	0.63	0.28	2.39	−1.40	1.09
20	527	74000	544	0.84	5.6	1.50	0.28	2.38	−1.41	1.06
21	526	84000	540	0.65	4.4	1.48	0.79	2.39	−1.42	1.08
22	529	71500	542	0.01	1.3	0.08	7.6			
23	524	68000	540	0.72	10.6	0.68	0.26	2.40	−1.39	1.08

[a] At a concentration of 5×10^{-7} M using Rhodamine 6G, as reference $\Phi = 0.78$ in water, $\lambda_{exc} = 488$ nm.[46] All Φ_F are corrected for changes in refractive index. [b] Calculated using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1 - \Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency. [c] Excited-state energies were estimated (±5%) by drawing a tangent on the high energy side of the emission. [d] Calculated excited-state oxidation potential vs SCE, $E°(B^+/B^*) = E°(B^+/B) - \Delta G_{ES}$. B = Bodipy. [e] Calculated excited-state reduction potential vs SCE, $E°(B^*/B^{\bullet-}) = E°(B/B^{\bullet-}) + \Delta G_{ES}$.

π^*) transition located at ca. 380 nm was also clearly evident for most of the new species.[43] On the basis of literature data, the peak appearing in the high energy region around 250 nm may be assigned to spin-allowed $\pi-\pi^*$ transitions centered on the phenyl ring of the dye.[44] For the derivatives **22** and **23**, the additional absorption bands around 270 and 370 nm for **22** and around 320 nm for **23** are tentatively assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions involving the dipyridinophenazine and indole sites, respectively (Figure S2. Supporting Information).[45] Finally, no long wavelength charge transfer (CT) absorption bands are observed for these neutral compounds.[12]

With the exception of all nitro, one diamino, and the phenazine compounds, these molecules exhibit strong fluorescence with quantum yields being measured using Rhodamine 6G.[46] The highest quantum yields were found for derivatives **14**−**17**, which have the highest oscillator strength for the corresponding absorption, likely induced by the substitution of the phenyl ring by urea functions. No marked difference in the quantum yield was found by changing the substitution patterns on the phenyl ring (e.g., compare **14** and **15**). The slight decrease in ϕ_{lum} observed for the thiourea derivatives is possibly due to the increase of the rate of nonradiative decay induced by the bulky and electron-rich sulfur atom. The weak Stokes shifts of about 500 cm^{-1} for the series of Bodipy fluorophores are in keeping with a singlet emitting state. Excitation spectra performed under similar conditions perfectly match the absorption spectra (Figures S1 and S2), allowing the conclusion that the emitted light originates from a single excited state with almost no contribution of a possible CT transition, despite the fact that these molecules contain both electron-donating groups such as Bodipy and electron-accepting fragments such as the urea or thiourea fragments. The absence of any significant dynamic quenching of the luminescence by molecular oxygen excludes the presence of an emissive triplet excited state.

Furthermore, the fluorescence decay profiles could be described by a single-exponential fit, with fluorescence lifetimes in the range of 1−12 ns, in accordance with a singlet excited state. In fact, most of the radiative rate constants of 1×10^{-8} s^{-1} are the same within experimental error (Table 2). However, the nonradiative rate constants are significantly higher for compounds **7** and **22** compared to the others, mostly because of the short excited-state lifetime, which may be attributed to the interaction of the emitting state with an energetically low-lying localized state. At this stage of our investigation, we do not have any evidence for the formation of a triplet excited state possibly able to readily quench the fluorescence. In the case of the nitro derivative, an electron-transfer process is likely responsible for the absence of emission. In addition, no significant solvatochromic effect was observed in the absorption and fluorescence spectra, confirming weak polarization of the ground and excited states. More importantly, the fluorescence spectrum shows good mirror symmetry with the lowest energy absorption transition, confirming that these transitions are due to the same state. These photophysical data are in keeping with related functionalized boron dipyrromethene dyes.[10,47]

