Special Collection

Synthesis and Structural Diversification of Circularly Polarised Luminescence Active, Helically Chiral, "Confused" *N,N,O,C*-BODIPYs**

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Helically chiral boron-chelated dipyrromethene (BODIPY) dyes are known to exhibit solution phase circularly polarized luminescence (CPL), but examples are limited to a few synthetically accessible molecular architectures. We report a B–N chelation, S_NAr, Suzuki cross-coupling, B–O chelation cascade reaction for the synthesis of understudied helically chiral, *N,N,O,C*-boron chelated, "confused" BODIPYs, from readily accessible 3,5-dibromo-BODIPY starting materials. Using this approach we have prepared a series of helically chiral "confused" BODIPYs with variation of the 3,5-subsitutents. Following resolution by chiral HPLC, absolute stereochemistry was assigned through comparison of the experimental and calculated ECD spectra, and solution phase chiroptical properties including CPL were determined ($|g_{lum}|$ from 2.1 to 3.7 × 10^{-3}; B_{CPL} from 11.3 to 27.2).

Introduction

Circularly polarised luminescence (CPL) is the spontaneous differential emission of left or right circularly polarised light from an excited state in the presence of a chiral field.[1] There is a burgeoning interest in the discovery of homochiral small organic molecules capable of efficient CPL emission in solution (CPL-SOMs), with numerous classes of CPL-SOMs thus far disclosed.[2]

Due to their typically high fluorescence quantum yields (ϕ_F) and molar extinction coefficients (ε), and their potential for facile modification of photonic properties through minor structural changes, boron-chelated dipyrromethenes or BODIPYs[3,4] have become attractive targets for the development of CPL-SOM architectures. Asymmetric perturbation of the inherently planar BODIPY core has been shown to result in chiroptical activity in such systems,[5] leading to a number of BODIPY based CPL-SOMs in which desymmetrisation has been achieved through the introduction of axial, helical, figure-of-eight and propeller-like chiralities.[6]

We recently reported an isolated example of a CPL-active helically-chiral BODIPY based on an unusual "confused" *N,N,O,C*-boron chelated motif.[6g] "Confused" *N,N,O,C*-BODIPY (***rac*-3 a**) was serendipitously formed as a by-product from a Suzuki-Miyaura cross-coupling reaction between 3,5-dibromo-BODIPY (**1**) and 2-hydroxyphenyl boronic acid, resulting in a structure in which one of the arylsubstituents at the 3,5-positions had been inverted in comparison to the parent *N,N,O,O*-boron chelated BODIPY (***rac*-2**). *N,N,O,O*-boron chelated BODIPY (***rac*-2**) is also formed under these conditions, the product of a double Suzuki-Miyaura reaction and *in situ* B–O chelation (Scheme 1a).

Unfortunately, this reaction proved highly capricious, with our initially reported yield of 36% proving to be unreproducible across nine reaction replicates, giving a range of yields from 2–36%. Due to our interest in the further investigation of the chiroptical properties of helically chiral "confused" BODIPYs, we decided to focus our efforts in this area on the development of a much more synthetically reliable route to these intriguing molecules.

Thus, herein we report a much improved synthesis of helically chiral 'confused' *N,N,O,C*-BODIPYs which also allows the flexible introduction of a range of substituted aryl-groups at the 3,5-positions (Scheme 1b).

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[**] BODIPY = boron-chelated dipyrromethene.

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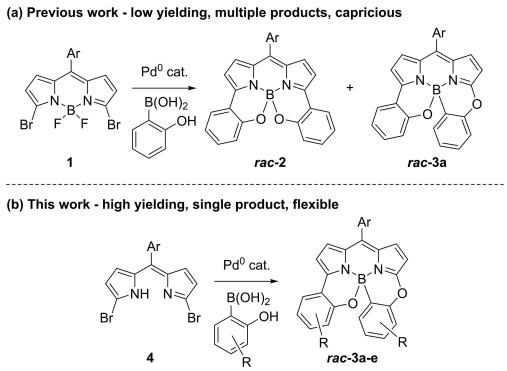
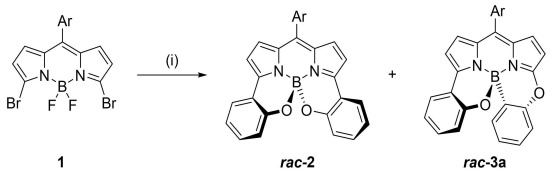
An invited contribution to a Special Collection on Circularly Polarized Luminescence



Scheme 1. (a) First reported synthesis of a helically chiral 'confused' *N,N,O,C*-BODIPY; (b) Improved route reported herein (Ar—=*p*-($MeCO_2$)C_6H_4–).

