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Title: Circularly Polarised Luminescence from Helically Chiral 'Confused' N,N,O,C-Boron-Chelated Dipyrromethenes (BODIPYs)

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Circularly Polarised Luminescence from Helically Chiral *N,N,O,C*-Boron-Chelated Dipyrrromethenes (BODIPYs)

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Abstract: Chiral organic fluorophores have significant promise in the development of efficient emitters of circularly polarized light. Herein we describe a helically chiral BODIPY with a hitherto unreported *N,N,O,C*-boron-chelation motif, synthesised via a one-pot boron metathesis, nucleophilic aromatic substitution (S_NAr), Suzuki coupling, boron chelation, cascade reaction. Resolution of the racemic BODIPY, by preparative chiral HPLC, allowed examination of the chiroptical properties of the resulting enantiomers ($\lambda_{max}(abs) = 593 \text{ nm}$, $\lambda_{max}(em) = 622 \text{ nm}$, $\gamma = 30,000 \text{ M}^{-1} \text{ cm}^{-1}$, $Z_F = 0.49$, $\Phi_{lum} = 3.7 \times 10^{-3}$ (hexane)). This is the first example of circularly polarised emission from a non- C_2 symmetric helically chiral *N,N,O,C*-BODIPY and as such provides a valuable benchmark for future developments in this compound series.

Introduction

Circularly polarised luminescence (CPL) is the spontaneous differential emission of left- or right-circularly polarized light from an excited electronic state in the presence of a chiral field.¹ Although many highly efficient condensed phase CPL systems have been disclosed,² CPL emitters presents an ongoing challenge. To this end chiral lanthanide complexes have been extensively studied,³ due to their high luminescence dissymmetry factors ($\Phi_{lum} \geq 1.38$)^{4,5} arising from magnetic dipole-allowed electric dipole-forbidden $f-f$ transitions,⁶ culminating in the development of a number of lanthanide based CPL probes for molecular sensing.⁷ However low fluorescence quantum yields (Z_F) for these systems can result in low overall CPL quantum efficiencies ($Z_F \cdot \Phi_{lum}$). Thus there is considerable interest in the development of homochiral small organic fluorophores capable of CPL emission (CPL-SOMs), which might provide a viable alternative to chiral lanthanide complexes.⁸ To date several classes of CPL-SOMs have been investigated including those based on helicenes,⁹

cyclophanes,¹⁰ and *ortho*-oligo(phenylene)ethynylenes¹¹ as well as some interesting recent examples of thermally activated delayed CPL.¹² Ourselves and others have focused on the study of chiral boron-chelated dipyrrromethenes (BODIPYs) due to their excellent photophysical properties (high extinction coefficients, fluorescence quantum yields, tuneable emission properties etc.) and synthetic accessibility.¹³ This has resulted in the disclosure of several CPL-SOM systems described as either axially¹⁴ or helically¹⁵ chiral BODIPYs in which the fluorophore core has been asymmetrically perturbed through the introduction of either covalent or steric restraints. However despite these advances in homochiral BODIPY design, their CPL quantum efficiencies are still limited by low luminescence dissymmetry factors (highest reported Φ_{lum} equal to 4.7×10^{-3} or 9×10^{-3} for monomeric or dimeric homochiral BODIPYs respectively^{15b,15e}). Future improvement of these Φ_{lum} values will require an improved understanding of the link between Φ_{lum} and molecular structure in the helically chiral BODIPY series.

The luminescence dissymmetry factor (Φ_{lum}) is given by $4(|\mathbf{m}| \cdot \cosh) / (|\mathbf{e}|^2 + |\mathbf{m}|^2)$ where \mathbf{m} and \mathbf{e} are the magnetic and electric transition dipole moment vectors respectively and θ is the angle between them.¹⁶ The relatively low Φ_{lum} values arise because $|\mathbf{m}|$ is typically three orders of magnitude smaller than $|\mathbf{e}|$ for the $d-d^*$ transition of a simple homochiral organic fluorophore, such as a chiral BODIPY. Consequently, molecular design must focus upon either increasing the magnetic transition dipole moment (\mathbf{m}) or decreasing the electric transition dipole moment (\mathbf{e}), assuming a fixed value of θ .

