

# Pyridylpyrrolides as alternatives to cyclometalated phenylpyridine ligands: synthesis and characterization of luminescent zinc and boron pyridylpyrrolide complexes †

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The synthesis, structure, and properties of six luminescent pyridylpyrrolide complexes and the first structural characterization of pyridylpyrrolide metal complexes are reported. A series of new zinc complexes, bis(pyridylpyrrolyl)-zinc,  $(R_2PyrPy)_2Zn$  ( $R = Me, Et, ^iPr, ^tBu, and Ph$ ), that vary in their substituents on the pyrrole ring ( $Me, Et, ^iPr, ^tBu, and Ph$ ), were prepared. Pyrrole substitution produced small structural changes in the complexes and affected the fluorescence properties very little. The zinc complexes were found to be luminescent, emitting at 495 nm ( $\Phi = 0.32, 0.32, 0.31, 0.19$  and  $0.57$ , respectively). A boron analog,  $(Me_2PyrPy)BF_2$ , was prepared and was found to share the luminescent properties with the zinc complexes, emitting at 505 nm ( $\Phi = 0.22$ ), but not their water-sensitivity. A total of four crystal structures are reported,  $^tBu_2PyrPyH, (Me_2PyrPy)_2Zn, (^tBu_2PyrPy)_2Zn$ , and  $(Me_2PyrPy)BF_2$ .  $^tBu_2PyrPyH$  crystallizes as a doubly hydrogen bonded dimer with non-coplanar pyridine and pyrrole rings. The solid-state structures of  $(Me_2PyrPy)_2Zn$  and  $(^tBu_2PyrPy)_2Zn$  revealed that despite the large change in steric bulk, the two compounds have very similar structures. The structure of  $(Me_2PyrPy)BF_2$  showed changes that are expected with the interaction between a smaller atom (B as compared to Zn). Molecular orbital calculations were performed on  $Me_2PyrPyH, (Me_2PyrPy)BF_2$ , and  $(Me_2PyrPy)_2Zn$  using Gaussian 98 methods. It was found that the main transition (HOMO–LUMO) for all three molecules is a  $\pi \rightarrow \pi^*$  transition and that in the inorganic complexes, the metal atom (zinc or boron) present has very little effect on transition, evidence that the optical properties are largely ligand based and that the B or Zn atom's main effect is lowering of the LUMO relative energy.

## Introduction

Luminescent metal complexes containing cyclometalated phenylpyridine (PhPy) ligands have received a great deal of attention in the last decade, driven by the search for improved light emitting diode (LED) materials.<sup>1</sup> The appeal of the PhPy complexes is their high luminescence quantum yields and the ability to tune their photoluminescent properties by varying the ligand structure.<sup>2</sup> The work with these ligands has thus far focused almost exclusively on a few key metal centers (Re, Ru, Os, Rh, Ir, Pd, Pt, Hg) that have the ability to undergo cyclometalation.<sup>1,3,4</sup> This limitation has led to very few studies with other metal centers, such as Mn(IV)<sup>5</sup> and Bi(III).<sup>6</sup> We have become interested in the use of pyridylpyrrolide (PyrPy) ligands as possible alternatives to PhPy. PyrPy ligands share the mono-anionic, bidentate coordination mode and steric profile of PhPy ligands (Fig. 1). They offer the advantage that the pyrrole N–H bond is considerably more acidic than the phenyl C–H bond in PhPy, which should lead to more facile coordination to a wider

variety of metal centers. In this work, we demonstrate this principle by preparing luminescent PyrPy Zn and B complexes.

The number of 2,2'-pyridylpyrrolide (PyrPy<sup>−</sup>) complexes in the literature are remarkably few in number.<sup>7–9</sup> Indeed, we are aware of no reports of such complexes since the work of Chiswell<sup>7</sup> and Perry and Weber,<sup>9</sup> over 30 years ago. This does not appear to be for lack of interest, as a number of reports of the closely related pyrrolide-imine<sup>10</sup> and pyridylindole<sup>11,12</sup> ligands have appeared recently. Rather, the relative rarity of PyrPy complexes is most likely due to the difficult syntheses of the free ligand, which commonly require many steps and result in low yields.<sup>13</sup> The recent development of a one-step synthesis of substituted pyridylpyrroles has removed this obstacle, and will hopefully lead to a wider exploration of the chemistry of PyrPy complexes.<sup>14</sup>

In the present study, we have chosen to focus on Zn and B complexes because they are representative of the types of centers for which it may be much easier to prepare PyrPy complexes than PhPy complexes. We also anticipated that they would be luminescent by analogy to luminescent zinc and boron complexes of other monoanionic ligands such as hydroxyquinolines,<sup>15</sup> pyridylamines,<sup>16</sup> azaindoles,<sup>17</sup> and indole derivatives (specifically pyridylindoles).<sup>11,12</sup> Here, we report the synthesis, characterization, and luminescent properties of five new bis(pyridylpyrrolyl)zinc complexes and a new boron complex, difluoro-(3,5-dimethyl-2-(2'-pyridylpyrrolyl))borane,  $(Me_2PyrPy)BF_2$ . We also report the first structural characterization of pyridylpyrrolide metal, (PyrPy)M, complexes.

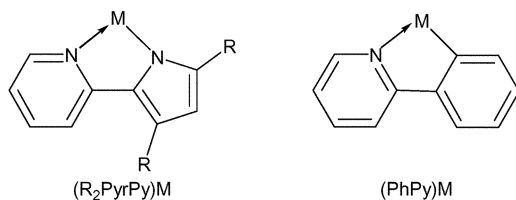


Fig. 1 General structures of pyridylpyrrolide and cyclometalated phenylpyridine metal complexes.

† Electronic supplementary information (ESI) available: Beer's Law plots and emission peak area vs. concentration plots for complexes; comparison of excitation and absorbance spectra; effect of triplet quencher isoprene on luminescence intensity. See <http://www.rsc.org/suppdata/dt/b3/b315523d/>

## Experimental

Chemicals that were purchased commercially and used without further purification include *p*-toluenesulfonic acid (Aldrich), 2-aminomethylpyridine (Aldrich), 2,4,6-collidine (Aldrich), boron trifluoride etherate (Aldrich), 3,5-heptanedione

(Chemika), 2,6-dimethyl-3,5-heptanedione (TCI America), trifluoroacetic acid (Spectrum) and 4 Å (8–12 mesh) molecular sieves (Acros). Diethylzinc (Aldrich), 1.0 M in hexanes or heptane, was transferred under vacuum prior to use. *n*-Butyllithium (Alfa Aesar) concentration (2.3 M) was determined by titration of diphenylacetic acid and it was filtered prior to use. Both toluene (Aldrich) and hexanes (Fisher) were dried by passage through an alumina column under nitrogen. THF (Fisher) and diethyl ether (JT Baker) were pre-dried over calcium hydride and distilled from sodium benzophenone ketyl.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were acquired on a Varian Unity, 300 MHz, Varian Inova, 500 MHz, or Varian Inova, 300 MHz. The  $^{19}\text{F}$  NMR was acquired on a Varian Unity 300 MHz with trifluoroacetic acid ( $\delta = 0.0$  ppm) used as a reference. GC-MS data were collected with an Agilent GC 6890 Series (column is HP-5MS crosslinked 5% PH ME Siloxane,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  film thickness) coupled to an Agilent MS 5973 Network Mass Selective Detector. High-resolution mass spectra (HRMS), using electron impact (EI), were acquired on a Finnigan MAT 95, matching the theoretical mass within 4.75 ppm and the calculated isotope patterns. Absorbance measurements were performed on a Jasco V-530 UV/VIS spectrophotometer and emission measurements were performed on a Jasco FP-6200 spectrofluorometer. Melting points were determined with a Büchi melting point apparatus, calibrated using the melting points of benzophenone and maleic acid. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

