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Full Paper

Thienyl Difluoroboron β-Diketonates in Solution and Polylactide Media*

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Difluoroboron β -diketonates (BF₂bdks) have impressive optical properties in both solution and the solid state. In particular, both fluorescence and room-temperature phosphorescence are present when the dyes are confined to a rigid matrix, such as poly(lactic acid) (PLA). To expand the current knowledge and colour range capabilities of this unique type of multi-emitting chromophore, a series of thienyl-substituted BF₂bdk complexes have been synthesized. The photophysical properties were investigated in dichloromethane solution and in the solid state as dye/PLA blends. By varying donor ability, i.e. methyl, phenyl, methoxy, and thienyl substituents, and by changing the dye loading in the PLA media (0.1–10 % dye loading) red-shifted emission was achieved, which is important for biological imaging applications. In dilute CH₂Cl₂ solution, complexes exhibited absorptions ranging from 350 to 420 nm, solid-state fluorescence in PLA ranging from 390 to 500 nm, and oxygen sensitive phosphorescence ranging from 540 to 585 nm in PLA blends. Promising candidates as dye/PLA blends serve as models for dye–polymer conjugates for application as biological oxygen nanoprobes.

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Introduction

The chemistry of boron-based materials has attracted significant interest, as tetra-coordinated boron complexes are at the forefront of advanced functional materials.^[1–3] For example, boron β -diketonates show strong emission in both solution and the solid state.^[4,5] In solution, difluoroboron β -diketonates (BF₂bdks) display large molar extinction coefficients,^[6,7] two-photon cross-sections,^[8,9] and high quantum efficiencies.^[10] Because of these desirable features, these materials have shown promise as molecular probes,^[11,12] organic lightemitting diodes (OLEDs),^[13,14] memory devices,^[15] and stimuli-responsive materials.^[16,17]

To tune the emissive properties of BF_2 complexes, a broad variety of chemical modifications have been investigated. One approach involves altering the ligand scaffold, such as extending the π -conjugation and/or the addition of heavy atoms.^[18] Anciliary ligands coordinated to the boron centre have also been studied; phenyl,^[19] pentfluorophenyl,^[20] or cyano groups^[21] have been explored. Some of these modifications lead to a smaller HOMO–LUMO energy gap, providing red-shifted absorption and emission. Such optical properties can expand the utility of BF₂bdks in biological applications, given deeper tissue penetration, reduced interference from auto-fluorescence, and minimal photo-damage to biological materials.^[22,23] However, extending the emission properties to the deep red or to the near-IR region by modifying the π -conjugation has limitations, such as thermally activated delayed fluorescence (TADF), which makes ratiometric oxygen sensing more challenging.^[24] Therefore, it is important to investigate new fluorophore scaffolds to gain meaningful insights into the design of dual emissive materials, with the hope of finding different ways to red-shift emission.

When BF₂bdks are confined to a rigid matrix, both fluorescence, and oxygen sensitive, room-temperature phosphorescence (RTP) can be present.^[5,25] In particular, BF₂bdks exhibit RTP in rigid poly(lactic acid) (PLA) media, a biodegradable polyester commonly used in biomedical applications. Large Stokes shifts, controllable oxygen sensitivity, and high colour tuneability make these single-component materials ideal candidates for oxygen sensing, for example, for tumour hypoxia imaging.^[18,24,26,27]

Current BF₂bdk–PLA materials have colour limitations, being that they emit mainly in the blue to yellow portion of the visible spectrum.^[27] Thiophene-based tetra-coordinated boron complexes have promising absorption and emission properties, making them a logical extension of dual-emissive

^{*}Dedicated to the memory of Professor Brice Bosnich, Cassandra Fraser's Ph.D. advisor at The University of Chicago, whose high standards, attention to detail, forthrightness, and thoughtful approach continue to inspire.

material design.^[28] For example, Yam et al. have reported the synthesis of a thienyl difluoroboron diketonate with near-IR photochromic properties,^[29] and a solution processable, dual-boron core memory device.^[15] Furthermore, Zhang et al. reported a synthetic strategy of forming β -diketone initiators via a one-step Claisen condensation between 2-acetylthiophene and ε-caprolactone, followed by lactide polymerization from the resulting hydroxy functionalized boron dye.^[30] The dyefunctionalized polymer thus obtained showed intense blue fluorescence ($\lambda_{max} = 397 \text{ nm}$) and green phosphorescence $(\lambda_{\rm RTP} = 530 \, \rm nm)$ under vacuum. Thiophene-based materials, mainly oligo- and polythiophenes, are most versatile conjugated materials.^[31,32] Weak emission in these materials is typically attributed to the inclusion of the heavy sulfur atom, as well as the efficient solid-state packing characteristic for thiophene-based materials, shown by Ono et al.^[33,34] However, the presence of an electron-rich thienyl ring can act as an electron-donating group, and the heavy atom inclusion may assist favourable dualemissive properties when confined to a rigid matrix.