The transition matrix elements for the former (\mathbf{m}) only operates upon the angular part of the wavefunction, and consequently can be seen as analogous to spin-orbit coupling.¹⁷ The low angular momentum components of the light elements used herein therefore represent a limitation when compared to the $f-f$ transitions exploited in chiral lanthanide complexes. In contrast the electric transition dipole moment operates on the spatial part of the molecular wavefunction, and can be minimised by creating a small overlap between the initial and final state wavefunctions, i.e. a charge transfer complex.¹⁸

Herein, we report a new structural class of helically chiral *N,N,O,C*-boron-chelated dipyrrromethenes (BODIPYs). By breaking the C_2 symmetry axis, ubiquitous amongst the reported helically chiral BODIPYs,¹⁵ we envisaged an increase in the charge transfer character of the emitting excited state, reducing the magnitude of electric transition dipole moment (\mathbf{e}). Chiroptical measurements in combination with computational and electrochemical analysis has allowed us to rationalize the impact of this structural change on the observed Φ_{lum} providing an insight into the link between the molecular structure and the chiroptical properties in helical BODIPY CPL-SOMs.

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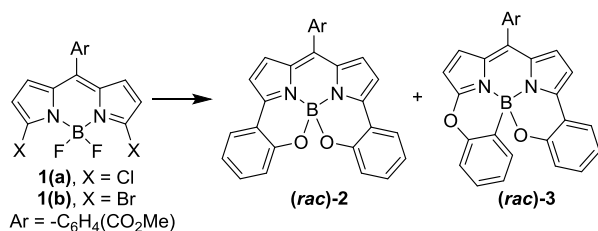
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Results and Discussion



Scheme 1. Synthesis of **(rac)-2** and **(rac)-3**. Conditions: **1a** X = Cl, (2-hydroxyphenyl)boronic acid, Na₂CO₃, 5 mol% Pd(PPh₃)₄, toluene, 1,4-dioxane, 90 °C, 24 hours, **2** = 63 %, **3** = 8 %. **1b** X = Br, (2-hydroxyphenyl)boronic acid Na₂CO₃, 5 mol% Pd(PPh₃)₄, toluene, 1,4-dioxane, 90 °C, 80 min, **2** = 43 %, **3** = 36 %.

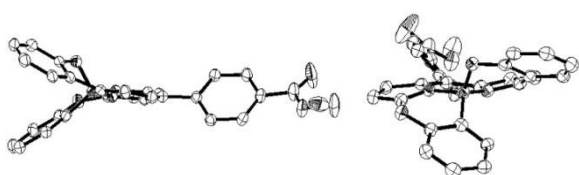


Figure 1. Two views of a molecule in the crystal structure of **(rac)-3** illustrating the asymmetry in the fluorophore core (H atoms are omitted for clarity, *M*-isomer shown).

While investigating improved methods for the synthesis of *N,N,O,O*-boron-chelated dipyrromethenes¹⁹ we examined the Suzuki coupling of **1a** with 2-hydroxyphenylboronic acid.²⁰ Surprisingly, alongside the expected BODIPY **(rac)-2**, we observed the formation, in 8% yield, of an unsymmetrical helically chiral BODIPY **3** containing a previously unreported *tetra-axial* *N,N,O,C*-boron-chelation motif, in which the binding of the one of the 3,5-*ortho*-phenolic substituents is inverted in comparison to that of the parent compound **2**.²¹⁻²³ Switching the starting material to the potentially more reactive 3,5-dibromo-BODIPY **1b**, resulted an improved 36% yield of **(rac)-3**. We propose that **(rac)-3** is formed through a complex series of reaction steps involving: metathesis of the BF₂ group with the boron of (2-hydroxyphenyl)boronic acid, nucleophilic aromatic substitution (S_NAr) of aryl bromide by the phenolic hydroxyl, Suzuki coupling with a second equivalent of (2-hydroxyphenyl)boronic acid and finally chelation of the boron by the free phenolic hydroxyl (Scheme 1).

Crystallization of **(rac)-3** provided material suitable for single crystal X-ray analysis, revealing an orthorhombic space group (Aea2) in which two pairs of enantiomers occupy the unit cell. Analysis of the crystal structure confirmed that the 3,5-*ortho*-phenolic substituents did indeed induce a twist into the fluorophore; a twist angle of approximately 7.7° being observed between the two planes as defined by the two pyrrolic rings (Figure 1).²⁴

Preliminary computational modelling of **(rac)-3** also showed an increase in excited state charge transfer character whilst absorption and emission spectra were consistent with those of a

