Synthesis, properties and reactivity of BCl_2 aza-BODIPY complexes and salts of the aza-dipyrrinato scaffold

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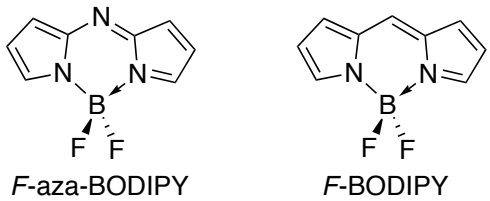
Abstract

The synthesis and characterisation of the BCl_2-chelated complexes of both archetypal aza-dipyrrin sub-types are presented. A stepwise halogen exchange, leading to a mixed-halide Cl-B-F intermediate, is implicated in the conversion of *F*-aza-BODIPYs to *Cl*-aza-BODIPYs upon treatment with BCl_3. The utility of the *Cl*-aza-BODIPY scaffold to facilitate substitutions at boron is demonstrated under mild conditions through treatment with aryl Grignard reagents. Additionally, the lability of the B-Cl bond enables facile removal of the BCl_2 group, i.e. deprotection of *F*-aza-BODIPYs, under aqueous conditions. Three aza-dipyrrin HX salts were also synthesised and characterised. The pK_a of the protonated aza-dipyrrin was determined to be 4, thereby providing insight regarding the storage and stability of such species.

Introduction

Aza-dipyrrins are a family of fully conjugated, strongly chromophoric heterocyclic compounds consisting of two pyrrolic units bridged by an imino-type nitrogen atom. They are formally related to the well-known dipyrrin (dipyrromethene) skeleton through replacement of the bridging nitrogen with a carbon-based substituent (Figure 1). Aza-dipyrrins and their coordination complexes, particularly the BF_2-chelated *F*-aza-BODIPYs (Figure 1, left), are of interest due to their remarkable red and near-infrared absorption and emission profiles, very high extinction coefficients, and excellent photostability. *F*-aza-BODIPYs are consequently attractive for use in photovoltaics,[1, 2] biological imaging,[3-7] and photodynamic therapy.[3] Synthetic routes[8] toward aza-dipyrrins produce two structural supertypes: a tetra-aryl variant, constructed via the condensation of an ammonia source and 4-nitro-1,3-diarylbutanones [or the condensation of an appropriate 2-nitrogen substituted pyrrole (amino, nitroso) with a pyrrole unsubstituted at the 2-position],[8] and a fused-ring variant typically made using aryl Grignard reagents and aromatic dinitriles along with an ammonia source.[8, 9] Given the constraints of these synthetic approaches, the range of substituents that can be introduced onto the aza-dipyrrin core is limited. Post-modification of the boron center thus provides an attractive approach to modifying the photophysical and chemical properties of aza-BODIPYs. Some such modifications on *F*-aza-BODIPYs have been reported, but most involve harsh conditions or bespoke substrates.[6, 8, 10, 11]



F-aza-BODIPY *F*-BODIPY

Figure 1. Scaffold of *F*-aza-BODIPY (left) and *F*-BODIPY (right).

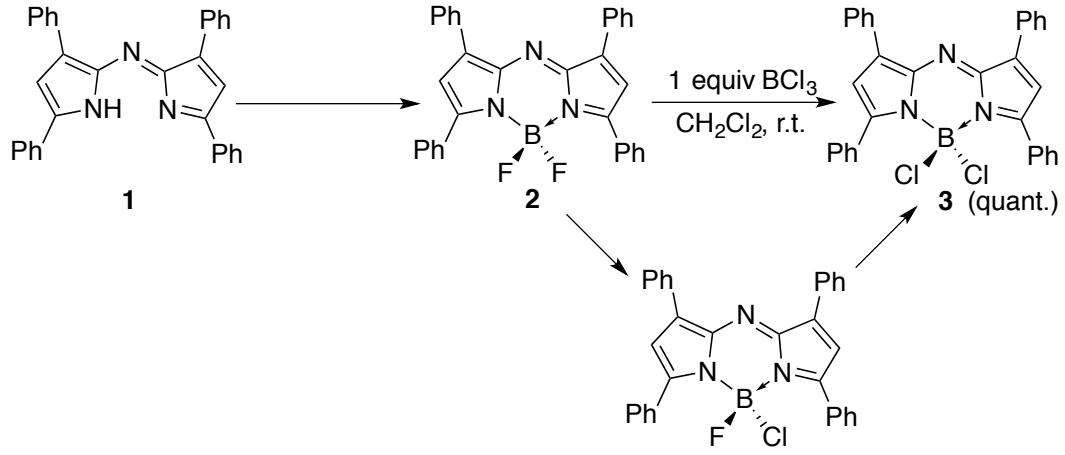
We hypothesised that *Cl*-aza-BODIPYs would present opportunities to introduce substituents at boron via reaction with nucleophiles. Indeed the weaker B–Cl bond of Cl-aza-BODIPYs cf. the B–F bond of *F*-aza-BODIPYs should enable facile substitution under mild conditions.[12] To the best of our knowledge, only one *Cl*-aza-BODIPY has been reported, an unisolated intermediate en route to an exotic aza-BODIPY construct featuring alkynylferrocene on boron.[9] Herein we synthesise, isolate and characterise the *Cl*-aza-BODIPYs of both archetypal aza-dipyrrin subtypes, and study the utility of the *Cl*-aza-BODIPY intermediate to facilitate substitutions at boron via reaction with Grignard reagents. In the course of this work, we also prepare the first series of HX salts of aza-dipyrrins.

