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dipyrrin complexes**

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Luminescence from open-shell, first-row transition metal dipyrriin complexes

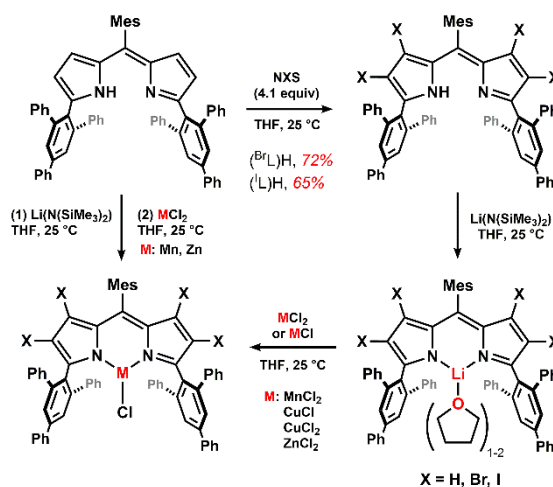
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Several first-row transition metal complexes of the 1,9-bis(2',4',6'-triphenylphenyl)-5-mesityl dipyrriinato ligand and its tetrahalogenated analogs have been synthesized and their luminescence spectra obtained. The protonated ligands, as well as the Li(I), Mn(II), Cu(I), Cu(II), and Zn(II) chelates show appreciable luminescence, despite the paramagnetism of the Mn(II) and Cu(II) ions. Fluorescence quantum yields (Φ_F) 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 dipyrriinato lithium salts, as well as from the non-halogenated Mn(II) complex.

The photophysical and photochemical properties of dipyrriin chelates have been well-studied, and those molecules have been used in light-harvesting arrays¹ and as fluorescence labels in biological systems,²⁻¹³ among many other applications.⁶⁻⁸ Examples of main-group chelates that display appreciable luminescence include the widely used boron-difluoride dipyrriin (BODIPY) dyes,⁹⁻¹² as well as chelates of Al,^{3, 14-16} Ga, Si, Ge,¹⁷⁻¹⁹ In,^{20, 21} and Sn.^{22, 23} A number of closed-shell transition metal and lanthanide complexes of dipyrriin ligands have also been shown to luminesce, notably several complexes of Zn(II), which have been shown to efficiently fluoresce with quantum yields (Φ_F) as high as 0.7.²⁴⁻²⁸ The phosphorescence of dipyrriin complexes of diamagnetic second- and third-row transition metals has been observed for Rh(III),^{29, 30} Re(I),³¹ Ir(III),^{32, 33} Pd(II), Pt(II),³⁴ and Cd(II),³⁵ and is uniformly weaker than the room-temperature fluorescence of analogous complexes, with the maximum reported Φ_p of 0.115.³⁶⁻³⁹

Luminescence from dipyrriin complexes is nearly always due to a ligand-based $\pi^* \rightarrow \pi$ emission, which is generally enhanced by extension of the dipyrriin π system,^{2, 3, 5} introduction of a



Scheme 1. Synthesis of halogenated dipyrriins and metal.

bulky aryl group at the *meso* position,⁴⁰ or rigidification of the ligand by chelation to a (closed shell) metal (or boron). Though fluorescence is the dominant mode of emission for most dipyrriin-based systems, those in which inter-system 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 ($\Phi \geq 0.01$) dipyrriin complex described to date has been diamagnetic. While several paramagnetic dipyrriinato complexes have been reported,⁴¹⁻⁵² their emission spectra have rarely been described, with the exception of a report of weak fluorescence from homoleptic Cu(II) dipyrriins,⁵³ though quantum efficiencies of luminescence were not reported. Both dia- and paramagnetic luminophores have potential utility as metal sensors,^{6, 54} in imaging applications,⁷ and for paramagnetic luminophores especially, as hybrid optical/MRI imaging agents.⁸

Following protocols for dipyrriin halogenation previously reported,⁴⁹ the parent dipyrriin (^AL)H ((^AL)H: 1,9-bis(2',4',6'-triphenylphenyl)-5-mesityl-dipyrriin) 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 dipyrriins was readily accomplished in a two-step procedure following deprotonation with lithium

