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Blue Thermally Activated Delayed Fluorescence from a Biphenyl Difluoroboron β -Diketonate

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Abstract

Optical properties of biphenyl difluoroboron β -diketonates were studied in poly(lactic acid) (PLA) blends. Increased conjugation lowered the emission energy, decreased the singlet-triplet energy gap and yielded blue thermally activated delayed fluorescence (TADF). The properties of these biphenyl dyes may inform organic light emitting diode (OLED) and bioimaging agent design.

Many applications benefit from the development of multicolour luminescent materials, such as bioimaging and displays. In bioimaging, fluorophores with distinct excitation and emission wavelengths can be used simultaneously, yet observed independently. This eliminates signal crosstalk, important for multiplexing in cell biology. For example, a DNA stain with blue fluorescence (4',6-diamidino-2'-phenylindole dihydrochloride; DAPI), an immunostain with green fluorescence (i.e. Alexa Fluors), and an oxygen sensor with red phosphorescence (i.e. platinum(II) 5, 10, 15, 20-tetrakis(pentafluorophenyl)porphyrin; PtPFPP) were used to correlate oxygen levels with target molecules of interest in cells with minimal signal interference.¹ While cell biology requires distinct red, green and blue (RGB) fluorophores to differentiate regions of interest, the summation of all three colours, blended, patterned or layered, is used to generate white light in organic light emitting diodes (OLEDs). In a report by Chujo et al., three RGB-emitting boron dyes, including a difluoroboron β -diketone (BF₂bdk) with blue fluorescence, a boron dipyrromethene (BODIPY) with green fluorescence and a boron di(iso)indomethene (BODIN) with red fluorescence, were combined to produce white light OLEDs.² Therefore, RGB dyes with unique optical properties can provide new opportunities for both imaging and OLED applications.

In emerging OLED devices, the most efficient materials utilize both the prompt and delayed emissions to overcome limitations from electronic excitation.³ For inorganic complexes, heavy atoms such as iridium or platinum enhance the rate of intersystem crossing (ISC) to siphon energy from the singlet-excited state to the triplet-excited state, producing primarily phosphorescence (no fluorescence). Because phosphorescence is inherently lower in energy

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than the fluorescence (redder decay), phosphorescence - based organic light emitting diodes (PHOLEDs) tend to be more green or red, making blue PHOLEDs very rare. In contrast to PHOLEDs that use heavy atoms to enhance phosphorescence and diminish the fluorescence, purely organic (heavy atom free) OLEDs access reverse intersystem crossing (RISC) to produce thermally activated delayed fluorescence (TADF). The TADF process siphons energy from the triplet-excited state to the singlet-excited state, diminishing phosphorescence and enhancing the fluorescence, to generate OLEDs more blue in nature. Purely organic luminophores are an emerging class of materials in this field to overcome the colour limitations of organometallic complexes. For example, Adachi and co-workers have pioneered the field of blue TADF emitters for OLED use.⁴ In particular, a 1,3,5-triazene with pendant phenyl-conjugated carbazoles produced a highly efficient electroluminescent device with external quantum efficiency of 20.6 % ($\pm$ 1.8%).⁵