Table 1. Investigation into the role of the Pd catalyst in the formation of *N,N,C,O*-BODIPY (***rac*-3**) (Ar—=*p*-($MeCO_2$)C_6H_4–). Reagents and conditions: (i) 2-hydroxyphenyl boronic acid (4 eq.), Pd catalyst (5 mol%), Na_2CO_3, toluene, 1,4-dioxane, 90 °C (Ar—=*p*-($MeCO_2$)C_6H_4–).



	Catalyst	[%] Yield of ***rac*-2** [a]	[%] Yield of ***rac*-3 a** [a]
1	$Pd(PPh_3)_4$	34	14
2[a]	none	0	0
3[b]	$Pd(PPh_3)_4$	9	16
4	$Pd(OAc)_2$	3	39

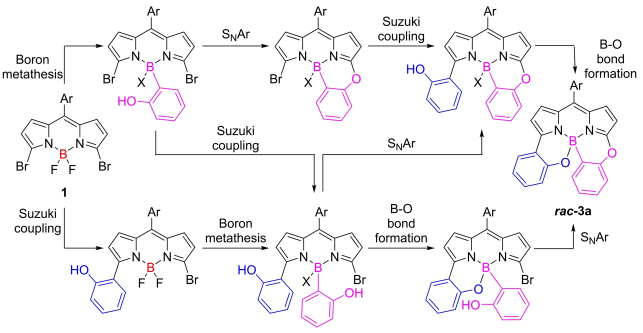
[a] Isolated yields. [b] Reaction performed in the presence of air.

Results and Discussion

Our first challenge in the development of new routes to helically chiral 'confused' *N,N,O,C*-BODIPYs (***rac*-3 a**) was to better understand the step order which was likely to have occurred under the previously discovered reaction conditions. We postulated four main steps in the reaction: boron metathesis, intramolecular S_NAr, Suzuki-Miyaura cross-coupling, and B–O bond formation. However, the likely ordering of these reaction steps was not immediately apparent, with a number of viable options available (Scheme 2).

A key step in the potential mechanisms for the formation of 'confused' *N,N,O,C*-BODIPYs (***rac*-3 a**) is boron metathesis, in which the BF_2 group is exchanged with the boron of the added 2-hydroxyphenyl boronic acid. Deborylation of BODIPYs is known, with examples mediated by Brønsted (e.g. TFA or HCl/MeOH)[7] or Lewis acids (e.g. BBr_3, then H_2O),[8] whilst spontaneous chelation of boronic acids by multidentate BODIPY like molecules has also been reported.[9] Thus we hypothesized that the boron metathesis may involve the loss of the BF_2 group mediated by Pd^{2+} acting as a Lewis acid, likely formed by the *in situ* oxidation of Pd^0, followed by rechelation with 2-hydroxyphenyl boronic acid.

To examine the role of Pd in the overall transformation, we began with a control reaction using 5 mol% $Pd(PPh_3)_4$, under our previously published reaction conditions (Table 1, entry 1), in which *N,N,O,O*-BODIPY (***rac*-2**) and *N,N,C,O*-BODIPY (***rac*-3 a**) were both formed in 34 and 14% yields respectively. Exclusion of the Pd catalyst gave rise to neither of these products (Table 1, entry 2), with some decomposition of the starting material and no detectable products arising from S_NAr chemistry. The use of 5 mol% $Pd(PPh_3)_4$ in the presence of air (Table 1, entry 3), to increase the availability of Pd^{2+} through air oxidation, resulted in a slight increase in the overall yield of *N,N,C,O*-BODIPY (***rac*-3 a**) to 16% as the major product isolated. Finally use of 5 mol% $Pd(OAc)_2$ gave a significant boost in the yield, 39% of *N,N,C,O*-BODIPY (***rac*-3**) isolated as the major component in the reaction with only trace *N,N,O,O*-BODIPY (***rac*-2**) observable (Table 1, entry 3).