### Synthesis of ligands

3,5-Dimethyl-2-(2'-pyridyl)pyrrole, **I**, 3,5-di-*tert*-butyl-2-(2'-pyridyl)pyrrole, **IV**, and 3,5-diphenyl-2-(2'-pyridyl)pyrrole, **V**, were prepared according to a previously published method.<sup>14</sup>

**3,5-Diethyl-2-(2'-pyridyl)pyrrole (II).** **II** was prepared by a modified literature procedure.<sup>14</sup> Into a sealed tube, one equiv. each of 3,5-heptanedione (1.06 g, 8.25 mmol) and 2-(aminomethyl)pyridine (0.900 g, 8.32 mmol) along with a catalytic amount of tosic acid (250 mg, 1.31 mmol) was added to xylenes (50 mL). Molecular sieves (4 Å, 80 mg) were added to the reaction mixture and the mixture was stirred at room temperature for 30 min. The sealed tube was evacuated and heated at 170 °C for 12 h. The reaction was monitored by GC-MS. The mixture was chromatographed (silica gel, 5 : 1 hexanes/ethyl acetate, 3% Et<sub>3</sub>N), and following removal of the solvent, product **II** (927 mg, 56.1%) was obtained as a yellow oil:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  1.30 (t,  $J = 7.5$  Hz, 3 H), 1.34 (t,  $J = 7.5$  Hz, 3 H), 2.68 (q,  $J = 7.5$  Hz, 2 H), 2.82 (q,  $J = 7.5$  Hz, 2 H), 5.96 (d,  $J = 3.3$  Hz, 1 H), 6.99 (ddd,  $J = 1.5, 4.8, 7.5$  Hz, 1 H), 7.47 (d,  $J = 8.1$  Hz, 1 H), 7.64 (td,  $J = 1.8, 7.8$  Hz, 1 H), 8.50 (dm,  $J = 4.8$  Hz, 1 H), 9.47 (br. s, 1 H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$  13.6, 14.7, 21.0, 21.2, 107.5, 118.6, 119.3, 124.9, 126.2, 135.5, 136.4, 149.0, 151.3; MS  $m/z$  200 (M<sup>+</sup>, 61.2%). Anal. calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.85; H, 8.16; N, 13.90.

**3,5-Di-isopropyl-2-(2'-pyridyl)pyrrole (III).** Following the same procedure employed for the synthesis of **II**, **III** was prepared by adding one equiv. each of 2,6-dimethyl-3,5-heptanedione (1.10 g, 7.01 mmol) and 2-(aminomethyl)pyridine (808 mg, 7.48 mmol) along with a catalytic amount of tosic acid (200 mg, 1.05 mmol) to xylenes (50 mL). The reaction was heated for 48 h at 170 °C. The mixture was chromatographed (silica gel, 5 : 1 hexanes/ethyl acetate, 3% Et<sub>3</sub>N). Following removal of the solvent, product **III** (1012 mg, 63.3 %) was obtained as a light yellow solid: mp = 84.0–85.0 °C;  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  1.298 (d,  $J = 6.6$  Hz, 6 H), 1.302 (d,  $J = 6.9$  Hz, 6 H), 2.95 (septet,  $J = 6.9$  Hz, 1 H), 3.30 (septet,  $J = 6.6$  Hz, 1 H), 5.95 (d,  $J = 3.2$  Hz, 1 H), 6.97 (ddd,  $J = 0.9, 4.8, 7.2$  Hz, 1 H), 7.46 (d,  $J = 8.4$  Hz, 1 H), 7.61 (td,  $J = 2.1, 8.4$  Hz, 1 H), 8.96 (m,

$J = 5.1$  Hz, 1 H), 9.21 (br. s, 1 H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$  22.4, 23.8, 26.1, 27.1, 103.4, 118.6, 119.1, 123.9, 131.3, 136.2, 139.8, 148.8, 151.2; MS  $m/z$  228 (M<sup>+</sup>, 48.2%). Anal. calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.85; H, 9.08; N, 12.15.

### Synthesis of zinc complexes

**Bis(3,5-dimethyl-2-(2'-pyridyl)pyrrolyl)zinc (1).** Under nitrogen atmosphere, **1** (54.6 mg, 0.317 mmol) was dissolved in THF (4 mL). Upon addition of diethylzinc (160  $\mu\text{L}$ , 1 M, 0.160 mmol), the solution turned bright yellow. Following removal of solvent *in vacuo*, a yellow solid remained. Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated solution in diethyl ether at  $-35$  °C (48.3 mg, 75%): mp = 168–171 °C;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.21 (s, 6 H), 2.44 (s, 6 H), 5.96 (td,  $J = 0.9, 6.7$  Hz, 2 H), 6.23 (s, 2 H), 6.87 (td,  $J = 1.8, 7.8$  Hz, 2 H), 7.17 (d,  $J = 5.2$  Hz, 2 H), 7.28 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  14.6, 16.1, 114.6, 115.7, 117.2, 124.6, 130.2, 138.2, 140.3, 146.4, 154.5. Anal. calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>Zn: C, 64.79; H, 5.44; N, 13.74. Found: C, 64.72; H, 5.47; N, 13.79. The solid-state structure was determined using X-ray diffraction, see details below.

**Synthesis of bis(3,5-diethyl-2-(2'-pyridyl)pyrrolyl)zinc (2).** Following the same procedure employed for **1**, diethylzinc (260  $\mu\text{L}$ , 1 M, 0.260 mmol) was added to a THF (4 mL) solution of 3,5-diethyl-2-(2'-pyridyl)pyrrole (93.8 mg, 0.468 mmol). The yellow solid was recrystallized from hexanes at  $-35$  °C (85.1 mg, 78.4%): mp = 89.5–92.0 °C;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.15 (t,  $J = 7.5$  Hz, 6 H), 1.37 (t,  $J = 7.5$  Hz, 6 H), 2.60 (q,  $J = 7.5$  Hz, 4 H), 2.86 (q,  $J = 7.5$  Hz, 4 H), 5.96 (t,  $J = 6.9$  Hz, 2 H), 6.68 (s, 2 H), 6.89 (td,  $J = 1.5, 7.2$  Hz, 2 H), 7.14 (d,  $J = 5.2$  Hz, 2 H), 7.31 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  14.5, 14.7, 22.1, 24.3, 110.8, 115.7, 117.3, 129.2, 131.7, 138.3, 146.5, 146.8, 154.4. Anal. calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Zn: C, 67.31; H, 6.52; N, 12.08. Found: C, 67.18; H, 6.58; N, 11.94.

**Synthesis of bis(3,5-di-isopropyl-2-(2'-pyridyl)pyrrolyl)zinc (3).** Following the same procedure employed for **1**, diethylzinc (125  $\mu\text{L}$ , 1 M, 0.125 mmol) was added to a THF (4 mL) solution of 3,5-di-isopropyl-2-(2'-pyridyl)pyrrole (48.3 mg, 0.211 mmol). The yellow solid was recrystallized from hexanes at  $-35$  °C (34.5 mg, 63%): mp = 139–140 °C;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.18 (d,  $J = 6.9$  Hz, 6 H), 1.21 (d,  $J = 6.9$  Hz, 6 H), 1.39 (d,  $J = 6.9$  Hz, 6 H), 1.43 (d,  $J = 6.6$  Hz, 6 H), 2.87 (septet,  $J = 6.9$  Hz, 2 H), 3.32 (septet,  $J = 6.9$  Hz, 2 H), 5.97 (td,  $J = 0.9, 2.7$  Hz, 2 H), 6.40 (s, 2 H), 6.92 (td,  $J = 1.8, 8.1$  Hz, 2 H), 7.13 (d,  $J = 3.7$  Hz, 2 H), 7.41 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  23.0, 23.6, 23.7, 23.9, 27.2, 30.4, 106.4, 115.8, 117.6, 128.5, 137.2, 138.4, 146.5, 151.5, 154.3. HRMS (EI) calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>Zn (M<sup>+</sup>) 518.2388, found 518.2374.