Results & Discussion

Tetraphenyl *Cl*-aza-BODIPY. Tetraphenyl *F*-aza-BODIPY **2**[5] features the tetra-aryl substitution pattern representative of this class of aza-dipyrrin ligand (Scheme 1). A solution of **2** in anhydrous dichloromethane was treated with 1 equiv boron trichloride (as a 1.0 M solution in dichloromethane). Upon addition, the colour of the solution changed immediately from the characteristic teal of **2** to a deep ultramarine blue. The solution was stirred for twenty minutes at room temperature, and the solvent then removed *in vacuo* to provide *Cl*-aza-BODIPY **3** as an iridescent blue residue in quantitative yield. As shown in Figure 2 (bottom), the ^{11}B NMR spectrum of the starting *F*-aza-BODIPY **2** reveals a triplet arising from ^{11}B coupling to the two fluoro substituents. The ^{11}B NMR spectrum of the *Cl*-aza-BODIPY **3** features a singlet shifted downfield cf. the fluorinated starting material (Figure 2, top). Interestingly, the ^{11}B NMR spectrum after the addition of 0.5 equiv BCl_3 to a solution of **2** in chloroform-d, followed by removal of volatiles and remaining BCl_3 and then redissolution in chloroform-d, revealed unconverted starting material along with a broad doublet (*ca*. 48 Hz coupling constant; Figure 2, middle) that is presumably due

to formation of a mixed halide intermediate, i.e. Cl-B-F complex (Scheme 1). Evidence of this mixed halide suggests step-wise halogen exchange and that, for this aza-dipyrrinato framework, the initial halogen exchange is fast. Using ^{19}F NMR spectroscopy to concurrently monitor the reaction of **2** with 0.5 equiv BCl_3 reveals a new, low-intensity quartet 7 ppm upfield of the starting material with the same 48 Hz coupling constant as observed in the ^{11}B NMR spectrum (Figure S1 in the Supplementary Information), further supporting the presence of the mixed halide Cl-B-F intermediate. Similar observations have been reported in the ^{19}F NMR spectra of F-B-CN aza-BODIPYs.[13] Addition of the remaining 0.5 equiv BCl_3 to the reaction mixture resulted in complete conversion to the *Cl*-aza-BODIPY **3**, as indicated by the presence of a singlet as the only ^{11}B resonance. As expected, all ^{19}F signals disappeared upon the addition of 1 equiv BCl_3. In contrast, our work with *meso*-carbon *F*-BODIPYs[12] showed that treatment with 0.5 equiv BCl_3 produced 50% yield of the corresponding *Cl*-BODIPY and enabled 50% recovery of the starting *F*-BODIPY. Presumably, in the case of the dipyrrinato framework, the second halogen exchange proceeds faster than the first. Clearly the aza-dipyrrinato framework is susceptible towards halogen exchange at boron, although the mechanistic pathway through which this occurs differs from that involving BODIPYs.

Scheme 1. Preparation of Cl-aza-BODIPY **3** via BCl_3-mediated halogen exchange of *F*-aza-BODIPY **2**



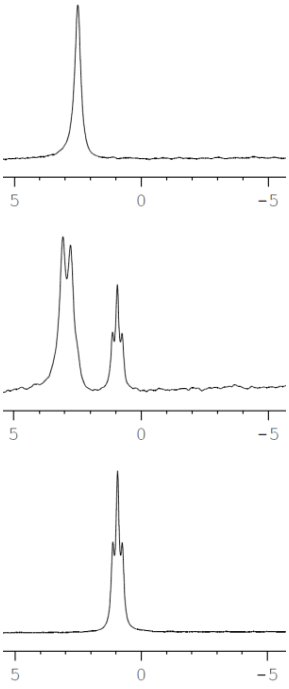
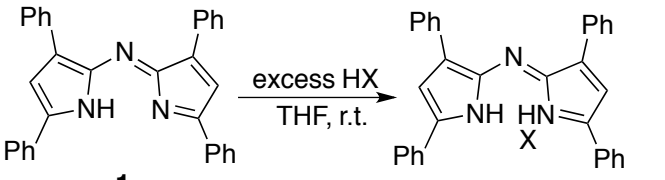


Figure 2. ^{11}B NMR spectra upon the addition of BCl_3 to a solution of **2** in chloroform-d; 0 equiv BCl_3 (bottom), 0.5 equiv BCl_3 (middle) and 1 equiv BCl_3 (top).

Salts of tetraphenyl aza-dipyrrin. *Cl*-aza-BODIPY **3** was found to be unstable. When exposed to air, the decomposition of a solution of **3** in chloroform-d was monitored using ^1H NMR

spectroscopy (see Figure S2 in the Supplementary Information). *Cl*-aza-BODIPY **3** completely decomposed after three days of exposure to air (with periodic agitation), with the onset of decomposition occurring after one hour. Two notable new signals appeared in the ^{1}H NMR spectrum over time: a broad singlet at 14.4 ppm, and a narrow doublet at 8.5 ppm. The intensity of the characteristic singlet in the ^{11}B spectrum fell to zero as the decomposition progressed. The singlet at 14.4 ppm in the ^{1}H NMR of the decomposition product integrated to 2H and is reminiscent of the pyrrolic N-H signal, which is typically suppressed in the ^{1}H NMR spectrum of the parent aza-dipyrrin **1** due to intramolecular hydrogen bonding. However, protonation of the Lewis basic nitrogen atom of the aza-dipyrrin would remove this intramolecular contact and reveal the two N-H resonances for the corresponding cation. Given this, and our observed lability of the BCl_2 chelate, we hypothesised the decomposition product to be the hydrochloride salt of **1**. To date, only one aza-dipyrrin salt has been reported. However, this salt was produced in only 32% yield.[14] In contrast, the HX salts of *meso*-carbon dipyrrins are well known: they are easily handled, crystalline derivatives that impart enhanced stability and are vital to the storage and manipulation of dipyrrins. Despite this utility, the analogous aza-dipyrrin salts have not been studied.

Scheme 2. Protonation of aza-dipyrrin **1** to yield **1HX** salts



1

1HCl, X = Cl, 92%
1HBr, X = Br, 80%
1HBF$_4$, X = BF_4, 88%

With evidence in hand for **1HCl** being formed as the decomposition product of **3** in air, we embarked upon the synthesis of a series of **1HX** salts via protonation of free-base aza-dipyrrins using excess concentrated acid (Scheme 2). In each case, protonation of **1** afforded an obvious and immediate colour change from dark blue/purple to an intense dark green. After treatment of **1** with hydrochloric acid, the proton spectrum of the resultant hydrochloride salt (**1HCl**) featured a broad, highly deshielded 2H singlet, consistent with protonation at nitrogen (Figure 3). It is of note that the chemical shift of this peak is unaffected by concentration, whereas the chemical shifts of charged N-H resonances often vary substantially with concentration and solvent. There is also a simplification of the signals in the aromatic region upon protonation, as shown in Figure S3 of the Supplementary Information. This is consistent with an increase in molecular symmetry upon protonation.[15] Furthermore, the ^{1}H NMR spectrum of **1HCl** matched that of the decomposition product of **3**, confirming that the *Cl*-aza-BODIPY decomposes to the dipyrrin hydrochloride salt upon exposure to air. Two further salts were synthesised via treatment of **1** with hydrobromic (**1HBr**) and hydrofluoroboric (**1HBF$_4$**) acids. Crystal structures of the three salts of **1** are included and discussed in the Supplementary Information.