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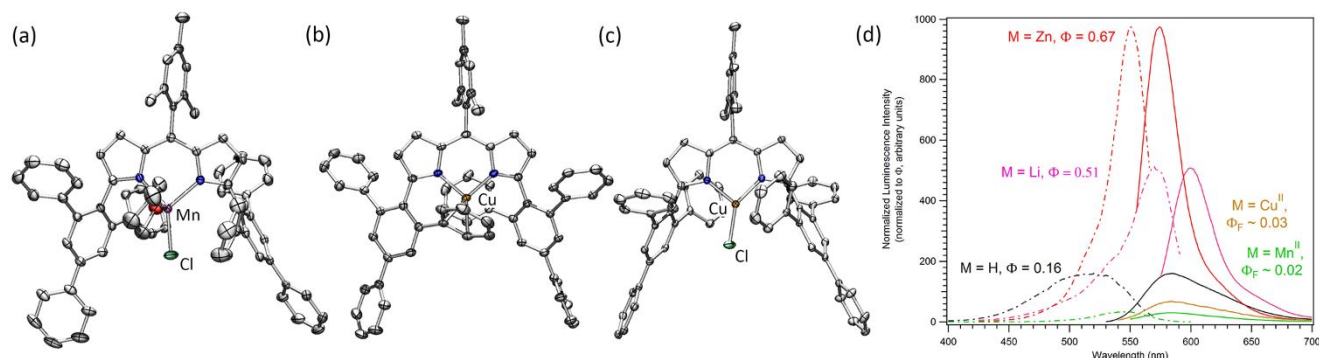


Figure 1. Solid-state molecular structures for (a) $(ArL)MnCl(THF)$, (b) $(ArL)Cu^I$, and (c) $(ArL)Cu^{II}Cl$. Thermal ellipsoids shown at 50% probability; H atoms and unbound solvents omitted for clarity. Colour scheme: C, gray; N, blue; Cl, green; O, red; Mn, orchid; Cu, green copper. (d) Fluorescence spectra of derivatives of (ArL) . Dashed lines are excitation spectra obtained with emission detected at λ_F and solid lines are emission spectra obtained with excitation at λ_{ex} . Black, $(ArL)H$; pink, $(ArL)Li(THF)_2$; red, $(ArL)ZnCl(THF)$; gold, $(ArL)Cu^{II}Cl$; purple, $(ArL)Cu^I$; green, $(ArL)MnCl(THF)$. Intensities are normalized to Φ .

bis(trimethylsilyl)amide bis(trimethylsilyl)amide in THF and transmetalation with metal chloride salts (i.e., $MnCl_2$, $CuCl$, $CuCl_2$, $ZnCl_2$) in THF, affording the desired transition metal complexes in 65-92% yield (Scheme 1). Crystals of $(ArL)MnCl(THF)$, $(ArL)Cu^I$, and $(ArL)Cu^{II}Cl$ suitable for X-ray diffraction were obtained from various mixtures of THF, benzene, and hexanes at $-35^\circ C$. The solid-state molecular structures are provided in Figure 1 and the crystallographic details are provided in the Supplementary Material.

In our exploration of the reactivity of base metal dipyrin complexes for the inter- and intra-molecular amination of C-H bonds,^{45-47, 55-57} we noticed in the course of these studies that both the parent dipyrin, $(ArL)H$, ($\Phi_F = 0.16$) and its lithium salt, $(ArL)Li(THF)_2$, ($\Phi_F = 0.51$) were visibly luminescent in solution, though none of the dipyrin-supported iron complexes^{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^{II} and Cu^I dipyrinato 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 ($\Phi_F = 0.67$), but complexation of the dipyrinato ligand to $Cu(I)$ had a significant quenching effect on the fluorescence of the ligand ($\Phi_F \sim 0.03$). We attribute this difference in fluorescence intensity to the significant difference in the coordination environment around the d^{10} centers. The 1H 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^2 fashion to the metal in the solid state (Figure 1b). 1H NMR in benzene- d_6 does not indicate desymmetrization of the ArL ligand, indicating the η^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), 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.

