Luminescence from open-shell, first-row transition metal dipyrrin complexes†

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Several first-row transition metal complexes of the 1,9-bis(2′,4′,6′-triphenylenphenyl)-5-mesityl dipyrrinato ligand and its tetrahalogenated analogues have been synthesized and their luminescence spectra obtained. The protonated ligands, as well as the Li(i), Mn(i), Cu(i), Cu(II), and Zn(i) chelates show appreciable luminescence, despite the paramagnetism of the Mn(i) and Cu(i) ions. Fluorescence quantum yields (ΦF) as high as 0.67 were observed for the zinc complex. Luminescence was partially quenched by the introduction of heavy halogens to the backbone of the ligand, as well as by the introduction of paramagnetic metal ions. Room-temperature, solution state phosphorescence was observed from the halogenated dipyrrinato lithium salts, as well as from the non-halogenated Mn(i) complex.

The photophysical and photochemical properties of dipyrrin chelates have been well-studied, and those molecules have been used in light-harvesting arrays and as fluorescence labels in biological systems, among many other applications. Examples of main-group chelates that display appreciable luminescence include the widely used boron difluoride dipyrrin (BODIPY) dyes, as well as chelates of Al, Ga, Si, Ge, In, Sn, and Sn. A number of closed-shell transition metal and lanthanide complexes of dipyrrin ligands have also been shown to luminesce, notably several complexes of Zn(i), which have been shown to efficiently fluoresce with quantum yields (ΦF) as high as 0.7. The phosphorescence of dipyrrin complexes of diamagnetic second- and third-row transition metals has been observed for Rh(iii), Re(iii), Ir(iii), Pd(II), Pt(II), and Cd(II), and is uniformly weaker than the room-temperature fluorescence of analogous complexes, with the maximum reported ΦP of 0.115.

Luminescence from dipyrrin complexes is nearly always due to a ligand-based π* → π emission, which is generally enhanced by extension of the dipyrrin π system, introduction of a bulky aryl group at the meso position, or rigidification of the ligand by chelation to a closed shell metal or boron. Though fluorescence is the dominant mode of emission for most dipyrrin-based systems, those in which intersystem crossing is enhanced by spin–orbit coupling (e.g., in the presence of a heavy metal or halogen) have also been shown to phosphoresce. To the best of our knowledge, nearly every luminescent (Φ ≥ 0.01) dipyrrin complex described to date has been diamagnetic. While several paramagnetic dipyrrinato complexes have been reported, their emission spectra have rarely been described, with the exception of a report of weak fluorescence from homoleptic Cu(i) dipyrrins, though quantum efficiencies of luminescence were not reported. Both dia- and paramagnetic luminophores have potential utility as metal sensors, in imaging applications, and for paramagnetic luminophores especially, as hybrid optical/MRI imaging agents.

Following protocols for dipyrrin halogenation previously reported, the parent dipyrrin (A)L(H) (A)LH: 1,9-bis(2′,4′,6′-triphenylenphenyl)-5-mesityl-dipyrrin) could be brominated with N-bromosuccinimide in tetrahydrofuran (THF) in good yield (72%, Scheme 1); whereas iodination with NIS required camphor sulfonic acid (CSA) catalysis and longer reaction times (65%). Metalation of the dipyrrins was readily accomplished in a two-step procedure: deprotonation with lithium bis(trimethylsilyl)amide in THF followed by transmetalation with metal chloride salts (i.e., MnCl2, CuCl, CuCl2, ZnCl2) in THF, afforded the desired transition metal complexes in 65–92% yield (Scheme 1). Crystals of MnCl(THF), CuCl, and CuCl2 suitable for X-ray diffraction were obtained from various mixtures of THF, benzene, and hexanes at ~35 °C. The solid-state molecular structures are provided in Fig. 1 and the crystallographic details are provided in the ESL.