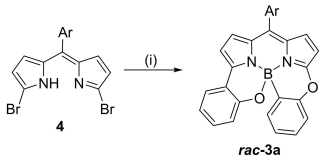
Scheme 2. Potential reaction step orderings *en route* to helically chiral 'confused' *N,N,O,C*-BODIPYs (***rac*-3 a**) (X=F or OH; Ar—=*p*-($MeCO_2$)C_6H_4–).

The observed change in selectivity from *N,N,O,O*-BODIPY (***rac*-2**) to *N,N,C,O*-BODIPY (***rac*-3 a**) upon use of a Pd^{2+} catalyst, either directly via $Pd(OAc)_2$ or via aerial oxidation of a Pd^0 species, supports the potential role of Pd^{2+} in a Lewis acidic mediated boron methathesis as a key early step in the formation of *N,N,C,O*-BODIPY (***rac*-3 a**). We reasoned that if the loss of the BF_2 moiety was indeed a key step, then starting instead from the corresponding unchelated α,α-dibromodipyrromethene **4**, a synthetic precursor to 3,5-dibromoBODIPY **1**, could lead to direct formation of *N,N,O,C*-BODIPY (***rac*-3 a**).

Indeed when we reacted dibromodipyrromethene **4**, prepared as previously,[6g] with 2-hydroxyphenyl boronic acid in the presence of 5 mol% $Pd(OAc)_2$, we observed the selective formation of the desired "confused" *N,N,O,C*-BODIPY (***rac*-3 a**). However, the yield was sub-optimal, owing to the lower overall activity of palladium(II) precatalysts in Suzuki-Miyaura cross-couplings. By instead using the palladium(0) catalyst, 5 mol% $Pd(PPh_3)_4$, we were able to selectively synthesise *N,N,O,C*-BODIPY (***rac*-3 a**) in a high isolated yield of 85% (Scheme 3).

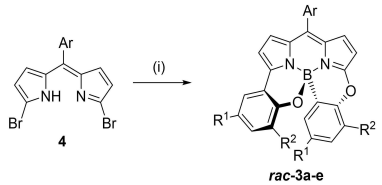
With our improved synthetic route in hand, we next sought to examine the scope of this approach towards functionalised *N,N,O,C*-BODIPYs. Thus dibromodipyrromethene **4** was reacted with a range of functionalised 2-hydroxyphenyl boronic acids leading to the isolation of *N,N,O,C*-BODIPYs ***rac*-3 a–e** in moderate to good yields (38–85%) (Table 2).

Following growth of a suitable crystal through slow evaporation of a chloroform solution, the structure of ***rac*-3 c**



Scheme 3. Synthesis of *N,N,C,O*-BODIPY (***rac*-3**). Reagents and conditions: (i) 2-hydroxyphenyl boronic acid (4 eq.), $Pd(PPh_3)_4$ (5 mol%), Na_2CO_3, toluene:1,4-dioxane (1:1), 90 °C (Ar—=*p*-$(MeCO_2)C_6H_4$–).

Table 2. Synthesis of an expanded range of *N,N,O,C*-BODIPY ***rac*-3 a–e**.



	R^1	R^2	Product	[%] Yield
1	H	H	**3 a**	85[a]
2	H	Me	**3 b**	38
3	Me	H	**3 c**	55
4	Cl	H	**3 d**	75
5	F	H	**3 e**	73

[a] Result from Scheme 3 included for comparison.

was confirmed through single crystal X-ray diffraction analysis. A twist angle of 8.2° between the two pyrrolic rings of ***rac*-3 c** was observed, a slight increase in the previously reported analogous twist angle of 7.7° observed in ***rac*-3 a**, suggesting that the aryl methyl groups of ***rac*-3 c** impart a higher degree of chiral perturbation to the planar BODIPY core, at least in the solid state (Figure 1).[10]

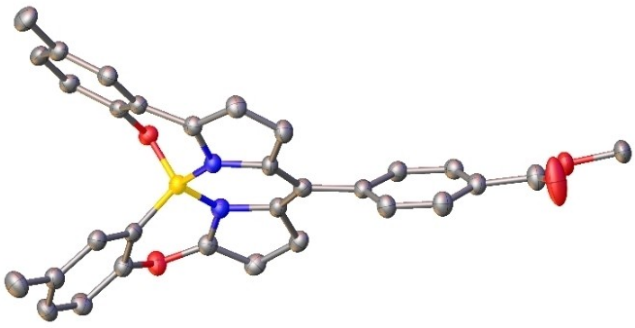


Figure 1. ORTEP diagram of a molecule in the crystal structure of ***rac*-3 c** (H atoms are omitted for clarity; *M*-isomer shown; thermal ellipsoids shown at 50%).[10]