Donor-acceptor (D-A) molecules, such as benzophenones,⁷ naphthalene diimides⁸ and sulfones,⁹ are organic dyes with the ability to access the triplet state for OLED and bioimaging. Carbonyl-based difluoroboron β -diketonates (BF₂bdks) have high extinction coefficients, efficient quantum yields and good photostability, making the dyes well suited for biological imaging^{10,11} as well as electronic devices.¹² For bioimaging, BF₂bdks have been used to spatially resolve differences in polarity,¹³ viscosity,¹⁴ metal analytes,¹⁵ and oxygen¹⁶ in living cells. In particular, when the dyes are confined to a rigid matrix, such as poly(lactic acid) (PLA), a polymer commonly used in biomedical applications, the BF₂bdks have both fluorescence and oxygen-sensitive room temperature phosphorescence (RTP).¹⁷ These single component, dual emissive BF₂bdkPLA materials were employed to quantify oxygen in cells and tumours via ratiometric techniques. We hypothesized that the oxygen sensitive RTP is activated by a restriction of molecular rotations in the amorphous PLA matrix (T_g = $\sim$ 60 °C), because in organic solvents (i.e. CH₂Cl₂) and poly(ϵ -caprolactone) (PCL) with a low glass transition temperature (T_g = $\sim$ 60 °C) RTP is not observed.¹⁸ Along with RTP, in heavy atom-free BF₂bdks, TADF is also observed as a result of RISC. Previous efforts from our group to obtain multicolour BF₂bdk derivatives employed aromatic π -conjugation as a general approach to red-shift emission (i.e. phenyl vs. naphthyl vs. anthracyl). With increased conjugation (naphthyl-naphthyl (dnm) vs phenyl-phenyl (dbm) dyes), the fluorescence red-shifted, however, the RTP surprisingly blue-shifted (i.e. λ_{RTP} ; BF₂dbmPLA = 506 nm, BF₂dnmPLA = 490 nm).^{11,16} For BF₂dnmPLA, the blue/green delayed emission was determined to be TADF, as the delayed emission at 77K (low temperature phosphorescence; LTP) red-shifted (585 nm). Given the molecular similarities of the dye with the classic TADF emitters (i.e. carbonyl, D-A), it is possible that the larger aromatic groups can destabilize planarization, causing a more twisted structure. Both dye planarization and π -conjugation have competing roles in producing TADF or RTP, and are important considerations in the design of next generation BF₂bdk materials.

In this report, we extend our work with π -conjugated materials using biphenyl substitution. In the crystal structure of a biphenyl boron dye elucidated by Mirochnik et al., a slight twist was observed between the two phenyl groups of the biphenyl moiety in the ground state.¹⁹ Systematic substitution of phenyl groups may provide insights into how these dyes interact within a polymer matrix. We hypothesized that a twisted structure induced by the biphenyl groups might result in blue-shifted delayed emission (TADF), whereas planar structures may

produce red-shifted delayed emission (RTP). Compounds **1** – **5** are characterized in PLA blends to evaluate potential OLED and bioimaging capabilities. Twisting-induced blue TADF will result in promising materials in OLEDs, while conjugation-induced red-shifted RTP can provide new scaffolds for developing dual-emissive oxygen sensors.

The dyes were prepared in two steps as previously described.^{19–21} First, a Claisen condensation was performed with the appropriate ketone-ester pair to generate the β -diketonate ligand. Then, boron coordination was achieved in anhydrous dichloromethane in the presence of boron trifluoride diethyl etherate to generate the difluorodioxaborine dye (e.g. Scheme S1). Solution spectral data (e.g. ¹H NMR, UV/Vis, fluorescence) of the ligands and boron dyes were in accordance with literature values. To analyse the solid-state luminescence properties, where dye-dye interactions play important roles in tuning the fluorescence maxima, blends of each dye were prepared in PLA. The polymer serves to activate the delayed emission at room temperature; the delayed emission is not observed in the dye powders or organic solvents (i.e. CH₂Cl₂).^{18,22} The blends also serve as models for dye-PLA conjugates.²⁰ Dye blends were prepared at three dye loadings (weight percent of dye; 5%, 2%, and 1%) (Figure S1). The fluorescence of the dye/PLA blends is dependent on both dye structure and dye loading. Different dye loadings correspond to variations in dye-dye interactions as previously described.^{16,23} At high dye loadings, increased dye-dye interactions resulted in red-shifted emission compared to the dilute dye/PLA blends. When the π -conjugation is increased, a larger range of fluorescence maxima can be achieved. In particular, the bis-biphenyl derivative, BF₂dbpm (**5**), can span from teal (510 nm) to blue (450 nm) fluorescence wavelengths. The less conjugated BF₂dbm showed a smaller range of colours in the PLA matrix (Figure S1, 420 nm to 396 nm). It is possible that the additional aromatic character increased the propensity of the dye to aggregate in the PLA matrix, a common observation in dye-PLA conjugates with naphthalene aromatic groups.¹⁶

The optical properties of the 1% dye/PLA blends are summarized in Table 1. Fluorescence wavelength is highly dependent on the number of phenyl rings in the dye structure. For example, when the 1% blends are analysed, BF₂mbm (one ring) had the most blue-shifted fluorescence at 371 nm. The addition of rings in BF₂dbm (**2**) and BF₂bpmm (**3**) resulted in

red-shifted fluorescence (λ_F ; **2** = 396 nm, **3** = 405 nm). This trend continued for dyes with three rings (BF₂bpbm; **4**) and four rings (BF₂dbpm; **5**) in the aromatic backbone of the dye (λ_F ; **4** = 440 nm, **5** = 451 nm). In summary, extending conjugation through the addition of *para*-substituted phenyl rings is an effective way to tailor the fluorescence wavelengths.