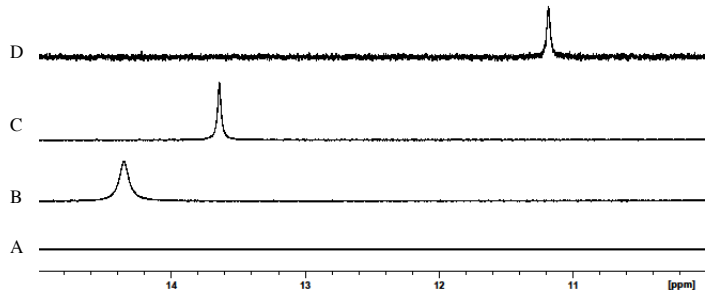


Figure 3. Low-field region of ^{1}H NMR spectra showing the N-H resonances of aza-dipyrrin **3** and three HX salts (A) **1**, no observable resonances; (B) **1HCl**; (C) **1HBr**; and (D) **1HBF$_4$**.

To further investigate the properties of the aza-dipyrrin salts, protonation was monitored using UV-visible spectroscopy. Aza-dipyrrin **1** was titrated with HBr to yield **1HBr**, whereupon

protonation was accompanied by a substantial bathochromic shift of 28 nm (Figure 4). For comparison, complexation of an aza-dipyrrin with BF_2 to give the aza-BODIPY typically results in a *ca*. 50 nm red-shift in absorbance. Titrations with other strong acids (including HCl, HBF_4, CF_3COOH, and H_2SO_4) revealed that the bathochromic shift observed upon protonation was independent of anion. Treatment of **1** with benzoic or tartaric acids failed to protonate the aza-dipyrrin, and treatment of any salt of **1** with water regenerated the free-base aza-dipyrrin thereby implicating **1HX** salts as weak acids. Indeed, the titration curves presented in Figure 4 enabled an apparent pK_a of 4.03 to be determined for **1HBr**,[16] thereby supporting the experimental observations regarding protonation.

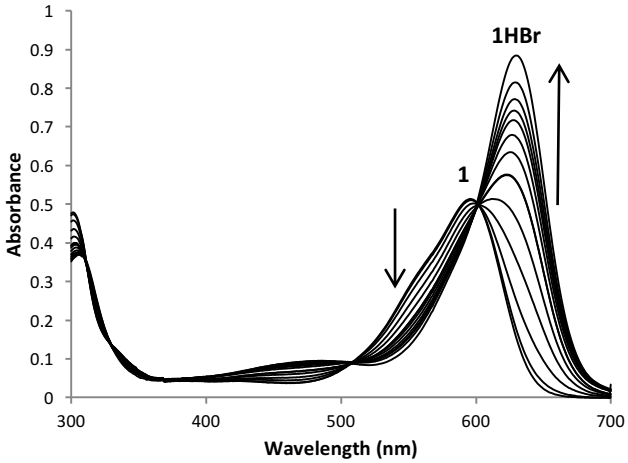
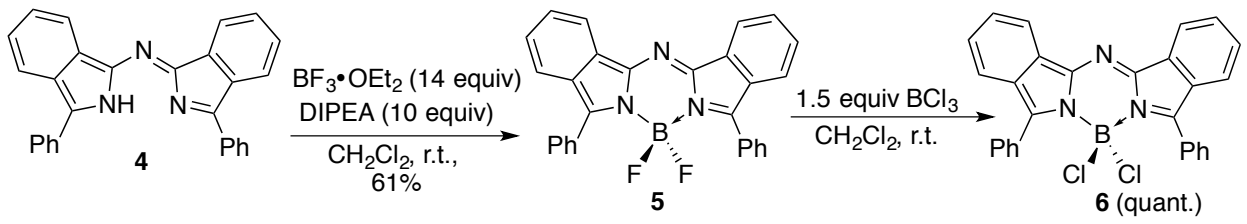


Figure 4. Spectrophotometric titration of a 0.1 mM solution of **1** in tetrahydrofuran acidified using a 7.0 mM solution of HBr in tetrahydrofuran. As the concentration of HBr increases, the peak at 630 nm increases in intensity while the peak at 598 nm decreases in intensity. λ_{max} of **1** = 598 nm and λ_{max} of **1HBr** = 630 nm. Note the two isosbestic points at 507 nm and 600 nm.

Benzannulated *Cl*-aza-BODIPY. With the tetraphenyl-substituted *Cl*-aza-BODIPY **3** synthesised and characterised, we turned our attention to the ring-fused subtype of aza-dipyrrins. Treatment of **4** with BF_3 gave *F*-aza-BODIPY **5**. Treatment of a solution of **5** in anhydrous

dichloromethane with 1 equiv boron trichloride (Scheme 3), as for **2**, caused an almost imperceptible lightening of the intense forest green color of the starting material, but afforded only 75% conversion to the corresponding *Cl*-aza-BODIPY **6** according to analysis using ^{11}B NMR spectroscopy. The course of the reaction was monitored via integration of the signals in the corresponding ^{11}B NMR spectrum (Figure 5): 25% conversion to **6** was achieved upon the addition of 0.5 equiv BCl_3; addition of 1 equiv BCl_3 resulted in 75% conersion; and complete conversion was achieved upon treatment of **5** with 1.5 equiv BCl_3. As for the conversion of **2** to **3**, a new doublet was observed after the addition of 0.5 equiv BCl_3 to **5**. This doublet persisted after the addition of 1 equiv BCl_3, accompanied by similar transient signals in the corresponding ^{19}F NMR spectra. These results again suggest the formation of a Cl-B-F complex as an intermediate. Studies of B,N-chelated BODIPYs[17] indicate that more strongly electron-withdrawing substituents are needed to stabilise the boron center, and our recent classification of the relative donor strengths of dipyrrins and aza-dipyrrins[18] shows that aza-dipyrrin **4** is a significantly poorer donor than **1**. This suggests that the boron chelate of **5** is more stabilised than that of **2**, hence the need for excess BCl_3 in order to drive the halogen exchange to completion. Compound **6** gave crystals of sufficient quality for X-ray analysis, the first reported crystal structure of a *Cl*-aza-BODIPY (see Supplementary Information).

Scheme 3. Preparation of *Cl*-aza-BODIPY **6** via BCl_3-mediated halogen exchange of *F*-aza-BODIPY **5**.