Detailed assignment of the two fluorine environments of ***rac*-3 e** (−117.0 and −123.1 ppm) was achieved through a combination of ^{19}F-^{13}C HMQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H ROESY and ^{1}H-{^{19}F} NMR experiments, the signal at −123.1 ppm being shown to correspond to the fluorine atom of the B–O bonded aryl substituent. ^{19}F-^{13}C HMQC showed correlations between the fluorines at −117.0 and −123.1 ppm and the carbons at 156.8 and 159.3 ppm respectively, with ^{1}H-^{13}C HMBC showing a correlation between the carbon at 156.8 ppm and the proton at 7.42 ppm. ^{1}H-{^{19}F} NMR confirmed a 3-bond AX coupling ($^{3}J = 8.2$ Hz) between the proton at 7.42 ppm and the fluorine at −123.1 ppm. Finally, ^{1}H-^{1}H ROESY showed that the aryl and pyrrolic protons at 7.42 and 6.84 ppm respectively, were close in space, allowing assignment of the proton at 7.42 ppm and thus the fluorine at −123.1 ppm to those of the isolated aromatic C–H and the fluorine of the B–O bonded aryl substituent (See SI).

Resolution of dyes *N,N,O,C*-BODIPYs ***rac*-3 b–e** was performed by semi-preparative HPLC on a chiral stationary phase to afford the dextro- and levoratory enantiomers of each *N,N,O,C*- BODIPY. Mirror image ECD spectra were obtained for each set of enantiomers showing good alignment with the recorded UV/Vis absorption spectra (Figure 2a). As we would anticipate, the ECD spectra of each enantiomer of *N,N,O,O*-BODIPYs **3 b–e** showed strong Cotton effects in the S_0–S_1 transition in each case.

In order to assign each enantiomer as either (*P*) or (*M*), Boltzmann-weighted ECD spectra were obtained from TD-DFT calculations at the cam-B3LYP/6-311++G(3df,2pd) level for the (*P*) enantiomer of each *N,N,O,C*-BODIPY (Figure 2b). By comparison of the calculated ECD spectra and the experimental ECD spectra, we were able to unambiguously assign the (*P*) and (*M*) isomers of *N,N,O,C*-BODIPYs **3 b–e** (Figure 2c).

CPL measurements for (*P*) and (*M*) isomers of *N,N,O,C*-BODIPYs **3 b–e** were undertaken using a home-built modular PEM-CPL spectrometer, and gave mirror image spectra with the magnitude of their luminesce dissymmetry factors ($|g_{lum}|$) in the range $2.1–2.6\times10^{-3}$ (Figure 3 and Table 3).[11] Unfortunately, comparison to the previously published CPL spectra of **3 a**[6d], showed no improvements in $|g_{lum}|$ values across the four derivatives **3 b–e**. However, the values obtained were typical of g_{lum} magnitudes observed for small organic molecules, including related mono-BODIPY systems, and as predicted for π-π* transitions in organic molecules through direct correlation with

Table 3. Photophysical and chiroptical properties of *N,N,O,C*-BODIPYs **3 a–e**.

	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	ϕ_F	$\lvert g_{abs}\rvert$	$\lvert g_{lum}\rvert_{calc}$[c]	$\lvert g_{lum}\rvert_{exp}$	B_{CPL} [$M^{-1}cm^{-1}$]
3 a[a]	622	30,000	0.49	3.1×10^{-3}	-	3.7×10^{-3}	27.2
3 b[b]	633	24,000	0.41	3.2×10^{-3}	3.1×10^{-3}	2.3×10^{-3}	11.3
3 c[b]	637	39,000	0.25	3.4×10^{-3}	2.2×10^{-3}	2.6×10^{-3}	12.7
3 d[b]	622	52,000	0.37	2.9×10^{-3}	2.2×10^{-3}	2.1×10^{-3}	20.2
3 e[b]	623	32,000	0.43	2.8×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	15.1

[a] Hexane. [b] DCM. [c] $|g_{lum}|_{calc}$ shown for conformer 1 of **3 b–d**. (Note: data for **3 a** previously published[6d], included for comparison).