**Synthesis of bis(3,5-di-*tert*-butyl-2-(2'-pyridyl)pyrrolyl)zinc (4).** Following the same procedure employed for **1**, diethylzinc (110  $\mu\text{L}$ , 1 M, 0.11 mmol) was added to a THF (4 mL) solution of 3,5-di-*tert*-butyl-2-(2'-pyridyl)pyrrole (54.4 mg, 0.21 mmol). The yellow solid was recrystallized from hexanes at  $-35$  °C (58.7 mg, 96%): mp = 145–150 °C;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.32 (s, 18 H), 1.61 (s, 18 H), 5.96 (t,  $J = 5.8$  Hz, 2 H), 6.60 (s, 2 H), 6.90 (td,  $J = 1.2, 8.4$  Hz, 2 H), 7.24 (d,  $J = 4.9$  Hz, 2 H), 7.87 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  31.2, 31.3, 109.1, 115.7, 120.2, 128.9, 137.6, 139.9, 146.3, 152.7, 154.0. HRMS (EI) calcd. for C<sub>34</sub>H<sub>46</sub>N<sub>4</sub>Zn (M<sup>+</sup>) 574.3014, found 574.3025. X-ray quality crystals were grown from a saturated solution in hexanes through slow evaporation of solvent. Solid-state structure was determined using X-ray diffraction (see below).

**Synthesis of bis(3,5-diphenyl-2-(2'-pyridyl)pyrrolyl)zinc (5).** Following the same procedure employed for **1**, diethylzinc

(110  $\mu\text{L}$ , 1 M, 0.110 mmol) was added to a THF (4 mL) solution of 3,5-diphenyl-2-(2'-pyridyl)pyrrole (54.0 mg, 0.182 mmol). Solvent was removed and a bright yellow solid was obtained. The yellow solid was recrystallized from hexanes/toluene (6 : 1) at  $-35^\circ\text{C}$ . From this solvent mixture, the compound crystallizes with 1 equiv. toluene (69 mg, 100% as  $5\cdot\text{C}_7\text{H}_8$ ); mp =  $154\text{--}156^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.78 (ddd,  $J = 1.2, 5.4, 7.2$  Hz, 2 H), 6.51 (td,  $J = 1.8, 7.6$  Hz, 2 H), 6.78 (tt,  $J = 1.2, 8.1$  Hz, 2 H), 7.01 (m, 6 H), 7.10 (m, 2 H), 7.20 (tt,  $J = 1.2, 7.2$  Hz, 2 H), 7.32 (tt,  $J = 0.9, 7.5$  Hz, 4 H), 7.54 (dt,  $J = 0.9, 8.4$  Hz, 2 H), 7.74 (dt,  $J = 1.5, 6.6$  Hz, 4 H), 7.88 (dt,  $J = 1.5, 6.9$  Hz, 4 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  114.2, 118.0, 118.5, 124.4, 125.7, 126.4, 128.4, 128.5, 129.6, 131.7, 132.0, 136.2, 138.3, 139.2, 143.3, 146.3, 154.2. HRMS (EI) calcd. for  $\text{C}_{42}\text{H}_{30}\text{N}_4\text{Zn}$  ( $\text{M}^+$ ) 654.1762, found 654.1793.

### Synthesis of the boron complex

#### Difluoro-(3,5-dimethyl-2-(2'-pyridyl)pyrrolyl)borane (6).

Compound **6** was prepared following a modified literature procedure.<sup>11</sup> In an evacuated sealed tube, boron trifluoride etherate (165  $\mu\text{L}$ , 1.30 mmol), **I** (222 mg, 1.29 mmol), 2,4,6-collidine (170  $\mu\text{L}$ , 1.29 mmol) and dry degassed THF (20 mL) were heated at  $80^\circ\text{C}$  for 4 h. Following removal of solvent *in vacuo*, a yellow residue remained. The residue was chromatographed (silica gel, 1 : 1 hexanes: ethyl acetate) to yield a bright yellow solid. Crystals suitable for X-ray diffraction were obtained from a saturated solution in hexanes at  $-20^\circ\text{C}$  (59 mg, 25%): mp  $153.2\text{--}155.0$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.99 (s, 3 H), 2.41 (s, 3 H), 5.78 (t,  $J = 6.6$  Hz, 1 H), 5.80 (s, 1 H), 6.38 (d,  $J = 8.4$  Hz, 1 H), 6.56 (t,  $J = 7.5$  Hz, 1 H), 7.50 (d,  $J = 5.7$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  11.6, 12.8, 115.1, 115.7, 116.6, 123.5, 127.5, 138.2, 139.7, 141.4, 148.5;  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$   $-81.506$  (q,  $J$  ( $^{19}\text{F}\text{--}^{11}\text{B}$ ) = 27.4 Hz). HRMS (EI) calcd. for  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{BF}_2\text{Na}$  [(M + Na)<sup>+</sup>] 243.0868, found 243.0876. The solid-state structure was determined using X-ray diffraction, see details below.

### Absorbance and emission measurements

**General.** Molar absorptivity determinations were performed with THF solutions of compounds **1–6** and **I** of known concentration. Luminescence quantum yields in THF were determined for the series of compounds, using 1,1,4,4-tetraphenylbutadiene in cyclohexane ( $\Phi = 0.60$  at excitation wavelength equal to 365 nm)<sup>18</sup> as a reference solution (eqn. (1)), where  $\Phi$  is defined as quantum yield,  $A$  = absorbance at  $\lambda$ ,  $n$  = refractive index,  $F$  = emission peak area resulting from excitation at  $\lambda$ ,  $s$  = sample solution, and  $r$  = reference solution.<sup>19</sup> The quantum yield calculations employed the molar absorptivity and the slope of the emission peak area vs. concentration plots (see ESI†) to avoid small errors in individual measurements. Since the sample and reference solutions were prepared in different solvents, an index of refraction correction was performed ( $n_{\text{THF}} = 1.4050$  and  $n_{\text{CycHex}} = 1.4266$ ).<sup>20</sup> The calculated quantum yields for the pyridylpyrrolyl complexes are summarized in Table 1. Instrument parameters: Absorbance, scan wavelength, 700–250 nm; scan speed, 400 nm  $\text{min}^{-1}$ ; data pitch, 1.0 nm; slit width, 2.0 nm; luminescence, scan wavelength, 300–700 nm; scan speed, 500 nm  $\text{min}^{-1}$ ; data pitch, 1 nm; excitation and emission slit widths, 5.0 nm.

$$\Phi_s = \Phi_r \left[ \frac{A_r}{A_s} \right] \left[ \frac{\eta_s^2}{\eta_r^2} \right] \left[ \frac{F_s}{F_r} \right] \quad (1)$$

**Me<sub>2</sub>PyrPyH, I.** For absorbance measurements, a solution of known concentration in THF was prepared and the molar absorptivity was determined. To determine the fluorescence quantum yield, a solution was prepared and purged with nitrogen to remove oxygen for at least 20 min. The concentration was then determined by measuring the absorbance of the

**Table 1** Molar absorptivities and quantum yields complexes **1–6**<sup>a</sup>

Compound	Absorbance		Emission	
	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\Phi$
<b>1</b>	337 <sup>b</sup>	29600 $\pm$ 2500	496	0.32 $\pm$ 0.03
	395	21600 $\pm$ 600		
<b>2</b>	339 <sup>b</sup>	25200 $\pm$ 1000	496	0.32 $\pm$ 0.02
	395	20300 $\pm$ 800		
<b>3</b>	335 <sup>b</sup>	22200 $\pm$ 500	492	0.31 $\pm$ 0.02
	395	19000 $\pm$ 500		
<b>4</b>	335 <sup>b</sup>	20800 $\pm$ 200	495	0.19 $\pm$ 0.01
	395	19300 $\pm$ 100		
<b>5</b>	300 <sup>b</sup>	31400 $\pm$ 3200	490	0.57 $\pm$ 0.06
	405	33900 $\pm$ 1000		
<b>6</b>	325 <sup>b</sup>	13800 $\pm$ 600	505	0.22 $\pm$ 0.04
	405	11200 $\pm$ 300		

<sup>a</sup> Experimental conditions: THF solvent,  $T = 22^\circ\text{C}$  (ambient).