Similar to the fluorescence, the room-temperature phosphorescence of the dyes also was dependent on dye structure. When 1% blends were studied under N₂ at room temperature, oxygen-sensitive phosphorescence wavelengths between 478 nm and 536 nm were achieved (Figure 1). In general, a red-shift in phosphorescence was observed with the addition of phenyl groups to the ligand scaffold. Compounds BF₂dbm (**2**) and BF₂bpmm (**3**) had the same number of phenyl rings (i.e. two), but BF₂bpmm (**3**) had a longer phosphorescence wavelength (**2** = 491 nm, **3** = 516 nm). This shows that extending conjugation along a single aromatic unit is a more effective means of red-shifting the phosphorescence than adding aromatic groups to both sides of the dioxaborine. This trend is likely a reflection of the energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of biphenyl compared to phenyl groups, as a biphenyl will have a smaller transition and therefore a redder emission.²¹ However, if a dye is already substituted with biphenyl on one side of the dioxaborine, additional phenyl groups on the other side can red-shift the phosphorescence (λ_P ; **4** = 529 nm, **5** = 536 nm).

While extended phenyl conjugation can tune the phosphorescence, it also decreases the singlet-triplet energy gap (E_{ST} , Table 1). Compound **1**, BF₂mbm, with a single phenyl ring had the largest gap (0.748 eV), while compound **5**, BF₂dbpm, with four phenyl rings had the smallest (0.436 eV). The change in the energy gap played a defining role in the delayed emission properties of these materials. In compound **5**, two distinct peaks were present in the delayed emission spectra under nitrogen at room-temperature, while only one peak was observed in the total emission spectrum under air. We hypothesize the blue-shifted peak is thermally activated delayed fluorescence (TADF; $\lambda_{TADF} \approx 450$ nm), and the redder transition is the room temperature phosphorescence (RTP) from the dye ($\lambda_{RTP} = 536$ nm). A blue peak is also observed for BF₂bpbm (**4**) around 440 nm, which may correspond to weak TADF. A larger energy gap (~0.4 eV) is characteristic of TADF-emitting BF₂dbks yet unconventional compared to most TADF materials, which typically have singlet-triplet energy gaps below 0.3 eV.^{16,20,24,25,26,27}

The TADF properties of BF₂dbpm (**5**) were confirmed by investigating the temperature and dye loading dependence of the delayed emission under nitrogen (Figure 2). No significant changes were observed in the delayed emission spectra under nitrogen of compound **5** in PLA films for various dye loadings. However, when the sample was submerged in liquid nitrogen (77 K) thermal back population was eliminated, resulting in only phosphorescence at 535 nm in the delayed emission spectrum. Conversely, when the sample was heated (< 60 °C), reverse intersystem crossing was promoted. Thus, TADF became the dominant feature in the delayed emission to produce a blue afterglow. Prolonged heating quenched all delayed emission. When PLA is heated above the glass transition temperature ($T_g = \sim 60$ °C), all delayed emission is turned off as a result of a change in the matrix and availability of non-radiative decay pathways.¹⁸ In previous work, Adachi *et al.* reported that enhanced twisting in a molecule induces TADF.⁷ We hypothesize that the enhanced TADF

of BF₂dbpm (**5**), compared to other dyes in this series, may be due to more opportunities for twisted conformations. For example, the TADF of BF₂bpbm (**4**) is noticeable, but much weaker than BF₂dbpm (**5**) as seen in the delayed emission spectra in Figure 3.