The weak fluorescence observed for the four nitro compounds and for the dipyridinophenazine derivative could be explained within the framework of a photoinduced electron transfer from the Bodipy excited state toward the nitro or phenazine fragments. In these cases, the Bodipy excited state is a good reductant, with E'^0 (Bodipy*/Bodipy$^{\bullet+}$) around −1.48 V (Table 2). The easy reduction of the nitro groups (Table 1) at reduction potentials around or lower than −1.0 V enables us to make an estimation of the photoinduced electron-transfer driving force (-480 mV $< \Delta G° > -710$ mV). For compound **23**, this driving force is decreased to −160 mV but still efficient quenching is

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observed. For all the others dyes, the absence of the electron accepting group results in efficient fluorescence of the Bodipy fragment.

Concluding Remarks

We have described the synthesis and redox and optical properties of a new class of mono- and disubstituted urea- and thiourea-based fluorescent probes. For the first time, reactive isocyanate and isothiocyanate F-Bodipy-based synthons have been prepared and display a good reactivity toward primary and aromatic amines without any degradation of the Bodipy core. A convenient condensation of the orthodiaminophenyl derivative with dione and formyl compounds readily allows the preparation of dipyridinophenazine and indole ligands. A strong electronic transition located about 530 nm is responsible for the very efficient fluorescence emission, reaching 86% in the best cases. For the nitro- and dipyridinophenazine compounds, the fluorescence is efficiently quenched owing to an intramolecular electron-transfer process from the F-Bodipy excited state to the nitro electron-accepting unit. The driving force is of the order of −710 mV in the case of compound **4**. Consideration of electrochemical and optical properties allows the conclusion that the Bodipy excited state is a good reductant and a modest oxidant. Coordination of zinc(II) cation to the dipyridinophenazine ligand results in resolution of the two cathodic processes due to successive reduction of the complexed phenanthroline fragment and the F-Bodipy core.

Taken together, these findings establish that these neutral and stable materials exhibit bipolar character and might behave as exciton carriers in optoelectronic devices. Ongoing efforts are focused on the use of these interesting isocyanate and isothiocyanate compounds in materials science for the engineering of block copolymers,[48] silica nanoparticles,[49] and derivatization of macrostructures.[50] The attachment of these dyes to the entry of zeolite nanochannels for directional energy transfer is currently in progress.

Experimental Section

General Procedure A for the Synthesis of Nitrobenzeneboradiazaindacene Derivatives. To a solution of 2,4-dimethyl-3-ethylpyrrole (2 equiv) in anhydrous dichloromethane was added the aroyl chloride (1 equiv). The solution was stirred at room temperature during 4 days, the color changing slowly from pale brown to deep red. Triethylamine (6 equiv) was then added (yellow brown solution), followed by a subsequent addition of boron trifluoride etherate (8 equiv) (purple solution). The mixture was stirred for 1 day at rt and then was washed 3 times with saturated aqueous $NaHCO_3$. The organic layer was then dried over $MgSO_4$ and filtered and the solvent removed. Chromatography on silica gel gave the pure compounds. Additional purification is performed routinely by recrystallization in adequate solvents.