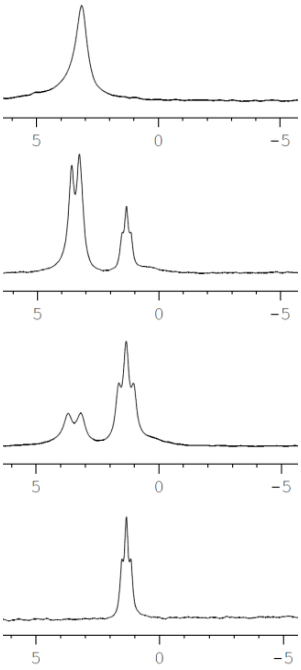
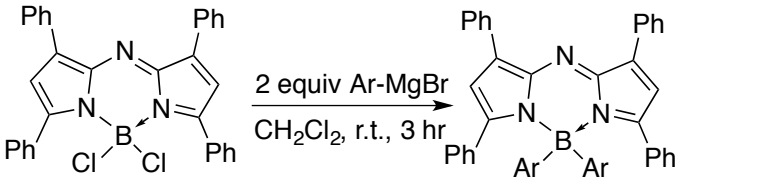


Figure 5. ^{11}B NMR spectra upon the addition of BCl_3 to a solution of **5** in CD_2Cl_2 (from bottom to top): 0 equiv, 0.5 equiv, 1 equiv, and 1.5 equiv

Functionalisation at boron. With a reliable route to *Cl*-aza-BODIPYS in hand, we investigated their susceptibility to nucleophilic substitution, using aryl Grignard reagents as model nucleophiles. In a one-pot procedure, **2** was converted to **3** via BCl_3-mediated halogen exchange and consequent removal of volatile materials. Once re-dissolved, Cl-aza-BODIPY **3** was treated with nucleophile to form B-functionalised products **7a-7c** (Scheme 4). **7a** is a known compound, typically accessed via treatment of F-aza-BODIPYs with excess Grignard reagent (3 equiv) in tetrahydrofuran at reflux temperature.[9] However, this method produces a slew of by-products that are difficult to separate via chromatography. In contrast, treatment of *Cl*-aza-BODIPY **3** with stoichiometric Grignard reagent at room temperature generated **7a-c** with the only byproduct being **1**, a remarkable improvement. Some care must be taken when handling **7a**, as it is not stable to silica or acidic conditions <pH 2.[10] Especially noteworthy is the high-yielding synthesis of **7c** using

this method, with no purification required. The ^{11}B chemical shift of this species (-2.56 ppm) falls within the range observed for dithienylboryl BODIPYs,[19] which substantially differs from any of the other species in the current study.

Scheme 4. Treatment of *Cl*-aza-BODIPY **3** with aryl Grignard reagents.



3

7a, Ar = Ph (53%)
7b, Ar = 2-naphthyl (37%)
7c, Ar = 2-thienyl (97%)

It is critical to note that addition of a nucleophile immediately after in situ formation of the *Cl*-aza-BODIPY **3** from **2** failed to effect *B*-substitution, instead returning either **2** or the parent free-base (i.e. deborylated) dipyrrin **1**. Removal of the solvent and re-dissolution in fresh solvent before adding the nucleophile is essential for substitution to proceed. To elucidate this behaviour, **3** was prepared again using a solution of **2** in chloroform-d, and an aliquot of the reaction mixture was analysed. The solvent was subsequently removed, then the residue re-dissolved in fresh chloroform-d and again analysed. Figure 6 shows the presence of four signals in the ^{11}B spectrum before removal of the solvent, one of which is the singlet expected of **3**: after the solvent is removed, only this singlet remains in the spectrum. This observation supports the postulate that reactive by-products remain dissolved until the solvent is removed and given that the *F*-aza-BODIPY was regenerated in some cases, one of these by-products is likely BF_2Cl. Thus, removal of the solvent and any such by-products is critical to quenching the halogen exchange reaction and achieving full conversion to the desired *Cl*-aza-BODIPY, a step not required in the synthesis of *meso*-carbon *Cl*-BODIPYs.

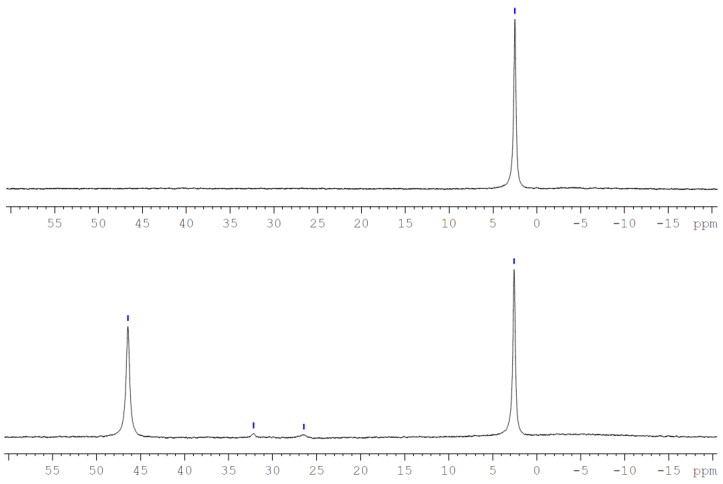
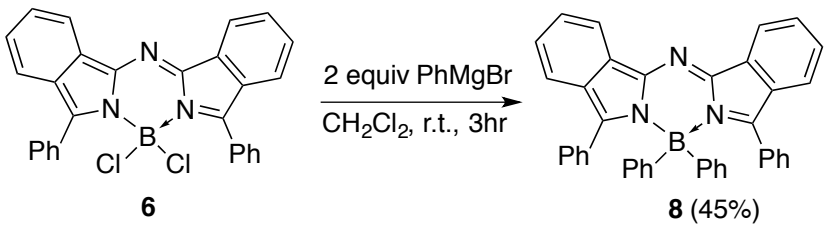


Figure 6. ^{11}B NMR spectra of the reaction mixture for formation of **3** before (bottom) and after (top) removal of the solvent.

B-functionalisation of the benzannulated system was also achieved via this method (Scheme 5). Treatment of a solution of **5** in CH_2Cl_2 with BCl_3, followed by removal of solvent, redissolution in CH_2Cl_2, and treatment with phenylmagnesium bromide afforded the diphenylboryl aza-BODIPY **8** in moderate yield. As with the preparation of **7a**, the only observed by-product was the parent free-base aza-dipyrrin, thus enabling facile purification. Treatment of either **3** or **6** with vinyl Grignard reagent led to a trace of the desired product alongside bulk decomposition, while treatment with methyl or ethyl Grignard reagents led only to decomposition of the aza-dipyrrinato unit.