Our investigation of boron β -diketonates and their structure– property relationships continues with a set of thienyl-substituted dyes presented herein. One aromatic unit is set as a thienyl group, while the opposing side is varied (i.e. methyl, phenyl, methoxyphenyl, and thienyl substituents), analogous to previously designed dyes (Chart 1).^[35]

Photophysical properties of the dyes are studied in CH_2Cl_2 solution and supported by computational results utilising density functional theory (DFT). To study the dual emissive properties, thienyl dyes were blended with PLA. This models how a dye–PLA conjugate would behave and serves as a valuable test and precursor to dye–polymer conjugate materials. Optical properties are tuned in two ways, by varying the dye scaffold, and by varying dye loading in PLA matrices. The purpose of attaching the C12 alkyl chain is to observe variations in dye aggregation, since C12 is a good solubilizing group.^[7] Dual emissive properties were analyzed for all dye/PLA blends, in order to identify good candidates for dual emissive oxygen sensitive nanoprobes.^[36]



5: BF₂dtm

Chart 1. Thienyl difluoroboron β -diketonates.

Experimental

Materials

Solvents CH₂Cl₂ and THF were dried over 3 Å molecular sieves that had been activated at 300° C.^[37] All other solvents were used as received without further purification. Boron trifluoride diethyl etherate (Aldrich, purified, redistilled) and other chemicals were reagent grade from Sigma Aldrich (methyl benzoate, methyl 4-hydroxybenzoate, methyl 4-methoxybenzoate, 1-bromododecane) and Alfa Aesar (2-acetylthiophene) and were used without further purification. Methyl 4-dodecyloxybenzoate was prepared via a Williamson ether synthesis as previously described.^[7] Ligands 1-(thiophen-2-yl)butane-1,3-dione (mtm),^[38] 1-phenyl-3-(thiophen-2-yl)propane-1,3-dione (tbm),^[39] 1-(4-methoxyphenyl)-3-(thiophen-2-yl)propane-1,3-dione (tbmOMe),[40] and 1,3-di(thiophen-2-yl)propane-1,3-dione (dtm)^[34] have been previously reported and the ¹H NMR data are in accordance with the literature. All BF2bdks 1-5 were obtained via the reaction of the appropriate ligand and boron trifluoride diethyl etherate in anhydrous CH_2Cl_2 solution, under nitrogen. Complex 5 was prepared as previously reported.^[34] The ¹H NMR spectra of previously reported ligands and dyes are in accordance with the literature. PLA (~13 kDa; polydensity index (PDI) = 1.02) was synthesized from ethylene glycol as previously described.^[24]