4,4-Difluoro-8-(3-nitrophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 2. Prepared according to general procedure A using 3-nitrobenzoyl chloride (0.31 mL, 2.7 mmol), 2,4-dimethyl-3-ethylpyrrole (0.73 mL, 5.39 mmol) in anhydrous CH_2Cl_2 (50 mL), triethylamine (2.3 mL, 16.2 mmol), and $BF_3{\cdot}Et_2O$ (2.7 mL, 21.5 mmol). Chromatography (silica gel, CH_2Cl_2/cyclohexane 50:50 to 100:0). Recrystallization in CH_2Cl_2/hexane afforded the desired compound as a purple powder (0.511 g, 46%), mp 240−242 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.39−8.35 (m, 1H), 8.23−8.22 (m, 1H), 7.74−7.65 (m, 2H), 2.54 (s, 6H), 2.3 (q, 4H, ^3J = 7.5 Hz), 1.25 (s, 6H), 0.98 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 155.2, 148.8, 137.8, 136.4, 135.0, 133.7, 130.5, 130.4, 124.1, 124.0, 17.2, 14.7, 12.8, 12.3. ^{11}B NMR ($CDCl_3$, 128 MHz): δ (ppm) = 3.82 (t, ^1J = 32 Hz). IR (KBr, cm^{-1}): ν = 2963, 2928, 2872, 1594, 1537 s, 1429 s, 1347, 1321, 1189 s, 1116, 1084, 980. UV−vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 530 (72000), 499 (sh, 23600), 382 (8000), 262 (13000). FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 426.2 ([M + H]$^+$, 100), 406.2 ([M − F]$^+$, 30). Anal. Calcd for $C_{23}H_{26}BF_2N_3O_2$: C, 64.96; H, 6.16; N, 9.88. Found: C, 64.74; H, 5.83; N, 9.55.

4,4-Difluoro-8-(3,4-dinitrophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 4. In a flame-dried Schlenk flask, under argon, to a stirred solution of 3,4-dinitrobenzoic acid (1 g, 4.7 mmol) in anhydrous CH_2Cl_2 (30 mL) were added oxalyl chloride (0.8 mL, 9.4 mmol) and three drops of distilled pyridine. The colorless solution, which slowly became turbid, was stirred overnight at room temperature. The excess oxalyl chloride and the solvent were then evaporated under vacuum, and 30 mL of freshly distilled CH_2Cl_2 was added. The solution was then tranferred via cannula to a stirred degassed solution of 2,4-dimethyl-3-ethylpyrrole (1.3 mL, 9.4 mmol) in 30 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred for 4 days at room temperature and progressively turned from pale brown to deep red in color. Triethylamine (4 mL, 28.3 mmol) was then added, and the solution turned brown. After 10 min, $BF_3{\cdot}Et_2O$ (4.8 mL, 37.7 mmol) was added and the reaction mixture turned purple. After being stirred for 24 h at room temperature, it was washed with three portions of saturated aqueous $NaHCO_3$ (3 × 40 mL). The organic layer was then dried over $MgSO_4$ and filtered and the solvent evaporated. The crude product was purified by chromatography on a column packed with flash silica gel, using CH_2Cl_2/cyclohexane (30:70 to 100:0) as eluent. Recrystallization in CH_2Cl_2/hexane afforded the desired compound as a purple powder (1.411 g, 64%), mp 228−230 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.12 (d, 1H, ^3J = 8.1 Hz), 7.90 (d, 1H, ^3J = 1.7 Hz), 7.76 (dd, 1H, ^3J = 8.1 Hz, ^4J = 1.7 Hz), 2.54 (s, 6H), 2.32 (q, 4H, ^3J = 7.5 Hz), 1.33 (s, 6H), 1.00 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 156.3, 143.7, 142.8, 142.4, 137.2, 134.3, 133.9, 133.4, 129.9, 126.0, 125.8, 17.2, 14.6, 12.8, 12.7. ^{11}B NMR ($CDCl_3$, 128 MHz): δ (ppm) = 3.72 (t, ^1J = 32 Hz). IR (KBr, cm^{-1}): ν = 2973, 2964, 2929, 1543 s, 1473 s, 1421 s, 1190 s, 1080, 979. UV−vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 536 (55000), 504 (sh, 21000), 386 (7500), 262 (14000). FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 471.2 ([M + H]$^+$, 100), 424.1 ([M − NO$_2$]$^+$, 35). Anal. Calcd for $C_{23}H_{25}BF_2N_4O_4$: C, 58.74; H, 5.36; N, 11.91. Found: C, 58.51; H, 4.95; N, 11.62.