Scheme 5. Synthesis of diphenylboryl benzannulated aza-BODIPY **8** via *Cl*-aza-BODIPY **6**.



6 **8** (45%)

The photophysical properties of the compounds synthesised in this work were examined. Table 1 contains spectrophotometric characterisation data for all aza-dipyrrins and aza-BODIPYs discussed herein. Complexation of the aza-dipyrrins **1** and **4** to form *F*-aza-BODIPYs **2** and **5**, respectively, leads to a substantial narrowing of the absorbance curves as expected for a molecule with such high symmetry, and a red shift in absorbance of ca. 60 nm. The addition of BCl_3 to **2** causes a loss of the distinctive greenish hue, which is reflected in the slight blue shift and curve broadening that accompanies its conversion to **3**. Other than a corresponding broadening of the emission curve and a loss of fluorescence quantum yield attributable to the heavy atom effect of chlorine, the fluorescence profiles of **2** and **3** are very similar, with virtually identical maxima. This translates to an increased Stokes shift for **3**. However, the addition of BCl_3 to **5** produces only a very slight color change that amounts to a lightening of the shade of green of the solution. This is again reflected in the spectra, with **6** having absorption and emission maxima only slightly red-shifted and broadened *cf*. those of **5**.

Substituting phenyl on boron such as in compound **7a** leads to a comparatively large hypsochromic shift of 35 nm compared to the analogous substitution of **2**. This substitution also effectively nullifies the fluorescence of the compound, as expected.[10] This loss of quantum yield can be attributed to efficient non-radiative relaxation pathways offered by the free rotation of the many phenyl groups on a compound such as **7a**, particularly of the β-phenyl moieties.[20] Virtually identical results follow for compounds **7b** and **7c** bearing other arenes (2-naphthyl and 2-thienyl, respectively) on boron. Substituting phenyl on boron for the benzannulated aza-BODIPY **5** yields **8**. The incorporation of the phenyl groups of **8**, which is an emerald green color in solution, results in a hypsochromic shift of 39 nm compared to **5**: the absorbance curve of **8** is sharp with a noticeable shoulder centered around 630 nm.

Table 1. Photophysical properties of solutions of aza-dipyrrin derivatives in toluene

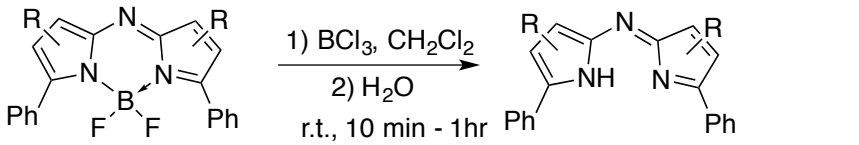
Compound	λ_{abs} (nm)	ε (log E)	Fwhm (nm)	λ_{em} (nm)	Stokes Shift (nm)	Φ[a]
1	599	4.39	74	N.f.	N.f.	N.f.
2	654	4.96	46	677	23	0.32
3	649	4.74	55	676	27	0.12
4	656	4.43	80	N.f.[c]	N.f.[c]	N.f.[c]
5	715	4.79	46	726	11	[d]
6	719	4.74	52	729	10	[b]
7a	619	4.62	63	658	39	[b]
7b	617	4.61	65	658	41	[b]
7c	622	4.75	61	659	37	[b]
8	676	4.89	38	694	18	[b]

[a]relative to 3,3'-diethylthiadicarbocyanine iodide in dichloromethane (Φ = 0.35);[21] [b]so weakly emissive that the quantum yield could not be accurately measured (Φ < 0.01); [c]N.f. = Not fluorescent at the wavelengths available for evaluation using our instrumentation; [d]not determined.

Aza-BODIPY deprotection. Finally, deliberate deborylation of the aza-BODIPY unit was attempted using a procedure based on our previous work[22] involving *Cl*-BODIPY derivatives of meso-carbon dipyrrins. There are two variants of the deborylation scheme. The first uses boron trifluoride diethyl etherate as a Lewis acid to activate the *F*-BODIPY BF_2 group, which becomes labile in the presence of ≤3 equiv of water. The second involves forming the *Cl*-BODIPY then dissolving it in a solution of 10% water in acetone to remove the BX_2 moiety. The former method is entirely ineffective on these *F*-aza-BODIPYs; no reaction occurred and the starting materials **2** and **5** were returned unchanged. Conversely, the latter method works well for these compounds.

Indeed, subjecting **2** to 1 equiv BCl_3, followed by excess water, gave the free aza-dipyrrin **1** in quantitative yield after ten minutes of stirring, with no purification required (Scheme 6). This contrasts with the results for *meso*-carbon BODIPYs, which return their hydrochloride salts under the same conditions. This result is rationalised given the low pK_a of **1HCl** and the comparatively large amount of water present. The same procedure was attempted using F-aza-BODIPY **5**. However, the *Cl*-aza-BODIPY **6** is insufficiently soluble in the acetone/water mixture: however, an alternative mixture using tetrahydrofuran as the organic component improved the solubility. The progression of the reaction was noted to be very dissimilar to the tetraphenyl analogue. Indeed, after ten minutes of stirring, the desired product was apparent in trace amounts. After fifteen minutes, the solution began to rapidly change color, culminating after one hour with the light blue characteristic of **4**. Although conversion was not quantitative, chromatographic separation to isolate the aza-dipyrrin **4** was facile.

Scheme 6. Deborylation of *F*-aza-BODIPYs via *Cl*-aza-BODIPY intermediate.



1, R = Ph, quant.
4, R = benzannulated, 53%

Conclusions

Cl-aza-BODIPYs of the two major classes of aza-dipyrrinato ligand were prepared via treatment of F-aza-dipyrrins with BCl_3. The F to Cl halogen exchange process was found to occur via a step-wise pathway, distinct from that involving *meso*-carbon BODIPYs. Use of the BCl_2-chelated *Cl*-aza-BODIPY[12, 23] as an intermediate for *B*-substitutions of aza-BODIPYs was explored, and was found to be an effective strategy for expedient replacement of fluorine for aryl moieties.

Furthermore, the first series of aza-dipyrrin HX salts was synthesised and characterised, and the pK_a of the protonated tetraphenyl-substituted aza-dipyrrin **1** determined. Finally, treatment of the *Cl*-aza-BODIPYs with excess water was shown to quickly and easily deborylate the complex. These studies expand the range of synthetic modifications that can be performed on the aza-dipyrrin/aza-BODIPY framework.