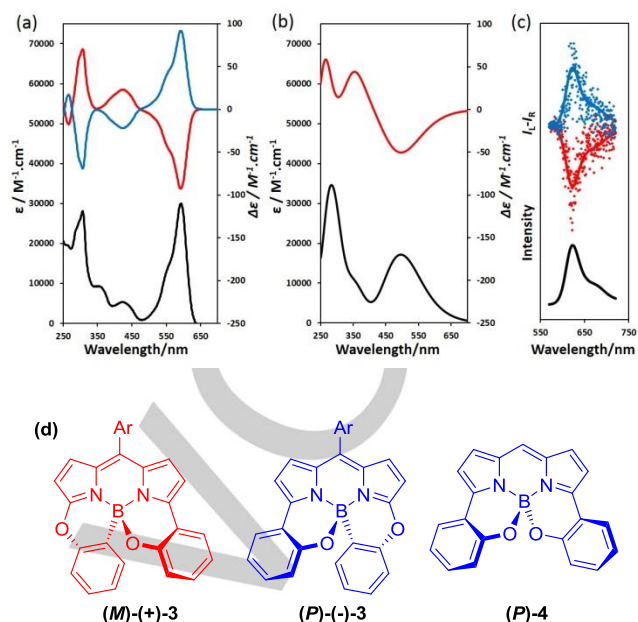


Figure 2. (a) Experimental ECD spectra [red = **(+)-3**, blue = **(-)-3**] and UV/Vis absorption spectra [black = **(rac)-3**]. (b) Calculated Boltzmann-weighted spectra, ECD [red = postulated **(M)-3** (wavelength uncorrected)] and UV/Vis absorption spectra [black = postulated **(M)-3** (wavelength uncorrected)]. (c) Normalised CPL [*I_L-I_R*] [red = **(+)-3**, blue = **(-)-3**] and fluorescence spectra, [black = **(rac)-3**]. (d) Structures of **(M)-(+)-3**, **(P)-(-)-3** and **(P)-4**.

highly fluorescent red-shifted BODIPY dye ($\lambda_{\text{max}}(\text{abs}) = 593 \text{ nm}$, $\lambda_{\text{max}}(\text{em}) = 622 \text{ nm}$, $\gamma = 30,000 \text{ M}^{-1} \text{ cm}^{-1}$ and $Z_F = 0.49$ in hexane) This serendipitous discovery of a stable, highly fluorescent, non-C₂ symmetric, helically chiral BODIPY provided the opportunity to examine the impact of this structural change on the chiroptical properties of the molecule.

Resolution by semi-preparative chiral HPLC gave the dextro- and levorotatory enantiomers **(+)-3** and **(-)-3** respectively by retention time. Mirror image electronic circular dichroism spectra (ECD) were recorded for the two enantiomers, showing good alignment to the UV/Vis absorption spectra of **(rac)-3**. Boltzmann-weighted ECD spectra for the postulated enantiomer were then obtained from TD-DFT calculations at the cam-B3LYP/6-311++G(3df,2pd) level for the *M* enantiomer of **3**, allowing the assignment of **(+)-3** as *M* and thus **(-)-3** as *P* (see ESI). CPL measurements for **(M)-(+)-3** and **(P)-(-)-3** also gave mirror image spectra with a $|g_{\text{lum}}| = 3.7 \times 10^{-3}$, which when combined with the fluorescence quantum yield ($Z_F = 0.49$) gave an overall CPL quantum efficiency ($|g_{\text{lum}}|Z_F$) of 1.8×10^{-3} in hexane (Figure 2).

Cyclic voltammetry of **(rac)-3** was carried out to provide supporting evidence for the involvement of charge transfer in the excited state. Oxidative scans revealed an irreversible one-electron wave with a peak potential of 0.84 V vs Ag/Ag⁺, which can be assigned as a preferential removal of an electron from the dipyrin unit, with a second irreversible oxidation at 1.01 V vs Ag/Ag⁺ suggesting the removal of an electron from the boron-chelated phenoxy rings. This suggests that the observed optical absorption transition is primarily a HOMO-LUMO transition

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localised on the BODIPY core with a charge-transfer state located slightly above the lowest-energy d-d* excited-singlet state (see ESI).

Unfortunately this increase in charge transfer character had not increased the observed $|g_{lum}|$ of **3** as desired, in comparison to the maximum values previously observed for a monomeric *N,N,O,O*-boron-chelated dipyrromethene (e.g. **4**, $|g_{lum}| = 4.7 \times 10^{-3}$, Figure 2).^{15b} To better understand this result, the excited states of both (**P**)-**3** and *N,N,O,O*-boron-chelated dipyrromethene (**P**)-**4** were calculated using DFT(PBE0) using with a def2-TZVP basis set (Table 1) as implemented within the ORCA quantum chemistry package.²⁵ Comparison of these two related molecular systems confirmed the presence of charge transfer character in the excited state of **3** along with the consequential decrease in electric transition dipole moment (μ).