Methods

¹H NMR spectra were recorded on a Unity Inova 300/51 instrument (300 MHz), or Varian VMRS/600 (600 MHz) in CDCl₃. Resonances were referenced to the signal for the residual protiochloroform peak at 7.26 ppm. ¹H NMR peak frequencies are reported in ppm (δ) and coupling constants in Hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constant (Hz), and integration. Mass spectrometry (MS) was performed on a Micromass Q-TOF Ultima spectrometer using electrospray ionization (ESI) MS techniques. UV-Vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer in CH₂Cl₂. Steady-state fluorescence emission spectra were recorded on a Horiba Fluorolog-3 model FL3-22 spectrofluorometer (doublegrating excitation and double-grating emission monochromators). The data were analysed using FluorEssence v 2.1 software also from Horiba Jobin Yvon. Phosphorescence spectra were recorded with the same instrument except that a pulsed xenon lamp ($\lambda_{ex} = 369 \text{ nm}$; duration < 1 ms) was used for excitation, and spectra were collected with a 2 ms delay after excitation. Fluorescence lifetime measurements (time correlated single-photon counting, TCSPC) were performed with a NanoLED-370 (369 nm) excitation source and DataStation Hub as the SPC controller. Phosphorescence lifetimes were measured with a 500 ns multichannel scalar card (MCS) excited with a pulsed xenon lamp ($\lambda_{ex} = 369 \text{ nm}$; duration < 1 ms). Lifetime data were analysed with DataStation v 2.4 software from Horiba Jobin Yvon. Thin films of dye/PLA blends were prepared on the inner wall of vials by dissolving dyes and PLA in CH₂Cl₂ to form a homogeneous solution and then evaporating the solvent by slowly rotating the vial under a stream of nitrogen. The films were dried under vacuum for 30 min before further measurements. Lifetimes were fit to single exponential decays in solution (fluorescence) and to double or triple exponential decays in solid-state films (fluorescence/total emission and phosphorescence). Fluorescence quantum yields (Φ_F) were calculated versus anthracene in EtOH as a standard using the following values: $\Phi_{\rm F}$ (anthracene) = 0.27,^[41] $n_{\rm D}^{20}$ (EtOH) = 1.361, $n_{\rm D}^{20}$ (CH₂Cl₂) = 1.424.^[42] Optically dilute CH₂Cl₂ solutions of BF₂ complexes **1–5** and EtOH solutions of the anthracene standard were prepared in 1 cm path length quartz cuvettes, and absorbances (A < 0.1, a.u.) and emission spectra ($\lambda_{\rm ex} = 350$ nm; emission integration range: 365–650 nm) were recorded. BF₂ complexes **1–3** were modelled using the *Gaussian 09* suite of programs utilising DFT.^[43] B3LYP/6–31+G(d) was employed for ground state geometry optimization of all compounds with a Tomasi polarized continuum for dichloromethane solvent. Single point energy calculations were used to generate the molecular orbital diagrams utilising 6–31G(d). Time-dependent density functional theory (TD-B3LYP/6–311+G(d)) was used for estimating the absorption spectra in dichloromethane at the optimized ground state geometries.^[44,45] Molecular orbitals were depicted by *GaussView 5* software.^[46]

Synthesis

1-(4-(Dodecyloxy)phenyl)-3-(thiophen-2-yl)propane-1,3-dione (tbmOC12)

Acetylthiophene (1.0 g, 7.92 mmol), methyl 4-dodecyloxybenzoate (3.0 g, 9.51 mmol), and THF (25 mL) were added sequentially to a 100 mL round-bottom flask. After the mixture was stirred for 10 min, a suspension containing NaH (380 mg, 15.8 mmol) in THF (20 mL) was added via cannula at room temperature under N_2 . The reaction was refluxed at 60°C in a nitrogen atmosphere, and monitored by TLC. Upon consumption of the limiting reagent, 2-acetylthiophene (21 h), the reaction mixture was removed from the heat and allowed to cool to room temperature and quenched with 1 M HCl (1 mL, pH 6-7). The THF was removed via rotary evaporation. Organics were extracted with CH_2Cl_2 (20 mL \times 2), washed with H_2O (20 mL \times 2) and brine (10 mL), and then dried over Na₂SO₄. After filtration and concentration under vacuum, the residue was purified by column chromatography on silica gel eluting with toluene/hexanes (5:1) to give an ivory solid (1.35 g, 41 %). $\delta_{\rm H}$ (600 MHz, CDCl₃) 16.51 (s, 1H, -OH), 7.90 (d, J 9.0, 2H, -ArH), 7.77 (d, J 3.6, 1H, -ArH), 7.60 (d, J 5.1, 1H, -ArH), 7.16-7.15 (m, 1H, -ArH), 6.95 (d, J 9.0, 2H, -ArH), 6.61 (s, 1H, -COCHCO-), 4.01 (t, J 6.6, 2H, -ArOCH₂-), 1.82–1.77 (m, 2H, -OCH₂CH₂-), 1.25 (br m, 18H, -C₉H₁₈-), 0.87 (t, J 6.3, 3H, -CH₂CH₃). HRMS (ESI, TOF) m/z 415.2302; calcd for $C_{25}H_{35}O_3S [M + H]^+$ 415.2307.

All BF₂bdks were obtained via the reaction of the appropriate ligand 1–5 and boron trifluoride diethyl etherate in CH_2Cl_2 solution under nitrogen. A representative reaction is provided for BF₂mtm (1).