Experimental Section

General methods and materials. All chemicals were used as received unless otherwise noted. For convenience, reactions involving boron substitution were performed in a glove box under a positive pressure of nitrogen gas although Schlenk techniques would be equally applicable. Prior to use in the glove box, glassware was dried overnight in an oven at 180 °C and then subjected to dynamic vacuum in the glove box antechamber overnight. Any items that could not be oven-dried were simply subjected to dynamic vacuum in the antechamber overnight. Compounds **2**[3] and **5**[9, 24, 25] were synthesised according to literature methods. These were dried overnight in a vacuum oven, then placed under dynamic vacuum in the antechamber for a further 18 hr before use. All solids were well treated with static removal devices (electronic ion generator, anti-static gun) to ensure the discharge of any static from the material that would interfere with mass determination.[15] Flash and thin-layer chromatography were performed using ultrapure silica (230-400 mesh) or Brockmann III standard grade neutral alumina (150 mesh). Air-sensitive samples (in NMR tubes or spectroscopy cuvettes) handled outside the glove box were sealed with a septum and/or Teflon tape, and Parafilm if the sample was to spend a prolonged amount of time outside the inert atmosphere. Mass spectrometry was performed using a TOF spectrometer in ESI^+ or APCI mode, as indicated. All NMR spectra were recorded using a Bruker AVANCE 500 MHz spectrometer unless otherwise noted. ^1H chemical shifts are reported in ppm relative to tetramethylsilane using

the solvent residual as an internal standard (δ = 7.26 for chloroform, 5.32 for dichloromethane). ^{13}C NMR spectra were recorded using the proton-decoupled UDEFT pulse sequence,[26] and chemical shifts are reported in ppm using the residual solvent as an internal standard (δ = 77.2 for chloroform and 53.8 for dichloromethane). It has been reported that carbon atoms directly bonded to boron in aza-BODIPYs are either weakly or not visible in ^{13}C spectra,[27] likely due to the quadrupolar relaxation of ^{11}B: the spectra of compounds **7a-c** are each missing one signal . Dichloromethane-d_2 was chosen as a deuterated solvent for derivatives of **1** due to the chloroform solvent residual obscuring some ^{1}H signals. ^{11}B chemical shifts are reported in ppm, externally referenced to boron trifluoride diethyl etherate (δ = 0.00). ^{19}F chemical shifts are reported in ppm, externally referenced to $CFCl_3$ (δ = 0.00). UV/Vis spectra were recorded using a 10 mm screw-cap quartz cell at room temperature. Spectra of air-sensitive compounds **3** and **6** were acquired under nitrogen. Fluorescence spectra are the composites of ten scans in all cases. Quantum yields were calculated relative to 3,3'-diethylthiadicarbocyanine iodide in dichloromethane (Φ = 0.35)[21] using the relationship $\Phi = \Phi_{std} \frac{I_{unk}}{A_{unk}} \frac{A_{std}}{I_{std}} \frac{n^2}{{n_{std}}^2}$, where I represents the integral of the emission spectrum of the standard (*std*) or compound under test (*unk*), A represents the absorbance at the excitation wavelength of the standard or test compound, and n represents the refractive index of the solvent used for the standard or test compound.[28] X-ray crystallography data were collected using a CCD-equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[29] Experimental parameters for each structure reported herein are included in the Supplementary Information.

4-Nitro-1,3-diphenyl-1-butanone

Following a literature procedure,[3] yet limiting the amount of nitromethane used, chalcone (6.09 g, 29 mmol), nitromethane (7.8 mL, 140 mmol) and diethylamine (15 mL, 140 mmol) were combined

and stirred for 6 hours at 60°C with the use of an oil bath. The resulting mixture was diluted with methanol (90 mL) and then acidified to pH ≈2 using 1 M HCl. The ensuing white precipitate was collected via suction filtration and washed with ice-cold hexanes followed by ice-cold methanol to yield the title compound as a white fluffy solid (7.4 g, 93% yield). R_f = 0.46 (EtOAc:Hex 1:4). M.P. 94-96°C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.90 (m, 2H), 7.58 (t, 1H, *J* = 7.5 Hz), 7.46 (t, 2H, *J* = 7.7 Hz), 7.32 (m, 2H), 7.28 (m, 3H), 4.86 – 4.66 (m, 2H), 4.23 (qu, 1H, *J* = 7.2 Hz), 3.46 (m, 2H) in accordance with reported data.[3]

Synthesis. 4,4-Dichloro-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (3). In the glove box, *F*-aza-BODIPY **2**[3] (10 mg, 0.020 mmol) was dissolved in anhydrous dichloromethane (3 mL). Boron trichloride as a 1.0 M solution in dichloromethane (22 μL, 0.022 mmol) was added, causing the teal solution to turn deep ultramarine blue. The mixture was stirred for twenty minutes at room temperature, after which the solvent was removed *in vacuo* to give the title compound as a shiny golden-blue residue in quantitative yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.09 – 8.00 (m, 8H), 7.51 – 7.42 (m, 12H), 6.93 (s, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.2, 144.6, 143.4, 132.9, 132.1, 130.50, 130.46, 130.1, 129.7, 128.9, 128.0, 121.4. ^{11}B NMR ($CDCl_3$, 160 MHz) δ: 2.51 (s). Mass spectra of this compound show only the free-base aza-dipyrrin **1**, indicating deborylation during ionisation.

*General Procedure 1 (GP1) for the synthesis of HX salts of **1***: To a stirring solution of **1** (20 mg) in tetrahydrofuran (5 mL), excess concentrated HX (X = Cl, Br, or BF_4) (0.1 mL) was added. Upon protonation, solutions of the free-base aza-dipyrrin changed from dark blue/purple to an intense dark green colour. Solvent and water were removed *in vacuo* and the resulting solid was dried in a vacuum oven overnight to yield salts without need for further purification.

***N*-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrochloride (1HCl)**. Following GP1, the title compound was isolated as a blue-green solid (20 mg, 92% yield). M.P. 284.0-287.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 14.40 (s, 2H, NH), 8.50 (d, 4H, *J* = 6.6 Hz), 7.68 – 7.53 (m, 10H), 7.43 (t, 2H, *J* = 7.3 Hz), 7.32 (s, 2H), 7.27 (t, 4H, *J* = 7.8 Hz, partially overlapping solv. residual). ^{13}C {^{1}H} NMR (CD_2Cl_2, 126 MHz) δ: 156.4, 148.4*, 136.2*, 132.8, 132.5, 130.6, 129.6, 129.5, 128.6, 116.0, one signal missing [*confirmed via 2D HMBC]. HRMS-ESI$^+$-TOF (*m/z*): [M-Cl+H]$^+$ calc'd. for $C_{32}H_{24}N_3$: 450.1970; found 450.1949.