Table 1. Calculated electric (**a**) and magnetic (**m**) transition dipole moments, the angle between them (h) and $|g_{lum}|_{calc}$ in comparison with $|g_{lum}|_{exp}$ for (**P**)-**3** and (**P**)-**4**.

Compound	a/au	m/au	h°	$ g_{lum} _{calc}$	$ g_{lum} _{exp}^a$
3	6.0×10^{-1}	7.3×10^{-4}	70	2×10^{-3}	3.7×10^{-3}
4	7.6×10^{-1}	1.4×10^{-3}	65	3×10^{-3}	4.7×10^{-3}

[a] $|g_{lum}|_{exp}$ given at the respective $\mu \cdot \max(\epsilon_{em})$, measured in hexane.

However any resultant increase in $|g_{lum}|$ had been offset by both a reduction in the magnetic transition dipole moment (**m**) and an unanticipated detrimental change in angle (h) between the two transition dipole moments (from 65° in **4** to 70° in **3**). The decrease in the former (**m**), is larger than that observed for the electric transition dipole moment (μ), due to a reduction in both wavefunction overlap in the case of (**P**)-**3** compared to (**P**)-**4** and in the change in the orbital angular momentum between the ground and excited state. The decrease in **m** of $\sim 50\%$ and change in h combining to give an overall decrease in both the calculated and experimental $|g_{lum}|$ of $\sim 20\%$. Interestingly examination of the calculated electric (**a**) and magnetic (**m**) transition dipole moments of **3** and **4** shows that **m** aligns with the helical axis whilst **a** aligns with the d-system in both molecules, in line with the previously observed orientation of both **a** and **m** in the carbo[*n*]helicenes series (for an animated graphical representation of the direction of both **a** and **m** with respect to the structures of **3** and **4**, see ESI).²⁶ Based on these results we propose that $|g_{lum}|$ in a CPL emissive helically chiral BODIPY maybe indeed be tuneable through the use of synthetic design to dictate both the magnitude and relative direction of **a** and **m** through simultaneous control of both the helical pitch and the extent of d-conjugation in the molecule. Thus the focus of our current research is to apply these new design principles to the synthesis of helically chiral dipyrromethenes with improved chiroptical properties.

Conclusions

We have synthesised the first example of a resolved helically chiral *N,N,O,O*-boron-chelated dipyrromethene and investigated its properties in the context of an efficient small organic molecular emitter of red-shifted circularly polarised light. Despite exhibiting a reduction in their electric transition dipole moment these systems exhibit an overall reduction in $|g_{lum}|$, arising as a consequence of the delicate and complex interplay between **a**, **m** and h . In this case the use of charge transfer states has been shown to be of limited value, as the desired decrease in $|g_{lum}|$ is intrinsically coupled to an undesirable decrease in **m**. Through our comparative investigation of the calculated and experimentally measured chiroptical properties of *N,N,O,O*-boron-chelated dipyrromethene **3** we have demonstrated the need to control **a**, **m** and h in future attempts to maximise CPL efficiency in the CPL-SOMs.

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Keywords: chiral "BODIPY" CPL "helical" ECD

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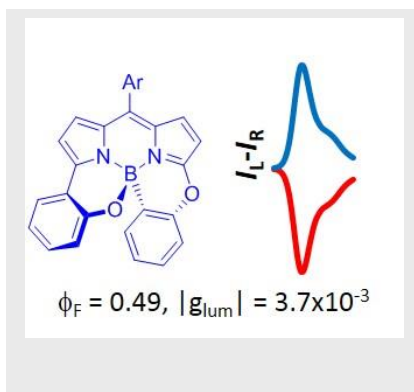
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CPL-SOMs: A helically chiral BODIPY with a *N,N,O,C*-boron-chelation motif is synthesised via a one-pot boron metathesis, nucleophilic aromatic substitution (S_NAr), Suzuki coupling, boron chelation, cascade reaction. Resolution allowed examination of the chiroptical properties ($\lambda_{max}(abs) = 593$ nm, $\lambda_{max}(em) = 622$ nm, $\epsilon = 30,000$ M⁻¹ cm⁻¹, $Z_F = 0.49$, $|g_{lum}| = 3.7 \times 10^{-3}$ (hexane)), demonstrating circularly polarised emission from a non- C_2 symmetric helically chiral BODIPY.



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Circularly Polarised Luminescence from Helically Chiral Γ 7cbZ gYX *N,N,O,C*-Boron-Chelated Dipyrromethenes (BODIPYs)