$BF_2mtm(1)$

Boron complex 1 was prepared by dissolving 1-(thiophen-2-yl) butane-1,3-dione (mtm) (80 mg, 0.48 mmol) in anhydrous CH₂Cl₂ (25 mL) in an oven-dried 50 mL round bottom flask. Boron trifluoride diethyl etherate (88 μ L, 0.71 mmol) was added via syringe and the solution turned brown. The reaction mixture was stirred at room temperature and monitored by TLC until the ligand was consumed (20 h). The reaction mixture was filtered and the solvent was removed by rotary evaporation. The product was purified by column chromatography with hexanes/EtOAc (3 : 1) as the eluent. A light yellow powder was obtained: 69 mg (67 %). $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.01 (d, *J* 3.9, 1H, -ArH) 7.88 (d, *J* 5.1, 1H, -ArH) 7.26–7.24 (br, 1H, -ArH) 6.36 (s, 1H, -COCHCO-) 2.38 (s, 3H, -COCH₃). HRMS (ESI, TOF) *m/z* 197.0244; calcd for C₈H₇BO₂FS [M – F]⁺ 197.0244.

$BF_2tbm(\mathbf{2})$

Boron complex **2** was prepared as described for **1**, using 1-phenyl-3-(thiophen-2-yl)propane-1,3-dione (tbm) as the ligand. The resulting complex was purified by recrystallization from hexanes to give a yellow powder: 61 mg (64%). $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.14–8.10 (m, 3H, -ArH) 7.90 (d, *J* 4.8, 1H, -ArH) 7.71–7.67 (m, 1H, -ArH) 7.58–7.53 (m, 2H, -ArH) 7.30–7.27 (m, 1H, -ArH) 6.98 (s, 1H, -COCHCO-). HRMS (ESI, TOF) *m/z* 259.0399; calcd for C₁₃H₉O₂SBF [M – F]⁺ 259.0400.

BF₂tbmOMe (3)

Boron complex **3** was prepared as described for **1** using 1-(4methoxyphenyl)-3-(thiophen-2-yl)propane-1,3-dione (tbmOMe) as the ligand. The product was purified by column chromatography using CH₂Cl₂ as the eluent to give a yellow powder: 86 mg (80%). $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.12 (d, *J* 9.3, 2H, -ArH), 8.05 (d, *J* 3.9, 1H, -ArH), 7.83 (d, *J* 5.1, 1H, -ArH), 7.26–7.24 (m, 1H, -ArH), 7.03 (d, *J* 9.3, 2H, -ArH), 6.90 (s, 1H, -COCHCO-), 3.94 (s, 3H, -ArOCH₃). HRMS (ESI, TOF) *m*/*z* 289.0505; calcd for C₁₄H₁₁BO₃FS [M – F]⁺ 289.0506.

BF₂tbmOC12 (4)

The complex **4** was prepared as described for **1** using 1-(4-(dodecyloxy)phenyl)-3-(thiophen-2-yl)propane-1,3-dione (tbmOC12) as the ligand. The resulting complex was purified by recrystallization from hexanes to give a yellow powder: 178 mg (80%). $\delta_{\rm H}$ (600 MHz, CDCl₃) 8.10 (d, *J* 9.0, 2H, -ArH), 8.04 (d, *J* 3.9, 1H, -ArH), 7.81 (d, *J* 4.8, 1H, -ArH), 7.25–7.24 (m, 1H, -ArH), 7.00 (d, *J* 9.0, 2H, -ArH), 6.87 (s, 1H, -COCHCO-), 4.06 (t, *J* 6.0, 2H, -ArOCH₂), 1.84–1.79 (m, 2H, -OCH₂*CH*₂-), 1.26 (br m, 18H, -C₉H₁₈-), 0.88 (t, *J* 6.6, 3H, -CH₂*CH*₃). HRMS (ESI, TOF) *m/z* 443.2231; calcd for C₂₅H₃₃O₃SBF [M - F]⁺ 443.2228.

Results and Discussion

Synthesis

The complexes 1–5 were obtained via a two-step synthesis. Claisen condensation in the presence of NaH in THF generated the β -diketone ligands followed by boronation with BF₂·OEt₂ in CH₂Cl₂. All of the ligands were obtained as tan solids and the complexes as yellow powders. ¹H NMR and MS analysis confirmed the structure and purity of the ligands and boron complexes.

Optical Properties in Solution

Optical properties of dyes 1–5 were first investigated in dilute CH_2Cl_2 solutions (10⁻⁶ M, A < 0.10) in air and at room temperature. Highly dilute solutions prevent aggregation or exciplex formation. Solution data are presented in Table 1 and Fig. 1.