<sup>b</sup> Excitation wavelength for quantum yield determination.

sample, and emission measurements were performed. The quantum yield was determined relative to a standard (reference solution was 1,1,4,4-tetraphenylbutadiene in cyclohexane).

**(R<sub>2</sub>PyrPy)<sub>2</sub>Zn complexes.** A solution of metal complex was prepared of known concentration under nitrogen atmosphere, in a glove box or glove bag. Prior to use, the cuvette was silated (5% dimethyldichlorosilane in  $\text{CCl}_4$ ), and then dried in a  $110^\circ\text{C}$  oven for at least three hours prior to use. Into a dry silated cuvette, a known volume (*ca.* 3 mL) of dry degassed THF was added. Diethylzinc (25  $\mu\text{L}$ , 1 M in heptane) was also added to remove any adventitious water. The cuvette was sealed with Teflon/silicone septa and cap. The cuvette was removed from the inert atmosphere and blank absorbance and emission measurements were taken. The cuvette was returned to the inert atmosphere, and the stock solution was added (*via* syringe) to prepare a known concentration solution in the cuvette. This procedure was repeated to determine the molar absorptivity and fluorescence quantum yield (reference solution was 1,1,4,4-tetraphenylbutadiene in cyclohexane).

**(Me<sub>2</sub>PyrPy)BF<sub>2</sub>, 6.** For absorbance measurements, a solution of known concentration in THF was prepared and the molar absorptivity was determined. To determine the quantum yield, a solution was prepared and purged with nitrogen to remove oxygen for at least 20 min. The concentration was then determined by measuring the absorbance of the sample and emission measurements were performed. The molar absorptivity and quantum yield were determined (reference solution was 1,1,4,4-tetraphenylbutadiene in cyclohexane).

**(Me<sub>2</sub>PyrPy)Li, 7.** The emission was measured for **7** in THF, with **7** being synthesized *in situ* for the experiment. The same procedure was followed for the zinc complexes except for the following changes. Into THF (3 mL), 50.0  $\mu\text{L}$  of filtered *n*-BuLi (2.3 M) in hexanes was added. The blank emission and absorbance measurements were taken, and a stock solution of **I** was added sequentially to the cuvettes to generate **7**. The absorbance and emission measurements were taken for the series of solutions.

### Crystal structure determinations

Crystal data for compounds **IV**, **1**, **4**, and **6** were collected at 173(2) K using a Siemens SMART Platform CD diffractometer. Data collection was carried out using Mo  $\text{K}\alpha$  radiation (graphite monochromator) with a frame time of 10 s, 30 s, 45 s, or 60 s for **1**, **4**, **IV**, and **6**, respectively. Frames were collected with  $0.30^\circ$  steps in  $\omega$  at four different  $\phi$  settings and a detector position of  $-28^\circ$  in  $2\phi$ . The intensity data were corrected for absorption and decay (SADABS).<sup>21</sup> Data was integrated

**Table 2** X-ray crystallographic data for <sup>t</sup>Bu<sub>2</sub>PyrPyH (**IV**), (Me<sub>2</sub>PyrPy)BF<sub>2</sub> (**6**), (Me<sub>2</sub>PyrPy)<sub>2</sub>Zn (**1**) and (<sup>t</sup>Bu<sub>2</sub>PyrPy)<sub>2</sub>Zn (**4**)

	<sup>t</sup> Bu <sub>2</sub> PyrPyH, <b>IV</b>	(Me <sub>2</sub> PyrPy)BF <sub>2</sub> , <b>6</b>	(Me <sub>2</sub> PyrPy) <sub>2</sub> Zn, <b>1</b>	( <sup>t</sup> Bu <sub>2</sub> PyrPy) <sub>2</sub> Zn, <b>4</b>
Formula	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub>	C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> BF <sub>2</sub>	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> Zn	C <sub>34</sub> H <sub>43.68</sub> N <sub>4</sub> Zn <sub>0.66</sub>
MW	256.38	220.03	407.81	554.58
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	19.140(5)	7.145(4)	11.929(3)	10.6415(14)
<i>b</i> /Å	11.221(3)	8.990(5)	12.286(3)	10.8583(15)
<i>c</i> /Å	14.343(4)	9.300(5)	13.777(4)	27.459(4)
<i>a</i> <sup>o</sup>		65.793(8)	81.694(5)	
<i>β</i> <sup>o</sup>		89.589(9)	83.582(5)	92.306(2)
<i>γ</i> <sup>o</sup>		75.611(9)	88.531(5)	
<i>V</i> /Å <sup>3</sup>	3086.9(13)	524.7(5)	1985.3(9)	3170.3(2)
<i>Z</i>	8	2	4	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.103	1.393	1.364	1.162
<i>μ</i> /mm <sup>-1</sup>	0.065	0.108	1.250	0.0551
<i>F</i> (000)	1120	228	848	1194
Crystal colour	Colourless	Yellow	Yellow	Yellow
Ind. reflns.	5435	1845	8957	5616
Obsd. reflns.	4809	1549	7225	4471
<i>R</i> <sub>int</sub>	0.0424	0.0243	0.0251	0.0515
GOOF on <i>F</i> <sup>2</sup>	1.035	1.012	1.025	1.007
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0611	0.0388	0.0338	0.0564
<i>wR</i> <sup>2</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.1556	0.0910	0.845	0.1404

(SAINT).<sup>22</sup> The structure was solved using SHELXS-97<sup>22</sup> (**IV**, **4**, and **6**) or SIR-92<sup>23</sup> (**1**) and refined using SHELXL-97.<sup>24</sup> Crystallographic data and refinement details for **IV**, **1**, **4**, and **6** are found in Table 2. The refinements for **IV**, **1**, and **6** were straightforward with facile convergence of the proposed and refined structures. The refinement of **4** proved to be more challenging. Due to partial occupancy of the zinc atom (0.66), the structure was refined as the superposition of (<sup>t</sup>Bu<sub>2</sub>PyrPy)<sub>2</sub>Zn and the dimeric free ligand, (<sup>t</sup>Bu<sub>2</sub>PyrPyH)<sub>2</sub>. The structure converged as the occupancy of the Zn/H ratio became consistent with the observed data. The refinement was heavily constrained (127 constraints applied).

CCDC reference numbers 225455–225458.

See <http://www.rsc.org/suppdata/dt/b3/b315523d/> for crystallographic data in CIF or other electronic format.

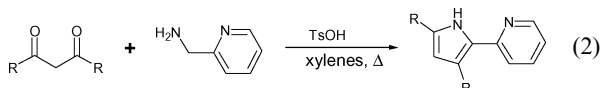
### Computational studies

Calculations for **1**, **4**, and **6** were performed using the Gaussian 98 program suite.<sup>25</sup> Hybrid density function theory (DFT) optimizations of all molecules were carried out by means of Becke's Three Parameter Hybrid Functional using the correlation functional of Lee, Yang, and Parr, B3LYP,<sup>26</sup> with the 6-31G(d) basis set. Frequency calculations were carried out for optimizations to verify the nature of the stationary point. Electronic excitation energies, molecular orbital transitions and oscillatory strengths associated with the electronic transitions, and molecular orbital electron densities were determined from time-dependent DFT (TD-DFT) calculations.<sup>27</sup> The TD-DFT calculations were performed at the TD-B3LYP/6-31G(d) level of theory starting from the optimized B3LYP/6-31G(d) ground state geometries.