***N*-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrobromide (1HBr)**. Following GP1, the title compound was isolated as a blue-green solid (14 mg, 80% yield). M.p. 263.9-267.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 13.64 (s, 2H, NH), 8.48 (m, 4H), 7.66 – 7.54 (m, 10H), 7.43 (t, 2H, *J* = 7.2 Hz), 7.32 (s, 2H), 7.27 (t, 4H, *J* = 7.6 Hz, partially overlapping solv. residual). ^{13}C {^{1}H} NMR (CD_2Cl_2, 126 MHz) δ: 156.7, 148.9, 135.9, 133.1, 132.4, 130.7, 130.0, 129.7, 129.5, 128.6, 128.1, 116.2. HRMS-ESI$^+$-TOF (*m/z*): [M-Br+H]$^+$ calc'd. for $C_{32}H_{24}N_3$: 450.1970; found 450.1957.

***N*-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrofluoroborate (1HBF$_4$)**. Following GP1, the title compound was isolated as a yellow-green solid (37.5 mg, 88% yield). M.P. 238.0-240.0 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 11.25 (s, 2H, NH), 8.19 – 8.07 (m, 4H), 7.69 (m, 10H), 7.51 (t, 2H, *J* = 7.4 Hz), 7.42 (s, 2H), 7.36 (s, 4H). ^{11}B NMR (CD_2Cl_2, 96 MHz) δ: -0.82 (s). ^{19}F NMR (CD_2Cl_2, 282 MHz) δ: -147.28 (s). HRMS-ESI$^+$-TOF (*m/z*): [M-BF_4+H]$^+$ calc'd. for $C_{32}H_{24}N_3$: 450.1970; found 450.1962.

N,N-Dichloroboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (6). In the glove box, compound **5**[9] (10 mg, 0.022 mmol) was dissolved in anhydrous dichloromethane (2 mL). Boron trichloride as a 1.0 M solution in dichloromethane (33

μL, 0.033 mmol) was added, resulting in a lightening of the green hue of the solution. The mixture was stirred for twenty minutes at room temperature, after which the solvent was removed *in vacuo* to give the title compound as a dark green residue in quantitative yield. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ: 8.11 (d, 2H, *J* = 8.0 Hz), 7.84 (m, 4H), 7.57 (m, 2H), 7.53 – 7.49 (m, 6H), 7.43 (m, 2H), 7.33 (m, 2H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 126 MHz) δ: 154.7*, 137.1*, 132.8*, 131.7, 131.3, 131.0, 130.8*, 130.4, 128.1, 127.8, 124.7, 121.2 [*signals elucidated via 2D HMBC]. ^{11}B NMR (CD_2Cl_2, 160 MHz) δ: 3.17 (s). Mass spectra of this compound show only the free-base aza-dipyrrin **4**, indicating that the compound is deborylated during ionisation.

4,4-Diphenyl-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7a). In the glove box, compound **2**[3] (50 mg, 0.10 mmol) was dissolved in anhydrous dichloromethane (10 mL). Boron trichloride as a 1.0 M solution in dichloromethane (110 μL, 0.11 mmol) was added, causing the teal solution to turn deep blue and indicating formation of **3**. The mixture was stirred for twenty minutes at room temperature, after which the solvent was removed *in vacuo* and in an anhydrous fashion. The residue was re-dissolved in fresh anhydrous dichloromethane (10 mL) and phenylmagnesium bromide as a 3.0 M solution in diethyl ether (67 μL, 0.20 mmol) was added. No substantial colour change occurred. The mixture was stirred for 3 hours at room temperature, after which the reaction vessel was capped and transferred out of the glove box. The reaction mixture was extracted into dichloromethane (2 x 70 mL) with water, then washed with saturated aqueous sodium chloride (70 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude blue solid was purified using flash chromatography on neutral alumina, eluting with 1/99 EtOAc/hexanes to yield the title compound as a copper-colored solid (20 mg, 53% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.15 – 8.10 (m, 4H), 7.47 (t, 4H, *J* = 7.7 Hz), 7.41 (m, 2H), 7.11 (t, 2H, *J* = 7.3 Hz), 7.03 – 6.93 (m, 10H), 6.90 (t, 4H, *J* = 7.5 Hz), 6.78 (s, 2H),

6.70 – 6.64 (m, 4H) in accordance with reported values.[10] We report further spectral data as follows: ^{11}B NMR ($CDCl_3$, 160 MHz) δ: 1.33 (s). HRMS-ESI$^+$ (*m/z*): [m+H]$^+$ calc'd. for $C_{44}H_{33}BN_3$: 614.2768; found 614.2762 in agreement with the literature.[10]

4,4-Di-(2-naphthyl)-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7b). In the glove box, compound **2**[3] (30 mg, 0.060mmol) was dissolved in anhydrous dichloromethane (10 mL). Boron trichloride as a 1.0 M solution in dichloromethane (67 μL, 0.066 mmol) was added, causing the teal solution to turn deep blue and indicating formation of **3**. The mixture was stirred for twenty minutes at room temperature, after which the solvent was removed *in vacuo* and in an anhydrous fashion. The residue was re-dissolved in fresh anhydrous dichloromethane (10 mL) and 2-naphthylmagnesium bromide as a 0.25 M solution in 2-methyltetrahydrofuran (480 μL, 0.120mmol) was added drop-wise. No substantial color change occurred. The mixture was stirred for 3 hours at room temperature. The reaction vessel was capped and transferred out of the glove box, and the mixture was extracted into dichloromethane (2 x 70 mL) with water, then washed with saturated aqueous sodium chloride (70 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude blue solid was purified using flash chromatography on neutral alumina, eluting with 1/99 EtOAc/hexanes to yield the title compound as a copper-colored solid (16 mg, 37% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.15 (d, 4H, *J* = 7.2 Hz), 7.71 (d, 2H, *J* = 7.9 Hz), 7.53 (d, 2H, *J* = 8.3 Hz), 7.49 (t, 4H, *J* = 7.7 Hz), 7.42 (t, 4H, *J* = 7.6 Hz), 7.34 (m, 7H), 7.28 (s, 1H, partially overlapping solv. residual), 6.95 (t, 2H, *J* = 7.4 Hz), 6.79 (s, 2H), 6.67 (t, 4H, *J* = 7.7 Hz), 6.58 (d, 4H, *J* = 7.2 Hz). ^{11}B NMR ($CDCl_3$, 160 MHz) δ: 1.60 (s). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.0, 144.2, 142.4, 133.7, 133.2, 133.1, 133.0, 132.5, 132.0, 129.51, 129.48, 129.1, 128.9, 128.8, 128.4, 127.4, 127.0, 126.3, 125.0, 124.8, 120.9. HRMS-APCI (*m/z*): [m+H]$^+$ calc'd. for $C_{52}H_{37}BN_3$: 714.3075; found 714.3075.