All boron complexes absorb light in the UV to violet range. Stronger absorption and bathochromic emission were obtained with increasing donor ability. The alkyl chain length in **3** versus **4** did not significantly affect the absorption bands (417 and 418 nm, respectively). The absorbance trend of dyes **1**–**4** was similar to that observed for previously reported BF₂bdk complexes.^[43] The exchange of a thienyl ring for a phenyl or naphthyl aromatic group resulted in red-shifted absorption, important for biological imaging. This may be assigned to the sulfur atom acting as a donor, thus raising the energy of the HOMO.

Table 1. Optical properties of boron complexes 1-5 in CH₂Cl₂

Sample		λ_{abs}^{A} [nm]	$\epsilon^{\rm B}[M^{-1}cm^{-1}]$	λ_{em}^{C} [nm]	$ au_{ m F}^{ m D}$ [ns]	$\Phi^{\rm E}_{\rm F}$
BF ₂ mtm	1	354	44 000	392	0.18	0.04
BF ₂ tbm	2	401	46 400	416	1.83	0.31
BF ₂ tbmOMe	3	417	56 000	441	2.06	0.38
BF ₂ tbmOC12	4	418	61 900	445	2.08	0.71
BF ₂ dtm	5	420	57 200	438	1.02	0.39

^AAbsorption maxima.

^BExtinction coefficients calculated at the absorption maxima.

 $^{\rm C}{\rm Fluorescence}$ emission maxima excited at 369 nm (except 1, excited at 350 nm).

^DFluorescence lifetime excited with a 369 nm light-emitting diode (LED) monitored at the emission maximum. All fluorescence lifetimes are fitted with single-exponential decay.

^ERelative quantum yield, with anthracene in EtOH as a standard.



Fig. 1. Optical properties in CH₂Cl₂. (a) Absorption spectra in CH₂Cl₂ (1×10^{-6} M). (b) Image of BF₂ complexes 1–5 in CH₂Cl₂ upon 365 nm light irradiation. (c) Steady-state emission spectra in CH₂Cl₂.

The absorbances of dyes **3** and **4**, containing terminal alkoxy groups, were slightly blue-shifted compared with **5**, as reported by Ono et al.^[34] This may suggest that the alkoxy-substituted phenyl rings and the thiophene moieties possessed similar electron donation and molecular geometry, for example, planarity in their ground states. The thienyl complexes **1–5** have high extinction coefficients (44000–61900) typical for π to π^* transitions, also characteristic for thiophene-based systems, such as oligothiophenes.^[34]

The fluorescence spectra for complexes 1–5 exhibited violetblue emission in CH₂Cl₂ ranging from 392–445 nm, and systematically displayed red-shifts with an increase of conjugation and donor ability (i.e. in CH₂Cl₂, λ_{Abs} : 1 = 354 nm, 2 = 401 nm, 3 = 417 nm, 4 = 418 nm, and 5 = 420 nm). Thienyl (5) and alkoxy-phenyl (3 and 4) derivatives had similar optical properties in CH₂Cl₂, suggesting that the two rings have similar electronic character.

As shown in Table 1, the fluorescence quantum yields and lifetimes increased with increasing electron donation for dyes 1–4. The quantum yield of complex 5 ($\Phi_F = 39.0$ %) was similar to the methoxy-substituted dye 3 ($\Phi_F = 38.0$ %). Overall, low quantum yields were characteristic for thiophene-based materials, compared with dbm-type boron dyes, which often have intense emission and quantum yields near unity.^[10] This can be attributed to fluorescence quenching due to the heavy atom effect of the sulfur atom. Complexes 2–4 have fluorescence lifetimes between 1.82 and 2.08 ns, similar values to symmetrically substituted phenyl BF₂bdks (~2.0 ns). The symmetric BF₂dtm dye 5 had a much shorter lifetime, 1.02 ns. The lowest quantum yield and lifetime was observed for 1, analogous to the phenyl-methyl dye.^[35]