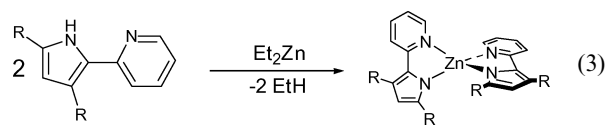
## Results and discussion

### Synthesis

The R<sub>2</sub>PyrPy ligands can be synthesized using a one-step procedure, involving the condensation of 2-aminomethylpyridine and 1,3-diketones (eqn. (2)).<sup>14</sup> The wide commercial availability of the suitable diketones makes this a good synthetic route. The zinc complexes were synthesized by addition of one equiv. of

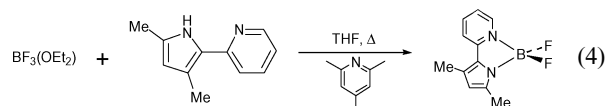


diethylzinc to a THF solution of two equiv. of free ligand (eqn. (3)). Zinc complexes were prepared with pyrrole ligands that have varying steric and electronic properties (Table 3). Initial attempts to prepare pure zinc complexes proved to be difficult, but subsequent attempts with diethylzinc solutions that were purified by vacuum transfer led to good success. We attribute this fact to the possible presence of chloride contamination in the diethylzinc. The complexes can be purified by either recrystallization or sublimation. Since both the pyridylpyrroles and the zinc complexes sublime, the complex must be free of the uncomplexed ligand to achieve purity through sublimation. The compounds are moisture sensitive, with hydrolysis yielding free ligand and zinc hydroxide. The complexes appear to be indefinitely stable in a nitrogen-filled dry box.



The (R<sub>2</sub>PyrPy)<sub>2</sub>Zn complexes are chiral, which is most clearly seen in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of (<sup>t</sup>Pr<sub>2</sub>PyrPy)<sub>2</sub>Zn. In these spectra, the four diastereotopic methyl groups appear as distinct signals. In the <sup>1</sup>H NMR spectrum of (Et<sub>2</sub>PyrPy)<sub>2</sub>Zn, the diastereotopic methylene proton resonances are not split noticeably.

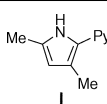
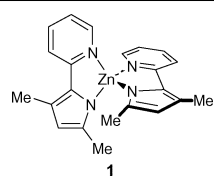
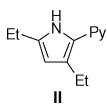
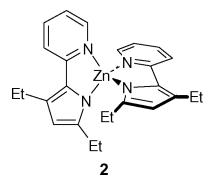
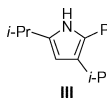
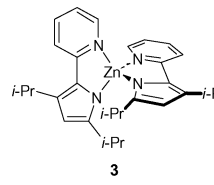
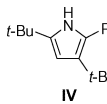
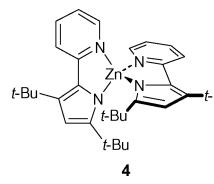
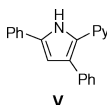
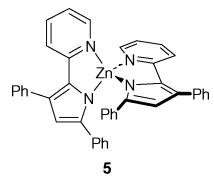
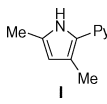
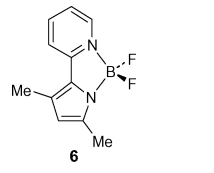
(Me<sub>2</sub>PyrPy)BF<sub>2</sub>, **6**, was prepared by a modified literature procedure (eqn. (4), Table 3).<sup>11</sup> A THF solution was heated to reflux with 1 equiv. each of boron trifluoride etherate, **1**, and base (2,4,6-collidine) for 4 h. The product, (Me<sub>2</sub>PyrPy)BF<sub>2</sub>, **6**, was purified by chromatography followed by recrystallization from hexanes, which yielded X-ray quality crystals. The yellow solid obtained sublimes and is air stable.

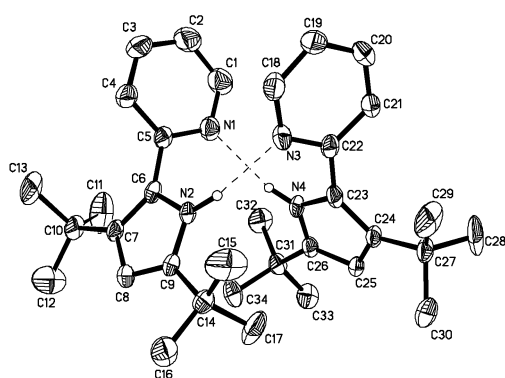


### X-ray crystallography

<sup>t</sup>Bu<sub>2</sub>PyrPyH, **IV**. X-ray quality crystals of **IV** were grown from a saturated solution (hexanes) at –20 °C. The compound crystallized as a dimer with two hydrogen bonds holding the two ligands together in a pseudo-tetrahedral fashion (Fig. 2). Placement of a centroid between the internal nitrogens shows that the dimer is pseudo-tetrahedral with a twist angle, angle between the two ligand planes, of 80.4°.

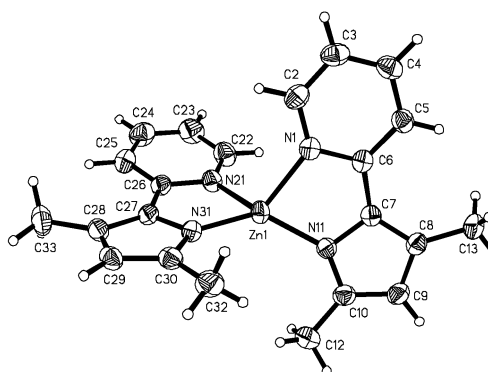
**Table 3** Complexes synthesized along with isolated % yields

Ligand	Complex	Isolated % yield
		75
		78
		63
		96
		100
		25



**Fig. 2** ORTEP diagram of  $(t\text{-Bu}_2\text{PyrPy})_2\text{H}_2$ , **IV**, as determined by X-ray diffraction, shown with all carbon-bound hydrogen atoms omitted. The compound exists as a doubly hydrogen bonded dimer in the solid state. The hydrogen bond lengths, based upon the calculated positions of H2A and H4A, are 2.964(3) (N2–H2A  $\cdots$  N3) and 3.019(3) (N4–H4  $\cdots$  N1).

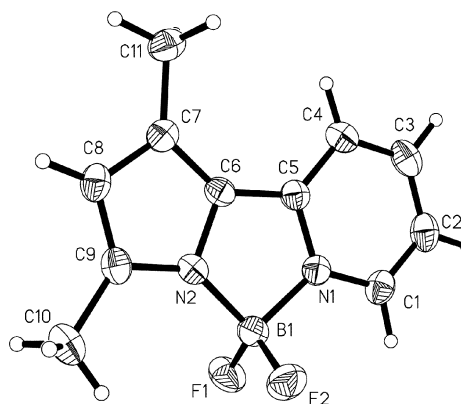
**(Me<sub>2</sub>PyrPy)<sub>2</sub>Zn, 1.** X-ray quality crystals of **1** were grown from a saturated solution (diethyl ether) at  $-20^\circ\text{C}$ . The zinc complex is pseudotetrahedral with two nearly identical molecules in the asymmetric unit (Fig. 3). The bite angle of **1** was found to be 82.67(8) and 83.65(8) $^\circ$ , which is larger than that



**Fig. 3** ORTEP diagram of  $(\text{Me}_2\text{PyrPy})_2\text{Zn}$ , **1**, as determined by X-ray diffraction. Only one of the two nearly identical molecules in the asymmetric unit is shown.