Density Functional Theory (DFT) calculations further support the TADF exhibited in the BF₂dbpm (**5**) (Figures S5 and S6, Tables S1-S4).²⁸ The geometry of the dye in the ground state shows twisting ($\theta_{S0} = 36^\circ$) about the phenyl-phenyl bond of the biphenyl moieties (Figure 3). In the HOMO, the electron density is delocalized around the phenyl rings. Electron density of the LUMO is localized around the dioxaborine subunit. Furthermore, from the ground state to the singlet excited state, a change in the torsion angles between the phenyl moieties on either half of the dye was observed. The dye appeared to planarize slightly upon excitation ($\theta_{S1} = 24^\circ$). These twisted structures, coupled with the charge transfer character induced by the dioxaborine moiety, produce twisted intramolecular charge transfer (TICT), a feature commonly linked to blue TADF emitting materials.²⁹

The phosphorescence lifetimes of the samples showed no apparent trends based on dye-structure or the E_{ST} . Noteworthy though, to our knowledge, compound **4** showed the longest room temperature phosphorescence lifetime ($\tau_p = 826$ ms) recorded for a boron β -diketone dye (Figure S7) in the literature. This long lifetime dye material could have potential applications in hypersensitive oxygen detection or organic light emitting diodes with extended delays.³⁰

Conclusions

In this report, five boron dyes were prepared via two -step synthesis. The optical properties of the dyes were studied in dilute PLA blends. Various fluorescence colours were achieved (400-500 nm), while the most conjugated derivative, BF₂dbpm (**5**), showed the greatest range upon varying the dye content in PLA ($\lambda_F = 60$ nm). This may be due to increased π -interactions and a greater propensity for these dyes to self-aggregate in the polymer matrix. Phosphorescence wavelengths were tuneable through extended π -conjugation. The addition of phenyl groups (2-4 rings) resulted in phosphorescence peaks ranging from 479 nm to 536 nm. Along with red-shifted phosphorescence, increased conjugation yielded thermally activated delayed fluorescence. The biphenyl rings are capable of producing TADF through molecular twisting, which is a common feature in TADF-OLED dyes.⁷ While trends in phosphorescence lifetimes of the dyes were noted, to our knowledge, BF₂bpbm (**4**) exhibited the longest phosphorescence lifetime recorded for a BF₂bdk at room-temperature.

These findings expand our understanding of BF₂bdk dyes in PLA. The materials showed a range of phosphorescence wavelengths ($\lambda_{RTP} = 58$ nm). Calculations (DFT) suggested that the phenyl groups are also free to twist and produce TADF. With rare blue TADF at 450 nm, these systems offer inspiration for OLED materials design. Furthermore, heavy atom substitution (Br, I) would likely suppress the TADF and yield strong RTP emitting materials.¹¹ In this way, these biphenyl-substituted boron dyes have potential for both RTP and OLED applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Fluorescence in air (A) and delayed emission spectra (RTP, TADF) under nitrogen (B) for dyes **1-5** as 1% dye/PLA thin films (λ_{ex} : **1** = 340 nm; **2-5** = 369 nm).

Figure 2.

Temperature dependent delayed emission of BF₂dbpm (5) as a 1% dye/PLA thin film under nitrogen. (Spectra: λ_{ex} = Xenon flash lamp, 369 nm, 2 ms delay. Images: λ_{ex} = 369 nm; UV lamp; taken immediately after UV lamp was turned off.)

Figure 3. DFT calculations of the optimized geometry of BF₂dbpm (**5**) and the torsion angles in the ground state ($\theta_{S_0} = 36^\circ$) compared to the singlet excited state ($\theta_{S_1} = 24^\circ$) (A). Molecular orbital diagrams of BF₂dbpm (**5**) (B).

Table 1

Luminescence Properties of 1% Dye/PLA Blends

BF₂bdk	λ_F^a (nm)	τ_F^b (ns)	λ_P^c (nm)	τ_P^d (ms)	E_{ST}^e (eV)
1	371	<i>f</i>	478	<i>f</i>	0.748
2	396	1.70	491	282	0.606
3	405	1.29	516	172	0.659
4	440	1.61	529	826	0.474
5	451	1.16	536	320	0.436

^aFluorescence maxima in air (λ_{ex} = 369 nm, except for **1**; λ_{ex} = 350 nm).^bFluorescence lifetime in air (λ_{ex} = 369 nm LED).^cPhosphorescence maxima at room temperature under nitrogen (λ_{ex} = Xenon flash lamp, 369 nm, 2 ms delay).^dPhosphorescence lifetime monitored at the phosphorescence maxima under nitrogen.^eEnergy gap between the singlet and triplet states^fLifetime too short or weak for detection (Figure S2).