Computational Studies

For most compounds, the computed absorption maxima (λ_{abs}) are in good agreement with the experimental values (Tables S3-S4, Supplementary Material). The one exception to this is complex 2, for which the computed λ_{abs} is blue-shifted $\sim 20 \text{ nm}$ compared with the experimental value. The absorption spectra are almost entirely dominated by HOMO to LUMO transitions. Furthermore, the HOMO to LUMO transitions appeared to be π to π^* corresponding to a $S_0 \rightarrow S_1$ transition, with no intramolecular charge transfer (ICT) bands evident from the experimental absorption spectra. All of the dyes exhibit relatively small Stokes shifts (i.e. $900-2739 \text{ cm}^{-1}$). It is typical for fluorophores with strong ICT character to exhibit large Stokes shifts corresponding to a dramatic change in excited state geometry. The computationally generated molecular orbital diagrams also support this qualitatively. Only a slight transfer of amplitude seems to occur from the aromatic rings to the BF2bdk moiety when going from the HOMO to the LUMO of these compounds (Fig. 2). This is an interesting result. In the past, we have observed transitions predominantly π to π^* in character when studying BF₂ complexes with symmetrical diarene ligands. However, when the compound contains an unsymmetrical diarene ligand, the HOMO to LUMO transition typically shows strong ICT. In this case, we observe unsymmetrical compounds with very little ICT character evident. Perhaps this is due to the thiophene ring being relatively similar in size and electronic character to the phenyl ring, in contrast to a naphthylene or anthracene moiety, for example in previous studies.^[43] In the case of the thiophene-methyl compound 1, the reason why no strong ICT is observed may be because the methyl moiety is slightly electron donating and would, therefore, be poor at accepting amplitude in any kind of charge transfer situation.



Fig. 2. Calculated HOMO and LUMO molecular orbitals for 1–3 indicating π to π^* character.

Table 2.	Fluorescence	properties	of	dye/PLA	blends in	air
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Dye loading [%]	1/PLA		2/PLA		3/PLA		4/PLA		5/PLA	
	$\lambda_{\rm em}^{\rm A}$ [nm]	$ au_{\mathrm{pw0}}^{\mathrm{B}}\left[\mathrm{ns} ight]$	$\lambda_{\rm em}^{\rm A}$ [nm]	$ au_{\mathrm{pw0}}^{\mathrm{B}}\left[\mathrm{ns} ight]$	$\lambda_{\rm em}^{\rm A}$ [nm]	$ au_{\mathrm{pw0}}^{\mathrm{B}}\left[\mathrm{ns} ight]$	$\lambda_{\rm em}^{\rm A}$ [nm]	$ au_{\mathrm{pw0}}^{\mathrm{B}} [\mathrm{ns}]$	$\lambda_{\rm em}^{\rm A}$ [nm]	$ au_{ m pw0}^{ m B}$ [ns]
0.1	393	C	415	C	438	1.23	435	2.68	433	1.06
1	395	C	433	0.95	453	2.24	441	2.50	448	1.32
2	397	C	438	0.67	458	2.00	464	2.42	457	1.23
5	400	C	440	0.47	442	1.00	469	2.31	493	2.68

^AFluorescence emission maxima excited at 369 nm (except for 1/PLA excited at 350 nm).

^BFluorescence lifetime excited with a 369 nm light-emitting diode (LED) monitored at the emission maximum. All fluorescence lifetimes are fitted with multiexponential decay.

^CSignal too weak to be detected with current LED excitation.

Dye loading [%]	1/PLA		2/PLA		3/PLA		4/PLA		5/PLA	
	$\lambda_{\rm RTP}^{\rm A}$ [nm]	$\tau^{B}_{pw0} [ms]$	$\lambda_{\rm RTP}^{\rm A}$ [nm]	$\tau^{\rm B}_{pw0} \ [ms]$	$\lambda_{\rm RTP}^{\rm A}$ [nm]	$\tau^{\rm B}_{pw0}[ms]$	$\lambda_{\rm RTP}^{\rm A}$ [nm]	$\tau^{\rm B}_{pw0}[ms]$	$\lambda_{\rm RTP}^{\rm A}$ [nm]	$ au_{pw0}^{B}$ [ms]
0.1	543	92.6	557	109.7	558	59.6	567	73.9	572	137.0
1	543	82.8	555	105.5	568	72.4	560	38.3	576	123.2
2	546	58.2	569	77.6	563	62.9	567	26.8	572	110.9
5	550	44.7	571	60.1	570	76.4	562	3.45	584	38.8

Table 3. Phosphorescence properties for dye/PLA blends under nitrogen

^APhosphorescence maxima under N₂ excited at 369 nm.

^BPre-exponential weighted lifetimes fitted to triple exponential decay.