found in bipyridine complexes (bite angle found is typically between 75 and 80 $^\circ$ ).<sup>28</sup> This is due primarily to the shorter Zn–N bond lengths found in **1**. The bond lengths were 1.9402(19) and 1.950(2) Å for the Zn–N(pyrrole) bond and 2.054(2) and 2.072(2) Å for the Zn–N(pyridine) bond. Zinc bipyridine complexes commonly have bond lengths of approximately 2.1 to 2.2 Å.<sup>28</sup> Zinc complexes of 2-(2'-pyridyl)indole (2-py-in) are structurally very similar (Zn–N(indole) 1.968(3) Å and Zn–N(pyridine) 2.189(4) Å),<sup>11</sup> as are zinc pyrrolide–imines (Zn–N(pyrrole) 1.97 Å and Zn–N(imine) 2.05 Å).<sup>29</sup>

**(Me<sub>2</sub>PyrPy)BF<sub>2</sub>, 6.** X-ray quality crystals of **6** were grown from a saturated solution (hexanes) at  $-20^\circ\text{C}$ . The boron compound was found to be pseudotetrahedral around boron with a bite angle of 96.93(12) $^\circ$  (Fig. 4). The boron nitrogen bond lengths were found to be 1.527(2) Å (for B–N(pyrrole)) and 1.612(2) Å (for B–N(pyridine)). These structural parameters are essentially identical to (2-py-in)BPh<sub>2</sub>, which has 1.55 Å (B–N(indole)) and 1.63 Å (B–N(pyridine)) for bond lengths. (2-py-in)BPh<sub>2</sub> has a bite angle of 94.8 $^\circ$ .<sup>11</sup>



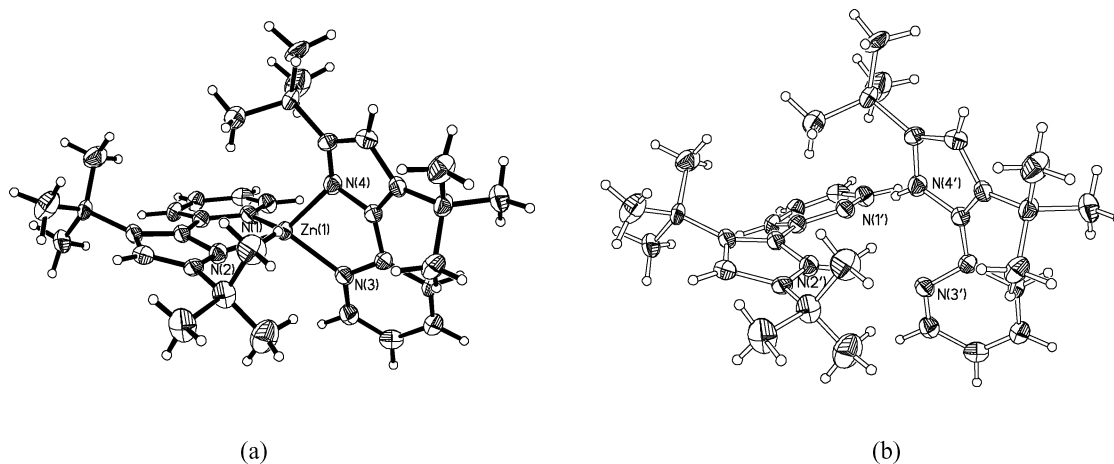
**Fig. 4** ORTEP diagram of  $(\text{Me}_2\text{PyrPy})\text{BF}_2$ , **6**, as determined by X-ray diffraction.

**(t-Bu<sub>2</sub>PyrPy)<sub>2</sub>Zn, 4.** X-ray quality crystals of **4** were grown through slow evaporation of solvent (hexanes) from a saturated solution of **4**, which contained some of the free ligand **IV**. During initial refinement, low electron density was observed at the zinc center. With further refinement, the structure was successfully modeled with partial occupancy of the zinc atom (0.66). The remainder of occupancy (0.34) was a dimeric structure of free ligand **IV** that had co-crystallized with complex **4** (Fig. 5). There was a large amount of disorder due to the partial occupancy of the ligand and complex, and a large number of restraints and constraints were needed for successful refinement. The bite angle for **4** was found to be 83.4(5) and 83.2(3) $^\circ$ , and the Zn–N bond lengths were found to be 1.966(11) and

**Table 4** Selected bond lengths and bond angles for pyridylpyrroles and their complexes

Compound	Bite angle/ $^{\circ}$	Torsion angle/ $^{\circ}$ <sup>b</sup>	Twist angle/ $^{\circ}$ <sup>c</sup>	M–N(pyrrole)/Å <sup>e</sup>	M–N(pyridine)/Å <sup>e</sup>
<b>1</b>	83.54(7) 83.59(7)	6.1(3) and 7.9(3) 2.3(3) and 7.7(3)	81.8	1.9385(17) 1.9407(17)	2.0591(18) 2.0705(18)
<b>4</b>	83.4(5) 83.2(3)	15.5(13) 20(4)	88.8	1.966(11) 1.994(18)	2.024(6) 2.044(5)
<b>6</b>	93.93(12)	0.02(17)		1.527(2)	1.612(2)
<b>IV</b>		57.0(3) 60.6(3)	80.4 <sup>d</sup>		
<b>IV<sup>a</sup></b>		33(3) 34(8)	76.0 <sup>d</sup>		

<sup>a</sup> As part of **4** crystal structure. <sup>b</sup> Angle defined as the N(pyrrole)–C–N(pyridine) that demonstrates the twist between the pyridine and pyrrole rings within one ligand unit. <sup>c</sup> Defined as the angle between the two ligand planes. <sup>d</sup> Twist angle was calculated by placement of a centroid between the 4 central nitrogen atoms. <sup>e</sup> M is Zn or B.



**Fig. 5** ORTEP diagram of (*t*Bu<sub>2</sub>PyrPy)<sub>2</sub>Zn, **4**, as determined by X-ray diffraction. The zinc atom shows partial occupancy due to co-crystallization of free ligand, **IV**, within the single crystal. The two parts are shown separately for clarity (a) metal complex (0.66 occupancy) and (b) free ligand dimer (0.34 occupancy).

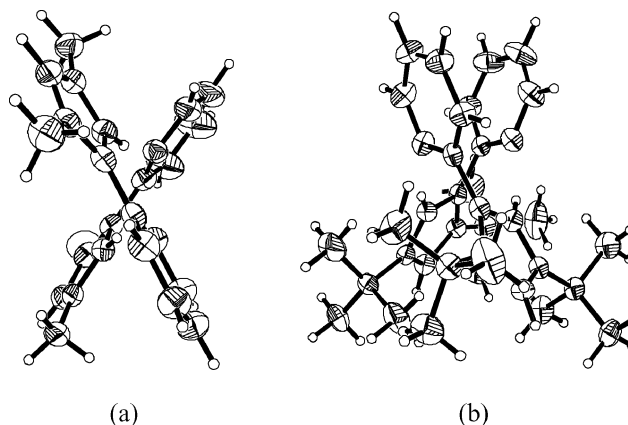
1.994(18) Å for Zn–N(pyrrole) and 2.024(6) and 2.044(5) Å for Zn–N(pyridine) bonds (very similar to **1**).

*t*Bu<sub>2</sub>PyrPyH, **IV**, has been found to crystallize as a hydrogen-bonded dimer. The disposition of the PyrPy groups in the structure of the free ligand and the zinc complex bear a striking resemblance and this may account for the co-crystallization of **IV** and **4**.

The twist angle between the pyridylpyrrole ligand planes was determined for **1** (81.8°) and **4** (88.8°), illustrating that both molecules are pseudotetrahedral around zinc. For comparison purposes, a centroid atom was placed between the four nitrogen atoms for **1** and **IV** (both in the pure sample and as part of the structure of **4**). This placement allows for a calculation of a twist angle for these compounds as well (Table 4). The calculated twist angle for **1** (51.5°) is much lower than **IV** (80.4°), as can be observed in Fig. 6. However the twist angle for the dimer, **IV**, (76.0°, as part of the structure of **4**) in the combined structure shows a slightly smaller angle than the pure sample, which is most likely due to the forces present due to packing of uncomplexed ligand with the zinc complex. Comparing the twist angles of **1** and **IV**, the larger angle of **IV** probably results from the steric effect from the *t*Bu group, forcing a larger angle between individual molecules (Fig. 6).