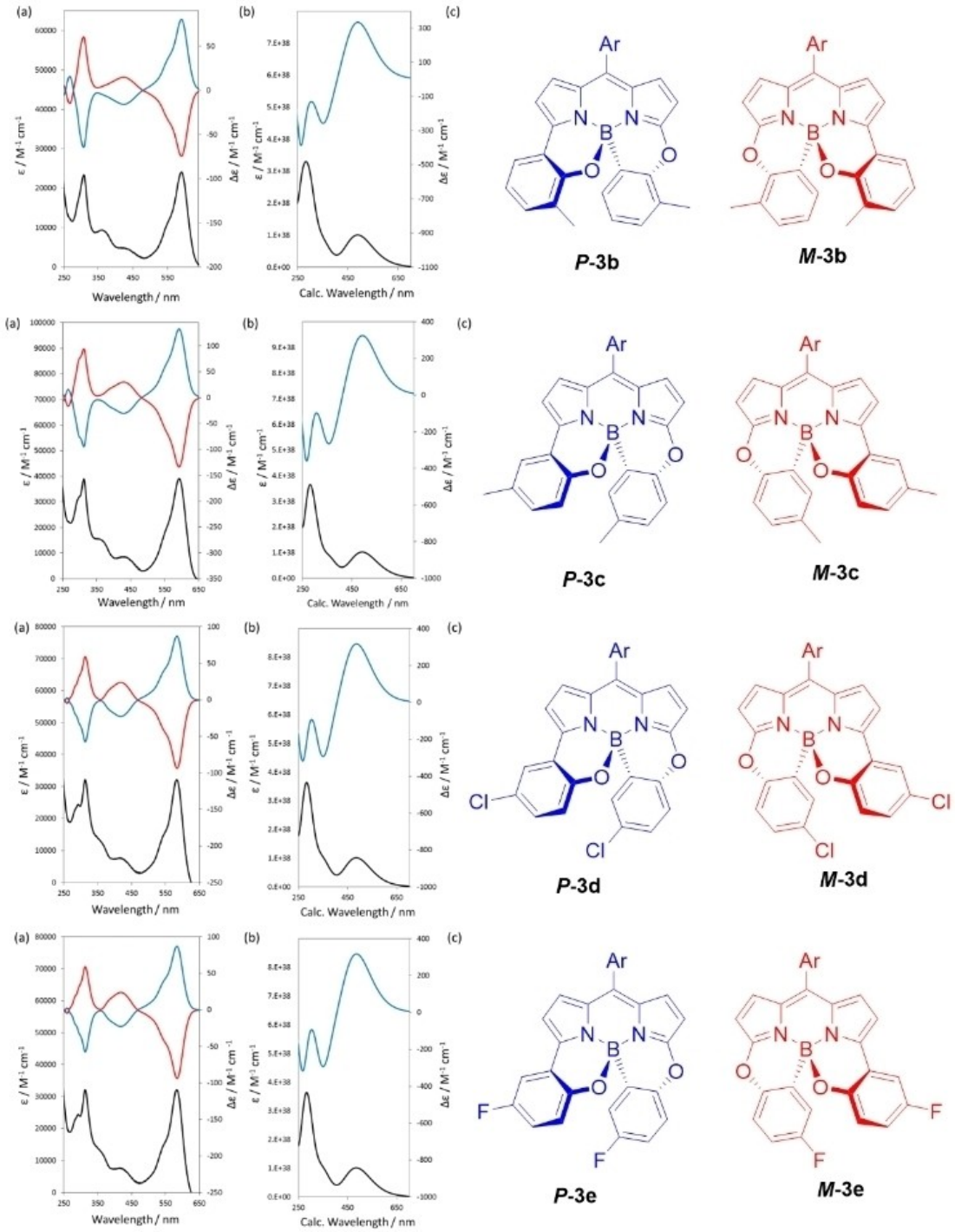


Figure 2. (a) Experimental ECD spectra (blue – **(*P*)-3 b–e**, red – **(*M*)-3 b–e**) and UV/Vis absorption spectrum (black – ***rac*-3 b–e**) measured in dichloromethane; (b) Calculated Boltzmann-weighted spectra, ECD (blue – postulated **(*P*)-3 b–e**, (wavelengths uncorrected)) and UV/Vis absorption spectra (black – postulated **(*P*)-3 b–e** (wavelengths uncorrected)); (c) Structures of blue – **(*P*)-3 b–e** and red – **(*M*)-3 b–e** (Note: Experimental and calculated ECD spectra for **3 a** were previously published[6g]).