As a result, we only observe a slight qualitative charge transfer in the molecular orbital (MO) diagrams from the thiophene ring to the BF₂ moeity. Ono et al. have previously performed calculations on compound **5** using similar methods to our own. As would be expected for the symmetrical BF₂bdk, the HOMO to LUMO transition of this compound is also π to π^* in character according to their generated MO diagrams.^[34]

Optical Properties of Dye/PLA Blends

Optical properties of the dyes were also analysed in PLA matrices. PLA is a biocompatible polymer commonly used in biomedical research, and creates a more rigid environment (high

glass transition temperature) necessary to produce multiemissive properties from boron dyes.^[5,47] Solutions of dye plus PLA mixtures were coated on the inner wall of vials, and dried under vacuum overnight before the measurements were taken. The solid-state photophysical properties, both fluorescence and phosphorescence, were studied in air and nitrogen (i.e. deoxygenated) environments. The fluorescence properties are listed in Table 2, and phosphorescence properties are presented in Table 3.

As shown previously in model studies of dye/PLA mixtures, the fluorescence is highly dependent on dye loading. In dilute dye/PLA blends (0.1 or 1.0%), the fluorescence maxima are

often similar to the corresponding data in CH₂Cl₂ (i.e. dye **3**, $\lambda_{\text{DCM}} = 441 \text{ nm}, \lambda_{\text{PLA (0.1 \%)}} = 438 \text{ nm}$). For dye blends at higher concentration, the emission maxima were significantly more red-shifted when compared with CH₂Cl₂ (Figs S1–S4,



Fig. 3. Dye dependent fluorescence of thienyl BF₂bdks in PLA. (a) Image showing emission (excitation by UV lamp) of 2% blends under ambient conditions. (b) Total emission spectrum for 2% blends (excitation = 369 nm).

Supplementary Material).^[9] When analysing higher dye loadings (~10%), a visible phase separation occurred and the emission became unreproducible and random. Depending on the analysed area on the vial, the fluorescence would change colours (Fig. S1, Supplementary Material). For higher dye loadings without phase separation, dye–polymer conjugates are preferable to dye/polymer blends. As shown in Fig. 3, all samples exhibited violet to blue emission, with a red shift in fluorescence wavelength with increased conjugation and donor ability (i.e. at 2% dye loading, λ_F : **1** = 397 nm, **2** = 438 nm, **3** = 458 nm, **4** = 464 nm, and **1** = 457 nm).

Establishing structure-property relationships of BF₂bdks in PLA is important for designing new dye materials. Previously, it was observed that π -conjugation played a key role in molecular weight (i.e. dye loading) colour tuneability. For example, difluoroboron dibenzoylmethane (BF2dbm) dyes reach a maximum blue-shift in ~ 20 kDa PLA polymers (~ 1.5 % dye),^[9] while difluoroboron dinaphthoylmethane (BF2dnm) dyes required ~30 kDa PLA polymers to maximally blue shift.^[24] The thiophene complexes 1–5 follow this trend as well. For dye 1 (BF_2mtm), with a single thiophene ring, the shift in fluorescence maxima from 5 % dye loading to 0.1 % dye loading ($\Delta \lambda$) is only 7 nm (5 %: $\lambda = 400$ nm, 0.1 %: $\lambda = 393$ nm). In contrast, dye 5 (BF₂dtm) has a $\Delta\lambda$ of 60 nm. For larger fluorophores with a tendency to associate (e.g. π stack) the likelihood of forming different aggregation states with different colours is a possible explanation for the different colour ranges among the dyes (Figs S2-S4, Supplementary Material). The presence of the alkyl chain in 4 had a surprising effect on the dye loading colour tuneability. Initially, we theorized that with the increased solubility of the fluorophore due to the alkyl chain, the propensity for aggregation would decrease, resulting in a blue-shifted emission. However, as seen in Fig. 4, the C12 chain in 4 resulted in a visible red-shifted emission, whereas the C1 derivative (3) only showed a weak red-shifted shoulder at $\sim 600 \,\mathrm{nm}$. It is



Fig. 4. Total emission spectrum for PhOMe and PhOC12 dyes 3 and 4 respectively as PLA blends showing fluorescence changes with dye loading (excitation = 369 nm).

possible that the C12 chain acted as an organizing group within the PLA, fostering assembly and microphase separation, as was previously seen for Rhodamine B-C12 dye in PLA reported by Zhang et al. Attaching organizing groups to the fluorophore may be an important new strategy for achieving red-shifted emission within PLA matrices.^[48]

While the fluorescence is sensitive to dye structure and dye loading, phosphorescence colour is only tuneable by dye structure. As previously reported, BF₂bdk dyes exhibit RTP in rigid media such as PLA ($T_g \sim 60^{\circ}$ C).^[25] All complexes showed phosphorescence in a nitrogen atmosphere (deoxygenated).