#### Optical absorbance and luminescent properties

**Me<sub>2</sub>PyrPyH, I.** To make a comparison between the optical properties of the free and bound ligand, absorbance and emission measurements of **I** were performed in THF. Compound **I** has absorbance maxima at 300 ( $\epsilon=14700 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 325 nm ( $\epsilon=16100 \text{ M}^{-1} \text{ cm}^{-1}$ ) and an emission maximum at 397 nm ( $\Phi_{\text{f}}(325 \text{ nm}) = 0.06$ ) in THF. The excitation profile matches the absorbance spectrum of **I** supporting the assignment of **I** as the emitting species (see ESI†).



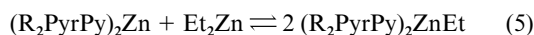
**Fig. 6** ORTEP diagrams for (a) (Me<sub>2</sub>PyrPy)<sub>2</sub>H<sub>2</sub>, **I**, and (b) (*t*Bu<sub>2</sub>PyrPy)<sub>2</sub>H<sub>2</sub>, **IV**, as determined by X-ray diffraction. The twist angle was determined for each of the two dimers and found to be 51.5° and 80.4° for **I** and **IV**, respectively.

**(R<sub>2</sub>PyrPy)<sub>2</sub>Zn.** Work done previously by Perry and Weber on the unsubstituted pyridylpyrrole zinc complex, (PyrPy)<sub>2</sub>Zn, reported absorbance maxima at 325 nm ( $\epsilon=33000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 378 nm ( $\epsilon=18800 \text{ M}^{-1} \text{ cm}^{-1}$ ), which is consistent with our findings. The molar absorptivities observed by Perry are close to the values found for complexes **1–4** in this study, however the values at 378 nm are slightly lower. This is possibly due to the instability of the zinc complexes and partial decay of the complex into free ligand. Perry noted this instability as well by stating that the zinc complexes are only stable in some solvents.<sup>9</sup>

The zinc complexes are much more luminescent than the free ligands, which is readily apparent through casual observation. Due to the water sensitivity of the complexes, the solutions for

analytical measurement were prepared and stored in a dry box. Further, cuvettes were silated to functionalize any surface silanol groups. Even with these precautions, water contamination remained a problem. Absorbance and emission spectra of all the complexes appeared to have a combination of free ligand and zinc complex present. Therefore, 25  $\mu\text{L}$  of diethylzinc (1 M in heptane) was added to the blank solution to remove adventitious water. This allowed for the rigorously water-free conditions required for the measurements of absorbance and emission. It should be noted that **4** appeared to be much less sensitive to reaction with water, presumably due to the increased steric bulk present on the ligand.

The presence of excess diethylzinc during fluorescence measurements raises some concerns, which need to be addressed. The presence of zinc hydroxide that would be generated from reaction of  $\text{Et}_2\text{Zn}$  and trace water was shown not to interfere in the absorbance or emission measurements. The presence of excess diethylzinc leads to the possibility that  $(\text{R}_2\text{PyrPy})_2\text{ZnEt}$  is present resulting from exchange in the solution between  $(\text{R}_2\text{PyrPy})_2\text{Zn}$  and  $\text{Et}_2\text{Zn}$  (eqn. (5)). We do not think this is a concern for several reasons. First, the luminescence excitation profile matches the absorbance spectrum of **1** supporting the assignment of **1** as the emitting species (see ESI†). Second, previous studies on the alkylzinc halides have shown that the equilibrium in question lies far to the left.<sup>30</sup> Third, when a titration was performed on  $\text{Me}_2\text{PyrPyH}$  (monitored by  $^1\text{H}$  NMR), we saw no evidence of alkylzinc bonds, based on  $^1\text{H}$  NMR shifts of other alkylzinc compounds.<sup>31</sup> Lastly, measurements performed on  $(\text{Me}_2\text{PyrPy})_2\text{Zn}$ , with both a small amount (5  $\mu\text{L}$ ) and a large excess (30  $\mu\text{L}$ ) of 1 M diethylzinc shows that no change is observed in the absorbance or emission spectrum.



Consider further that since  $\text{Zn}^{2+}$  is closed-shell, and the absorbance and emission properties of the complexes are believed to be completely ligand based,<sup>32</sup> the trace presence of  $(\text{R}_2\text{PyrPy})_2\text{ZnEt}$  should not perturb the measurements since the concentration of “ $\text{R}_2\text{PyrPy}^-$ ” is the important parameter. To further test this idea, the emission properties of  $(\text{Me}_2\text{PyrPy})\text{Li}$ , **7**, in THF were examined.

The complex,  $(\text{Me}_2\text{PyrPy})\text{Li}$ , was synthesized *in situ*, by addition of free ligand to a solution of *n*-BuLi (*n*-butyllithium) in THF, and its emission was measured. The fluorescence emission of **7** was found to be the same within error as the emission of **1**, strong evidence that the emission observed is ligand-based.

The molar absorptivity was determined for all of the inorganic compounds and are presented in Table 1 (Beer's Law plots can be found as ESI†). Absorbance spectra for **1**, **2**, **3**, and **4** were found to be very similar with two features around 335 and 395 nm (Fig. 7). The similarity is an indication that these four complexes have very similar structures, despite their steric differences. Further, the molar absorptivities for all four com-

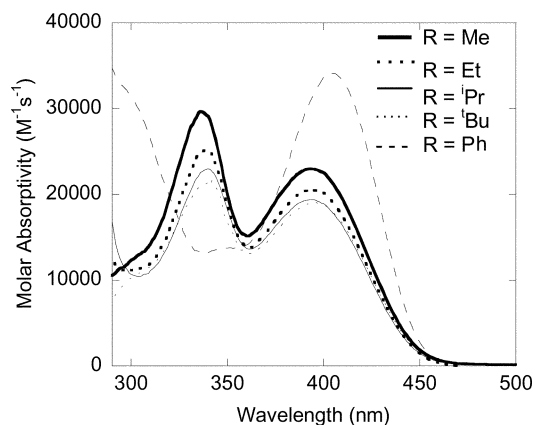


Fig. 7 Absorbance spectra of  $(\text{R}_2\text{PyrPy})_2\text{Zn}$  complexes in THF.

plexes, **1**, **2**, **3**, and **4**, are similar, with a decrease in molar absorptivity observed with an increased amount of steric bulk.

The presence of phenyl substituents at the 3 and 5 positions of the pyrrole ring in complex **5** results in significant differences in the electronic absorption spectrum (Fig. 7). The increased conjugation induces a red-shift of the low-energy band seen at 395 nm in the alkyl substituted complexes to 405 nm. The high-energy band observed at 335 nm in the alkyl substituted complexes is also apparently shifted to the red to 350 nm and diminished in intensity. A new intense absorbance band appears below 300 nm.

The emission spectra were collected by excitation at each complex's absorbance maxima. The solutions for emission measurements were prepared in the same manner as those for absorbance. All five zinc complexes proved to have similar emission properties, emitting one band with a maximum at 490–496 nm (Table 1), consistent with emission from one excited state.

The quantum yields of complexes **1**, **2**, and **3**, are all approximately 0.32, while complex **4** shows a diminished quantum yield (0.19). The origin of the lower quantum yield for **4** is not known, but is presumably attributable to the steric bulk of the *tert*-butyl groups. The solid-state structures of **1** and **4** show that the angle between the ligand rings, as measured by the N–C–N torsion angle, is significantly larger in **4** (15–20°) than in **1** (2–8°). The lower degree of coplanarity in **4** and the resulting perturbation of the Franck–Condon factors may lead to a decreased rate of fluorescence, an increased rate of non-radiative relaxation, or both. The presence of phenyl substituents in **5** results in an increase in quantum yield (0.57).