General Procedure B for the Reduction of the Nitrobenzene−Bodipy. To a stirred, degassed CH_2Cl_2/EtOH (20 mL/20 mL) solution of nitrophenyl−Bodipy (1 equiv) was added under argon Pd/C 5% (5% mol.). The reaction mixture was stirred under H_2 (atmospheric pressure) until total consumption of the starting material was observed by TLC (SiO_2, CH_2Cl_2). After 24 h, the solution was then filtered through Celite, and the solvents were evaporated. The crude product was purified by chromatography. Additional purification is performed routinely by recrystallization in adequate solvents.

4,4-Difluoro-8-(3-aminophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 6. Prepared according to general procedure B: **2** (0.400 g, 0.89 mmol), Pd/C 5% (0.100 g). Chromatography (silica gel, CH_2Cl_2/cyclohexane 80:20 to 100:0). Recrystallization in CH_2Cl_2/hexane gave the title compound as an orange powder (0.317 g, 85%), mp 291−293 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.28−7.23 (m, 1H), 6.80−6.61 (m, 3H),

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3.78 (br s, 2H), 2.54 (s, 6H), 2.33 (q, 4H, ^3J = 7.5 Hz), 1.44 (s, 6H), 1.01 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.6, 147.3, 140.7, 138.6, 136.9, 132.7, 130.8, 130.1, 118.4, 115.3, 114.7, 17.2, 14.8, 12.6, 11.7. ^{11}B NMR ($CDCl_3$, 128 MHz): δ (ppm) = 3.86 (t, ^1J = 32 Hz). IR (KBr, cm^{-1}): ν = 3370, 2965, 2924, 2871, 1601 s, 1537 s, 1450 s, 1317, 1190 s, 1062, 978. UV−Vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 524 (85000), 491 (sh, 25000), 376 (8000), 287 (7000). FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 396.2 ([M + H]$^+$, 100), 376.2 ([M − F]$^+$, 30). Anal. Calcd for $C_{23}H_{28}BF_2N_3 \cdot {}^1/_2H_2O$: C, 68.33; H, 7.23; N, 10.39. Found: C, 68.40; H, 6.82; N, 10.38.

4,4-Difluoro-8-(4-isocyanatophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 9. In a round-bottomed flask, under argon, trichloromethyl chloroformate (0.014 mL, 0.12 mmol) was added to a stirred solution of **5** (0.092 g, 0.23 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred at room temperature during 45 min and then heated at 60 °C during 30 min. The solvent was then evaporated, and the resulting isocyanate was used without further purification (0.098 g, 100%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.23 (m, 4H), 2.53 (s, 6H), 2.30 (q, 4H, ^3J = 7.5 Hz), 1.31 (s, 6H), 0.98 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.3, 138.9, 138.2, 134.3, 133.6, 133.2, 130.9, 130.0, 129.7, 125.6, 17.2, 14.7, 12.7, 12.0. IR (KBr, cm^{-1}): ν = 3410, 2957, 2927, 2864, 2256 s, 1779, 1534 s, 1471 s, 1312 s, 1184 s, 1112, 1051 s, 974 s.

4,4-Difluoro-8-(4-isothiocyanatophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 12. In a round-bottomed flask, under argon, was added dropwise a solution of thiophosgen (0.013 mL, 0.18 mmol) in distilled CH_2Cl_2 (5 mL) to a solution of **5** (0.05 g, 0.13 mmol) in anhydrous CH_2Cl_2/NEt_3 (20 mL/0.2 mL) maintained at 0 °C. As soon as total consumption of the starting materiel was observed by TLC (one spot, about 5 min), the reaction was quenched with water (10 mL). The organic layer was then washed with water (3 × 20 mL), dried over anhydrous $MgSO_4$, and filtered, and the were solvents evaporated. The residue was then passed through a very short pad of silica gel and the resulting isothiocyanate used without further purification for the following reaction (0.055 g, 100%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.32 (m, 4H), 2.53 (s, 6H), 2.30 (q, 4H, ^3J = 7.5 Hz), 1.30 (s, 6H), 0.98 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.5, 138.4, 138.1, 137.2, 135.1, 133.3, 132.3, 130.7, 130.1, 126.5, 17.2, 14.7, 12.7, 12.1. IR (KBr, cm^{-1}): ν = 2962, 2929, 2867, 2095 s, 1743, 1546, 1470, 1316, 1259 s 1186, 1018 s, 975, 799 s.