4,4-Di-(2-thienyl)-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7c). In the glove box, compound **2**[3] (30 mg, 0.060 mmol) was dissolved in anhydrous dichloromethane (10 mL). Boron trichloride as a 1.0 M solution in dichloromethane (67 μL, 0.066 mmol) was added, causing the teal solution to turn deep blue and indicating formation of **3**. The mixture was stirred for twenty minutes at room temperature, after which the solvent was removed *in vacuo* and in an anhydrous fashion. The residue was re-dissolved in fresh anhydrous dichloromethane (10 mL) and 2-thienylmagnesium bromide as a 1 M solution in tetrahydrofuran (120 μL, 0.120 mmol) was added drop-wise. This addition caused a very slight color change toward blue-green, which persisted throughout. The mixture was stirred for 3 hours at room temperature. The reaction vessel was capped and transferred out of the glove box, and the mixture was extracted into dichloromethane (2 x 70 mL) with water, then washed with saturated aqueous sodium chloride (70 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to yield the title compound as bronze-colored flakes without need for further purification (37 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.14 (d, 4H, J = 7.5 Hz), 7.48 (t, 4H, J = 7.6 Hz), 7.42 (t, 2H, J = 7.5 Hz), 7.15 (m, 4H), 6.99 (t, 4H, J = 7.6 Hz), 6.78 (m, 6H), 6.75 – 6.71 (m, 2H), 6.63 – 6.60 (m, 2H). ^{11}B NMR ($CDCl_3$, 160 MHz) δ: -2.59 (br s). ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz) δ: 161.3, 143.9, 142.8, 132.98, 132.96, 131.5, 129.5, 129.4, 129.2, 128.81, 128.75, 127.1, 127.0, 126.8, 120.9. HRMS-ESI$^+$ (*m/z*): [m+Na]$^+$ calc'd. for $C_{40}H_{28}BN_3S_2$: 648.1716; found 648.1710.

N,N-Diphenylboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (8). In a glove box, compound **5**[9] (30 mg, 0.067 mmol) was dissolved in anhydrous dichloromethane (10 mL). Boron trichloride as a 1.0 M solution in dichloromethane (101 μL, 0.101 mmol) was added, resulting in a lightening of the green hue of the mixture and indicating the formation of **6**. The mixture was stirred for twenty minutes at room temperature, after which

the solvent was removed *in vacuo* and in an anhydrous fashion. The residue was re-dissolved in fresh anhydrous dichloromethane (10 mL) and phenylmagnesium bromide as a 3.0 M solution in diethyl ether (45 μL, 0.134 mmol) was added. This addition briefly caused the solution to turn black, yet the dark green colour returned over time. The mixture was stirred for three hours at room temperature. The reaction vessel was capped and transferred out of the glove box, where it was extracted into ethyl acetate (60 mL) with water, then washed with saturated aqueous sodium chloride (60 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude green solid was purified using flash chromatography on neutral alumina, eluting with 1/99 EtOAc/hexanes and dried *in vacuo* to give the title compound as a copper-colored solid (17 mg, 45% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ: 8.20 (d, 2H J = 8.1 Hz), 7.52 (m, 2H), 7.21 (m, 6H), 6.99 (m, 6H), 6.88 (m, 8H), 6.53 – 6.50 (d, 4H). ^{11}B NMR (CD_2Cl_2, 160 MHz) δ: 1.66 (s). ^{13}C {^{1}H} NMR (CD_2Cl_2, 126 MHz) δ: 154.1, 137.8, 134.0, 133.08, 133.07, 131.4, 130.5, 129.8, 129.0, 127.6, 127.3, 126.5, 126.3, 123.2, 120.5. HRMS-ESI^{+} (m/z): $[m+H]^{+}$ calc'd. for $C_{40}H_{29}BN_3$: 562.2455; found 562.2449.

Deprotection of aza-BODIPYs.[22] In the glove box, boron trichloride as a 1.0 M solution in dichloromethane (67 μL, 0.066mmol) was added to a solution of **2**[3] (30 mg) in anhydrous dichloromethane (10 mL) and the mixture stirred for twenty minutes. The solvent was removed *in vacuo* to yield the corresponding *Cl*-aza-BODIPY **3** as a residue. The reaction vessel was capped and transferred out of the glove box, and the residue was re-dissolved in a 5.55M [10% v/v] solution of water in acetone (10 mL) and stirred at room temperature for ten minutes. The mixture was extracted into dichloromethane with water, and the organic layer dried over anhydrous sodium sulfate. Removal of solvent *in vacuo* quantitatively yielded the corresponding aza-dipyrrin **1** as a dark purple-black solid, with no further purification required.

In the glove box, boron trichloride as a 1.0 M solution in dichloromethane (67 μL, 0.066 mmol) was added to a solution of **5**[9] (18 mg) in anhydrous dichloromethane (10 mL) and the mixture stirred for twenty minutes. The solvent was removed *in vacuo* to yield the corresponding *Cl*-aza-BODIPY **6** as a residue. The reaction vessel was capped and transferred out of the glove box, and the residue was re-dissolved in a 5.55 M [10% v/v] solution of water in tetrahydrofuran (10 mL) and stirred at room temperature for one hour. The mixture was extracted into ethyl acetate with brine, and the organic layer dried over anhydrous magnesium sulfate. The mixture was concentrated in vacuo and purified using a short neutral alumina column, eluting with 25/75 dichloromethane/hexanes to yield the aza-dipyrrin **4** as a dark blue powder (8 mg, 58% yield).

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Conflicts of interest

The authors declare no competing financial interest.

[†]Electronic supplementary information (ESI) available

Characterisation data (NMR spectra, crystallographic data, photophysical data).

X-ray data

CCDC 1955376-1955380 contain the crystallographic data for this paper.

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