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In our exploration of the reactivity of base metal dipyrrin complexes for the inter- and intra-molecular amination of C–H bonds,\textsuperscript{45–47,55–57} we noticed in the course of these studies that both the parent dipyrrin, (ArL)H, (Φ_F = 0.16) and its lithium salt, (ArL)Li(THF)\textsubscript{2}, (Φ_F = 0.51) were visibly luminescent in solution, though none of the dipyrrin-supported iron complexes\textsuperscript{45–47,49,55,56} were noticeably luminescent. Given the importance of related chromophores in a wide array of applications, we were interested to explore whether transition metal chelates of (ArL) and related ligands would exhibit luminescence. To this end, we synthesized the closed-shell Zn\textsuperscript{II} and Cu\textsuperscript{I} dipyrrinato complexes (ArL)ZnCl(THF) and (ArL)Cu, respectively, anticipating that they should in fact luminesce. Unsurprisingly, the zinc complex showed significant fluorescence at room temperature (Φ_F = 0.67), but complexation of the dipyrrinato ligand to Cu(I) had a significant quenching effect on the fluorescence of the ligand (Φ_F ~ 0.03). We attribute this difference in fluorescence intensity to the significant difference in the coordination environment around the d\textsuperscript{10} centers. The \textsuperscript{1}H NMR and combustion analysis of (ArL)ZnCl(THF) indicates a four-coordinate species with THF bound to Zn, whereas crystallographic characterization of (ArL)Cu revealed a three-coordinate Cu(i) ion with one of the flanking phenyl units bound in an η\textsuperscript{2} fashion to the metal in the solid state (Fig. 1b). \textsuperscript{1}H NMR in benzene-\textsubscript{d}_\textsubscript{6} does not indicate desymmetrization of the ArL ligand, indicating the η\textsuperscript{2}-bound phenyl group is fluxional in solution. Notably, the emission spectrum of (ArL)Cu showed excitation wavelength dependence, indicative of the presence of multiple emissive species present in solution, consistent with the hypothesis that the solution-state structure of (ArL)Cu is fluxional. The addition of acetonitrile to the solution results in a single emission spectrum (Fig. S17 in ESI\textsuperscript{†}), consistent with the formation of a static 3-coordinate acetonitrile adduct, which displays only very weak fluorescence. The presence of multiple species in non-coordinating solvents makes the determination of quantum yields challenging, but we can estimate Φ by comparison to related spectra obtained in this study.

Given the dearth of reported paramagnetic, luminescent dipyrrin complexes in the literature, we synthesized several open-shell complexes of the fluorescent ligand (ArL). While the Fe\textsuperscript{III} complex showed extremely weak fluorescence (Φ_F < 0.001), both the Mn\textsuperscript{II} and Cu\textsuperscript{II} complexes (ArL)MnCl(THF) and (ArL)CuIICl luminesced at room temperature in benzene solutions (Fig. 1d). Though there was appreciable quenching of the luminescence in both complexes relative to the metal-free ligand (ArL)H, presumably due to the bound paramagnetic metals, fluorescence with appreciable quantum yield was observed for both species. Fluorescence spectral details of the derivatives of (ArL)\textsuperscript{−} are compiled in Table 1. Notably, (ArL)MnCl(THF) also showed appreciable near-infrared (NIR, λ\textsubscript{max} = 757 nm) phosphorescence, a very rare phenomenon for paramagnetic complexes in solution at room temperature (Fig. S13\textsuperscript{†}). When pure, crystalline samples of (ArL)MnCl(THF) were dissolved in benzene, they showed excitation wavelength-dependent phosphorescence emission maxima (Fig. S25\textsuperscript{†}), an
apparent violation of Kasha’s Rule. As determined by X-ray crystallography, (ArL)MnCl(THF) exists as a four-coordinate trigonal pyramidal THF adduct in the solid state (Fig. 1a), thus we surmised that the complex’s excitation wavelength-dependent phosphorescence spectrum was likely due to an equilibrium mixture of the 4-coordinate THF adduct and the 3-coordinate complex (ArL)MnCl with dissociated THF akin to the 3-coordinate iron analogue previously reported. Addition of excess THF to a benzene solution of (ArL)MnCl(THF) supported this hypothesis, as the excitation wavelength dependence disappeared under these conditions (Fig. S26†). We note that the proposed 3-coordinate complex has a significantly red-shifted phosphorescence emission from that of the 4-coordinate material; the two materials have λ<sub>P</sub> values of 777 and 757 nm, respectively. Alternative potential solution state structures for (ArL)MnCl include a Cl-bridged dimer (though this is unlikely under the extremely dilute (10<sup>−7</sup> M) conditions), various ligand ary group adducts, or solvento adducts.

The phosphorescent (ArL)MnCl(THF) is, to the best of our knowledge, the first phosphorescent molecular complex of Mn<sup>II</sup>. While Mn<sup>II</sup> is often used as a dopant in phosphorescent glasses, nanoparticles, and quantum dots reports of solution-state, room-temperature phosphorescence from a molecular species containing manganese are rare. There is a single report of the phosphorescence of Mn<sup>III</sup> tetraphenylporphyrin, which showed weak NIR phosphorescence (λ<sub>P</sub> = 840 nm, Φ<sub>P</sub> = 3 × 10<sup>−4</sup>) in methycyclohexane glass at 77 K, and one report of discrete molecular manganese species exhibiting solid-state phosphorescence.