General Procedure C: For the Synthesis of Urea or Thiourea with Phenyl Isocyanate or Isothiocyanate. In a flame-dried Schlenk flask, under argon, to a stirred solution of aminophenyl-Bodipy (1 equiv) in anhydrous CH_2Cl_2/CH_3CN (3 mL/3 mL) was added phenyl iso(thio)cyanate (1.5 equiv per amino group). The reaction mixture was stirred under reflux until complete consumption of the starting material was observed by TLC. Water was then added, and the solution was extracted with CH_2Cl_2. The organic layer was dried on $MgSO_4$ and filtered, and the solvents were evaporated. Purification was performed by chromatography. Additional purification is performed routinely by recrystallization in adequate solvents.

4,4-Difluoro-8-(3-phenylureaphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 15. Prepared according to general procedure C using **6** (0.05 g, 0.13 mmol) and phenyl isocyanate (0.19 mmol, 0.02 mL). Chromatography (silica gel, CH_2Cl_2/cyclohexane, 80:20 to 100:0). Recrystallization in CH_2Cl_2/hexane afforded the desired compound as a red powder (0.045 g, 70%), mp >150 °C dec. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.65 (m, 1H), 7.43−7.30 (m, 5H), 7.15−7.08 (m, 2H), 6.99−6.94 (m, 1H), 6.88 (s, br, 1H), 6.73 (s, br, 1H), 2.52 (s, 6H), 2.28 (q, 4H, ^3J = 7.5 Hz), 1.34 (s, 6H), 0.97 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.9, 152.9, 139.6, 139.5, 138.6, 137.9, 136.7, 133.0, 130.8, 130.1, 129.6, 129.5, 124.8, 124.7, 123.4, 121.6, 120.1, 119.5, 17.2, 14.7, 12.7, 11.9. IR (KBr, cm^{-1}): ν = 3399, 2959, 2925, 2868, 1646, 1599, 1538 s, 1474 s, 1441 s, 1310, 1191 s, 1062, 976. UV−vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 525 (77000), 493 (sh, 24000), 376 (9000), 251 (42000). FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 515.1 ([M + H]$^+$, 100), 495.1 ([M − F]$^+$, 20). Anal. Calcd for $C_{30}H_{33}BF_2N_4O$: C, 70.04; H, 6.47; N, 10.89. Found: C, 69.69; H, 6.12; N, 10.65.