Data are collected in Table 3. Because the complexes do not have a halide heavy atom substituent, such as bromide or iodide typically used to enhance the phosphorescence properties of BF₂bdks,^[24] there is little to no change in the total emission spectra when going from an oxygenated to a deoxygenated environment. In some thienyl dye/PLA blends, the total emission spectra under nitrogen revealed red shoulders and broadening peaks, attributed to phosphorescence. In dilute blends (1%) of compounds 1 and 5, phosphorescence shoulders are evident. It is possible that sulfur is acting as the heavy atom in this situation, as these two compounds have the highest



Fig. 5. Room-temperature phosphorescence properties of 1 % dye/PLA blends of thienyl BF₂bdks. Image: (F) blends under N₂ ($\lambda_{ex} = 369$ nm), (RTP) picture taken with light source turned off. Spectra: total emission in air (solid lines) and N₂ (dashed lines) and delayed emission spectra (grey lines). Excitation of dyes = xenon lamp set to 369 nm, except for **1** was excited at 350 nm. Delayed emission spectra taken with a 2 ms delay.

percent sulfur content. However, the effect is much less dramatic when compared with halide heavy atoms, such as bromide or iodide.^[24] For example, 5% blends of 1–3 show noticeable red peaks and 4 shows a slight peak broadening under nitrogen. The phosphorescence properties of the thienyl dyes varied similarly to their fluorescence; with increasing conjugation length and donor ability (-OMe), the phosphorescence red-shifted (i.e. at 1% dye loading $\lambda_{\rm P}$: 1 = 543 nm, 2 = 555 nm, 3 = 568 nm, 4 = 560 nm, and 5 = 576 nm) (Fig. 5). The dye/PLA blends show an impressive range of colours from green to yellow and orange RTP, except for 1, for which the phosphorescence was faintly visible to the naked eye. However, it was readily detected via more sensitive optical instrumentation.

Conclusions

A new series of thienyl-substituted BF₂bdk complexes was synthesized and characterized to study the effects of conjugation and substituents on optical properties. The photophysical properties were investigated in dichloromethane solution and in the solid state as dye/PLA blends. The emission wavelengths were tuned in two ways: by varying the ligand structure (i.e. methyl, phenyl, methoxyphenyl, and thienyl substituents) and by varying dye loading in PLA matrices (0.1–10% dye loading).

In CH₂Cl₂ solution, all boron complexes absorb light in the UV to violet range and exhibit violet-blue emission. Stronger absorption and bathochromic emission were obtained with increasing donor ability. The absorption spectra of the boron compounds were entirely dominated by HOMO to LUMO transitions which appeared to be π to π^* corresponding to a $S_0 \rightarrow S_1$ transition. The fluorescence spectra in the solid state were highly sensitive to the ligand structure and dye loading. All dyes exhibited violet to blue emission, with a red-shift in fluorescence wavelength with conjugation and donor ability. The most red-shifted emissions were achieved for the symmetric dye, BF₂dtm (**5**) in PLA blends, despite the fact that in CH₂Cl₂ solution, substituted phenyl derivatives **3** and **4** had more red-shifted maxima.

There is little to no change in the total emission spectra for the thienyl-substituted dyes in air versus nitrogen, most likely because the complexes do not have halide, heavy atom substituents, such as Br or I.^[26] However, all blends showed a phosphorescence afterglow in an oxygen-free nitrogen atmosphere. The phosphorescence properties of the thienyl dyes displayed red-shifted emission with increasing conjugation length and donor ability, and showed an impressive range of colours from green to orange. Future research will be extended to a series of compounds containing bromide and iodide heavy atom substituents, to obtain materials with intense and well separated fluorescence and phosphorescence peaks for ratiometric sensing.^[27] In addition, dye–polymer conjugates will be prepared.

Supplementary Material

Computational data of compounds 1-3, total emission spectra of 10 % dye/PLA blends, and the dye loading effects of compounds 1, 2, and 5, are available on the Journal's website.

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