To ascertain whether phosphorescence could be enhanced to a greater degree, the 2,3,7,8-tetrahalogenated variants (BrArL)<sub>2</sub>H and (IArL)<sub>2</sub>H, respectively, were examined (Table 2). Halogenation is known to increase the rate of intersystem crossing in luminescent molecules by enhancing spin-orbit coupling, thereby increasing the proportion of phosphorescence to fluorescence. Indeed, the lithium complexes (BrArL)Li(THF) and (IArL)Li(THF)<sub>1.5</sub> displayed measurable phosphorescence at room temperature, albeit with significantly lower quantum yields than for fluorescence emission (Fig. S23 and S24†). We can attribute the quenching of fluorescence upon introduction of halogens to two phenomena: the enhancement of spin-orbit coupling, and the dipyrrin deplanarization upon halogenation. Upon complexation of the (BrL)<sub>2</sub>Mn<sup>II</sup>, phosphorescence was totally quenched, and the only observable emission was by fluorescence, albeit quite weakly (Φ<sub>F</sub> = 0.02, Fig. S22†).

In conclusion, complexes of the fluorescent dipyrrin ligand (ArL) are shown to also display appreciable fluorescence in the orange portion of the visible spectrum (λ = 567–605 nm), even in the presence of heavy atoms (Br or I) or paramagnetic transition metal ions (Mn<sup>II</sup> or Cu<sup>II</sup>). Quantum yields of up to 0.67 were observed for the Zn<sup>II</sup> complex. Room-temperature phosphorescence was observed from the halogenated dipyrrin lithium salts, as well as for the non-halogenated Mn complex (ArL)MnCl(THF), the first reported molecular manganese species to exhibit room temperature, solution state phosphorescence. These luminescent complexes represent some of the first significantly luminescent paramagnetic dipyrrin complexes, and may have potential applications in metal sensing, biological fluorescence labeling, or as hybrid optical/MRI imaging agents.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
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### Table 1: Fluorescence spectral details for derivatives of (ArL)<sub>2</sub>H

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<tr>
<th>Complex</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>λ&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>Stokes shift (nm)</th>
<th>Φ&lt;sub&gt;F&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
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<tr>
<td>(ArL)H</td>
<td>520</td>
<td>584</td>
<td>64</td>
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<tr>
<td>(BrArL)&lt;sub&gt;2&lt;/sub&gt;H</td>
<td>570</td>
<td>600</td>
<td>30</td>
<td>0.51</td>
<td>0</td>
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<tr>
<td>(BrArL)MnCl(THF)</td>
<td>532</td>
<td>579</td>
<td>47</td>
<td>0.015</td>
<td>5/2</td>
</tr>
<tr>
<td>(IArL)&lt;sub&gt;2&lt;/sub&gt;H</td>
<td>519</td>
<td>583</td>
<td>64</td>
<td>&lt;0.001</td>
<td>2</td>
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<tr>
<td>(IArL)ZnCl(THF)</td>
<td>504</td>
<td>588</td>
<td>64</td>
<td>0.03</td>
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<td>(BrArL)CuI</td>
<td>532</td>
<td>567</td>
<td>35</td>
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<td>(IArL)CuI</td>
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<td>574</td>
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### Table 2: Luminescence spectral details of halogenated complexes

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<th>Complex</th>
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<th>λ&lt;sub&gt;P&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>Stokes shift (nm)</th>
<th>Φ&lt;sub&gt;P&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Φ&lt;sub&gt;F&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Φ&lt;sub&gt;p&lt;/sub&gt;</th>
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<tr>
<td>(BrArL)&lt;sub&gt;2&lt;/sub&gt;H</td>
<td>535</td>
<td>583</td>
<td>0.005</td>
<td>48</td>
<td>—</td>
<td>—</td>
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<tr>
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<td>569</td>
<td>589</td>
<td>0.21</td>
<td>20</td>
<td>760</td>
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<tr>
<td>(BrArL)MnCl(THF)</td>
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<td>585</td>
<td>0.002</td>
<td>53</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(IArL)MnCl(THF)</td>
<td>532</td>
<td>579</td>
<td>0.015</td>
<td>47</td>
<td>757</td>
<td>0.015</td>
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<tr>
<td>(BArL)MnCl</td>
<td>532</td>
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<td>∼0.02</td>
<td>47</td>
<td>777</td>
<td>0.015</td>
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*Excitation maximum. †Emission maximum. ‡Quantum yields were determined by comparison to Rhodamine 6G in absolute ethanol (Φ<sub>F</sub> = 0.95 ± 0.005). See the ESI for further details. a Two emission and excitation maxima were observed for (ArL)CuI; it is unclear how the two emissive species differ.
Notes and references