4,4-Difluoro-8-(dipyrido[3,2-*a*:2′,3′-*c*]phenazin-11-yl)phenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 22. To a solution of **8** (0.05 g, 0.12 mmol) in EtOH (15 mL) was added 1,10-phenanthroline-5,6-dione (0.026 g, 0.12 mmol). The reaction mixture was refluxed during 15 h, and after cooling, the red precipitate was filtered and washed with three portions of EtOH (3 × 5 mL). The analytically pure compound was recovered as a red powder (0.056 g, 79%), mp> 280 °C dec. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 9.71−9.62 (m, 2H), 9.31−9.28 (m, 2H), 8.53 (d, 1H, ^3J = 8.7 Hz), 8.37 (d, 1H, ^4J = 1.3 Hz), 7.88−7.79 (m, 3H), 2.57 (s, 6H), 2.29 (q, 4H, ^3J = 7.5 Hz), 1.25 (s, 6H), 0.97 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.7, 153.1, 148.78, 148.76, 142.3, 142.23, 142.22, 142.1, 138.5, 138.1, 138.0, 134.1, 134.0, 133.4, 131.4, 130.7, 129.6, 127.54, 127.49, 124.44, 17.2, 14.7, 12.7, 12.3. ^{11}B NMR ($CDCl_3$, 128 MHz): δ (ppm) = 3.93 (t, ^1J = 32 Hz). IR (KBr, cm^{-1}): ν = 1541 s, 1475 s, 1442 s, 1404 s, 1320, 1190 s, 1115, 1071, 979. UV−vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 529 (71500), 496 (sh, 24000), 384 (32000), 365 (27000), 294 (31000), 270 (74000). FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 585.2 ([M + H]$^+$, 100), 565.2 ([M − F]$^+$, 35). Anal. Calcd for $C_{35}H_{31}BF_2N_6$: C, 71.92; H, 5.35; N, 14.38. Found: C, 71.78; H, 5.29; N, 14.22.

4,4-Difluoro-8-(1*H*-benzimidazole-2-(6-methyl-2-pyridinyl)-5-yl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene 23. To a solution of **8** (0.100 g, 0.24 mmol) in EtOH (20 mL) were added 6-methylpyridine-2-carboxaldehyde (0.03 g, 0.25 mmol) and *p*-toluenesulfonic acid (10% mol., 0.005 g). The reaction mixture was heated under reflux while air was bubbled through the solution. After 1 h, total consumption of the starting material was observed. After cooling, the solution was washed with water (3 × 10 mL), the organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel (CH_2Cl_2/cyclohexane 80:20 to 100:0, then CH_2Cl_2/MeOH 100:0 to 98:2), followed by recrystallization in CH_2Cl_2/hexane, afforded the desired compound as a red powder (0.103 g, 83%), mp > 291 °C dec. ^{1}H NMR (CD_3OD, 300 MHz): δ (ppm) = 8.14 (d, 1H, ^3J = 8.1 Hz), 7.90−7.84 (m, 2H), 7.60 (s, br, 1H), 7.39 (d, 1H, ^3J = 7.5 Hz), 7.24 (d, 1H, ^3J = 7.9 Hz), 2.67 (s, 3H), 2.50 (s, 6H), 2.35 (q, 4H, ^3J = 7.5 Hz), 1.30 (s, 6H), 0.99 (t, 6H, ^3J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 158.5, 153.8, 153.6, 152.4, 147.2, 145.1, 144.9, 138.7, 137.6, 134.1, 133.9, 132.9, 131.5, 131.4, 130.2, 124.7, 124.2, 123.2, 121.0, 120.2, 118.8, 112.1, 111.3, 24.6, 17.2, 14.8, 12.6, 11.9. ^{11}B NMR ($CDCl_3$, 128 MHz): δ (ppm) = 3.93 (t, ^1J = 32 Hz); IR (KBr, cm^{-1}): ν = 3436, 2960, 2925, 2853, 1597, 1541, 1434 s, 1320, 1191, 1115, 1082, 980. FAB$^+$-MS *m*/*z* (nature of peak, relative intensity): 512.2 ([M + H]$^+$, 100). UV−vis (CH_2Cl_2) λ (nm) (ϵ, M^{-1} cm^{-1}) = 524 (68000), 494 (sh, 21600), 371 (10500), 316 (28000). Anal. Calcd for $C_{30}H_{31}BF_2N_5$: C, 70.46; H, 6.31; N, 13.69. Found: C, 70.33; H, 6.28; N, 13.57.

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Supporting Information Available: General experimental procedure, reagents, materials, and experimental details for compounds **1**, **3**, **5**, **7**, **8**, **10**, **11**, **13**, **14**, and **16**−**21**. Detailed X-ray crystal structure determination and geometrical parameters (Table S1) for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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