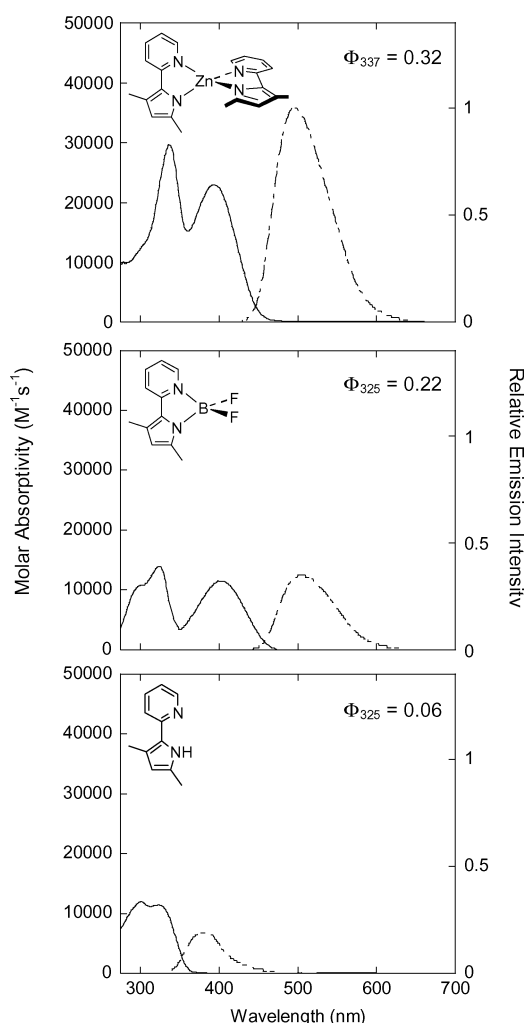
$(\text{Me}_2\text{PyrPy})\text{BF}_2$ . The molar absorptivity and quantum yield of  $(\text{Me}_2\text{PyrPy})\text{BF}_2$  (**6**) were determined in THF (Table 1). Unlike the zinc complexes, **6** is air and water stable, and the absorbance measurements were made in air. Oxygen was removed for fluorescence measurements, but no other special precautions, as needed by the zinc complexes, were taken. The luminescence intensity was completely unaffected by the addition of 120 mM isoprene, a triplet quencher (see ESI†), and was affected very little by the presence of  $\text{O}_2$ . The luminescence energy, the lack of quenching by isoprene, and the computational results all point toward the luminescence being fluorescence from the lowest excited singlet state.

The optical properties of  $(\text{Me}_2\text{PyrPy})_2\text{Zn}$ , **1**, and  $(\text{Me}_2\text{PyrPy})\text{BF}_2$ , **6**, are very similar. Both contain an absorption band around 330 nm and another absorption band around 400 nm (Fig. 8). Both compounds also have similar fluorescence quantum yields, with **6** (0.22) having a lower quantum yield than **1** (0.32).

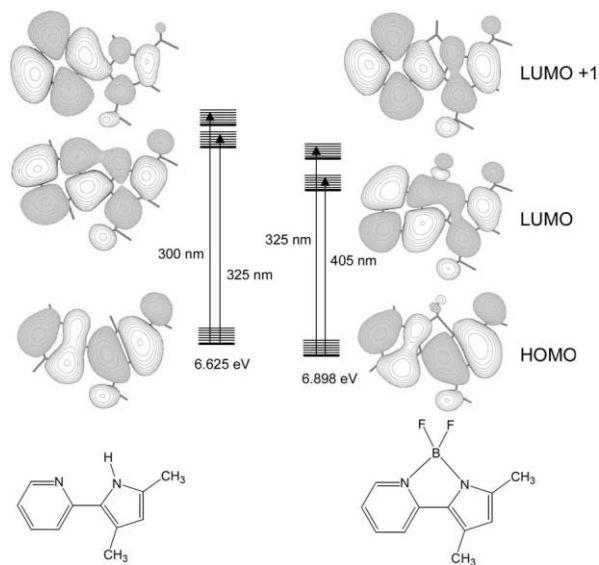
### Computational studies

To gain insight into the nature of the electronic transitions, we performed density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations on the free ligand, **I**, and on its Zn and B complexes, **1** and **6**. These calculations indicate that the Frontier Molecular Orbitals (FMOs) are nearly identical for **I**, **1**, and **6**, in terms of their contributions (*i.e.*, coefficients and phase) from the ligand-based atomic orbitals. While, the Zn and B complex FMOs are nearly indistinguishable, B complex orbitals in **6** are much easier to visualize because there is only one ligand per complex. Fig. 9 illustrates the HOMO, LUMO and LUMO+1 for **I** and **6**, and the following discussion will focus on these two species. All of the same arguments can be applied to the more difficult to visualize Zn complex, **1**.

The FMOs in both **I** and **6** are  $\pi$  symmetry orbitals, and so the two main UV-visible absorbance features are best described as  $\pi \rightarrow \pi^*$  transitions. The lowest energy absorbance for **I** and **6** is calculated to be a transition between the HOMO and a



**Fig. 8** Absorbance and emission spectra of  $(\text{Me}_2\text{PyrPy})_2\text{Zn}$ , **1**,  $(\text{Me}_2\text{PyrPy})\text{BF}_2$ , **6**, and  $\text{Me}_2\text{PyrPyH}$ , **I**, in THF.



**Fig. 9** Representations of the HOMO, LUMO, LUMO+1 orbitals calculated using DFT and electronic transitions for compounds **I** and **6**. The HOMO energies are calculated ionization energies and the transitions are labeled with the wavelengths of the experimentally observed absorbance maxima.

superposition of anti-bonding orbitals, which is mostly LUMO in character. Likewise, for both **I** and **6**, the second lowest energy absorbance is calculated to be from the HOMO to a superposition that is mostly LUMO+1 in character. The calculated transition energies agree very well with the observed

energies (Table 1). These results indicate that the low energy absorbance ( $\sim 400$  nm) in **1** and **6** does not arise from a different type of transition than the low energy (330 nm) absorbance of the free ligand, such as  $n \rightarrow \pi^*$ . Rather, both are due to  $\pi \rightarrow \pi^*$  transitions between essentially identical molecular orbitals, and the difference in transition energies between **I** and its complexes is due to changes in the relative energies of the FMOs. All of the FMO energies decrease going from **I** to **6**, but it is the LUMO energy that is the most stabilized, causing the red shift of the lowest energy absorbance. Inspection of the wavefunctions provides a rationalization for this greater stabilization, since among the HOMO, LUMO, and LUMO+1, it is the LUMO that has the largest coefficient on the B atom in **6** (Fig. 9).

## Conclusions

A series of 3,5-substituted PyrPy complexes have been prepared and three of these complexes have been structurally characterized by X-ray diffraction. These structures represent the first structural characterization of metal-PyrPy complexes. The  $(\text{R}_2\text{PyrPy})_2\text{Zn}$  and  $(\text{Me}_2\text{PyrPy})\text{BF}_2$  complexes exhibit blue-green luminescence with quantum yields ranging from 0.19 to 0.57, and may have applications in light emitting devices. Our calculations suggest that the visible absorbance and emission transitions are largely ligand-based, and therefore we expect PyrPy complexes of other closed-shell metal centers to exhibit similar optical properties. The  $\text{PyrPy}^-$  ligand is isolobal and roughly isosteric with cyclometalated 2-phenylpyridine ligands and may offer an interesting alternative to these ligands, which have received much recent attention due to their complexes' luminescent properties.<sup>1</sup>

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