recorded $|g_{abs}|$ values ($|g_{lum}| \approx 0.8\ |g_{abs}|$).[12] Additionally, the $|g_{lum}|$ values obtained for *N,N,O,C*-BODIPYs **3 b–e** are consistent across the series, which suggests that modifications to the 3,5-aryl rings can be performed without detriment to the CPL capability of the dye and thus that it should be possible in the future to maintain a predictable CPL output while introducing additional functionality. Indeed $|g_{lum}|$ were calculated for the major ground state conformers of **3 a–e** from the excited S1 optimised geometry by TD-DFT (CAM-B3LYP/6-311++G-(3df,2pd)),[13] and gave generally good agreement with the experimentally observed values. CPL brightness (B_{CPL}), the product of the molar extinction coefficient (ε), fluorescence

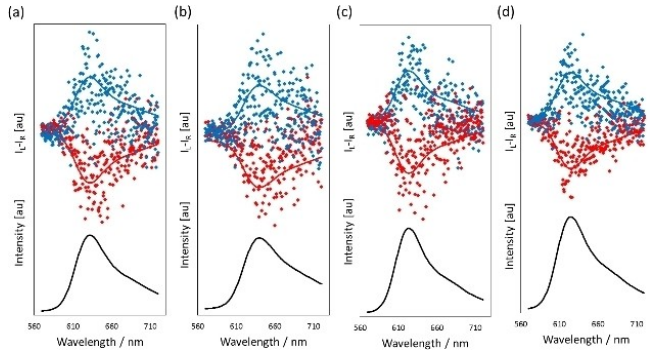


Figure 3. (a) Normalised CPL (I_L-I_R) (red – **(*M*)-3 b**, blue – **(*P*)-3 b** and fluorescence spectra (black – ***rac*-3 b**) measured in dichloromethane; (b) Normalised CPL (I_L-I_R) (red – **(*M*)-3 c**, blue – **(*P*)-3 c** and fluorescence spectra (black – ***rac*-3 c**) measured in dichloromethane; (c) Normalised CPL (I_L-I_R) (red – **(*M*)-3 d**, blue – (*P*)-**3 d** and fluorescence spectra (black – ***rac*-3 d**) measured in dichloromethane; (d) Normalised CPL (I_L-I_R) (red – **(*M*)-3 e**, blue – **(*P*)-3 e** and fluorescence spectra (black – ***rac*-3 e**) measured in dichloromethane (Note: CPL spectra for **(*M*)-3 a** and **(*P*)-3 a** were previously published[6g]).

quantum yield (ϕ_F) and half the luminesce dissymmetry factor ($|g_{lum}|/2$) was also calculated giving values from 11.3 to 27.2, also typical of simple chiral BODIPYs (Table 3).[14]

It should also be noted that in this series of helically chiral *N,N,O,C*-BODIPYs, in the case where one enantiomer absorbs circularly polarised light with a particular handedness, then it also emits light with the same handedness, also in line with previously reported cases of related helically chiral BODIPYs.

Conclusions

In summary, following an initial mechanistic investigation into the formation of confused helically chiral *N,N,O,C*-BODIPY (***rac*-3 a**), we have developed a reliable high yielding synthetic route towards these molecules tolerant of functional group variations coming from the aryl boronic acid component. This has allowed the synthesis of a number of *N,N,O,C*-BODIPYs (***rac*-3 a**–**e**) facilitating further study of the chiroptical properties of molecules in this class. *N,N,O,C*-BODIPYs **3 b**–**e** were resolved into their corresponding enantiomers, by chiral HPLC, and displayed chiroptical properties in keeping with related chiral BODIPYs published. Future work will focus on the extension of halogen functionalised *N,N,O,C*-BODIPYs, such as **3 d**, allowing the expansion of the chiral π-system with the potential for improved CPL-SOM design.[15]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: BODIPYs · cascade reactions · circularly polarised luminescence · electronic circular dichroism spectroscopy · helically chiral compounds

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