Table 1. Fluorescence spectral details for derivatives of (ArL)

Complex	λ_{ex} (nm) ^a	λ_F (nm) ^b	Stokes shift (nm)	Φ_F^c	S
$(ArL)H$	520	584	64	0.16	0
$(ArL)Li(THF)_2$	570	600	30	0.51	0
$(ArL)MnCl(THF)$	532	579	47	0.015	$5/2$
$(ArL)FeCl(THF)$	519	583	64	<0.001	2
$(ArL)Cu^{II}Cl$	504 (br)	588	64	0.03	$1/2$
$(ArL)Cu^I$ ^d	532	567	35	~0.03	0
	544	605	61		
$(ArL)ZnCl(THF)$	550	574	24	0.67	0

^aExcitation maximum. ^bFluorescence emission maximum. ^cQuantum yields were determined by comparison to Rhodamine 6G in absolute ethanol ($\Phi_F = 0.95 \pm 0.005$).¹⁸ See the ESI for further details. ^dTwo emission and excitation maxima were observed for $(ArL)Cu^I$; it is unclear how the two emissive species differ.

Given the dearth of reported paramagnetic, luminescent dipyrin complexes in the literature, we synthesized several open-shell complexes of the fluorescent ligand (ArL) . While the Fe^{II} complex showed extremely weak fluorescence ($\Phi_F < 0.001$), both the Mn^{II} and Cu^{II} complexes $(ArL)MnCl(THF)$ and $(ArL)Cu^{II}Cl$ luminesced at room temperature in benzene solutions (Figure 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 (Φ_F) was observed for both species. Fluorescence spectral details of the derivatives of (ArL) are compiled in Table 1. Notably, $(ArL)MnCl(THF)$ also showed appreciable near-infrared (NIR, $\lambda_{max} = 757$ nm) phosphorescence, a very rare phenomenon for paramagnetic complexes in solution at room temperature (Figure S13). When pure, crystalline samples of $(ArL)MnCl(THF)$ were dissolved in benzene, they showed excitation wavelength-dependent phosphorescence emission maxima (Fig. S25), an

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Table 2. Luminescence spectral details of halogenated complexes.

Complex	λ_{ex} (nm) ^a	λ_{f} (nm) ^b	Φ_{f} ^d	Stokes shift (nm)	λ_{p} (nm) ^c	Φ_{p} ^d	$\Phi_{\text{f}}/\Phi_{\text{p}}$
(^{BrAr} L)H	535	583	0.005	48	--	--	--
(^{BrAr} L)Li(THF)	569	589	0.21	20	760	0.002	105
(^I ArL)H	532	585	0.002	53	--	--	--
(^I ArL)Li(THF) _{1.5}	583	603	0.017	20	772	0.008	2.1
(^{Ar} L)MnCl(THF) ^e	532	579	0.015	47	757	0.015	1.0
(^{Ar} L)MnCl ^f	532	579	~0.02	47	777 ^g	~0.02	~1.0

^aExcitation maximum. ^bEmission maximum for fluorescence. ^cEmission maximum for phosphorescence. ^dQuantum yields were determined by comparison to Rhodamine 6G in absolute ethanol ($\Phi_{\text{f}} = 0.95 \pm 0.005$),⁵⁸ See ESI for further details. ^eData taken from the solution with added THF. ^fThis compound was not isolated; the listed values are from the excitation dependent spectrum which we presume contained both the 3- and 4-coordinate complexes (Fig. S25); therefore, quantum yields could not be reliably determined. ^gThis value was measured with $\lambda_{\text{ex}} = 565$ nm.

apparent violation of Kasha's Rule.⁵⁹ As determined by X-ray crystallography, (^{Ar}L)MnCl(THF) exists as a four-coordinate trigonal pyramidal THF adduct in the solid state (Figure 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 (^{Ar}L)MnCl with dissociated THF akin to the 3-coordinate iron analogue previously reported.⁴⁷ Addition of excess THF to a benzene solution of (^{Ar}L)MnCl(THF) supported this hypothesis, as the excitation wavelength dependence disappeared under these conditions (Figure 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_{p} values of 777 and 757 nm, respectively. Alternative potential solution state structures for (^{Ar}L)MnCl include a Cl-bridged dimer (though this is unlikely under the extremely dilute ($\sim 10^{-7}$ M) conditions), various ligand aryl group adducts, or solvent adducts.

The phosphorescent (^{Ar}L)MnCl(THF) is, to the best of our knowledge, the first phosphorescent molecular complex of Mn^{II}. While Mn^{II} is often used as a dopant in phosphorescent glasses,⁶⁰ nanoparticles,⁶¹ and quantum dots,⁶² reports of solution-state, room-temperature phosphorescence from a molecular species containing manganese are rare. A single report of the phosphorescence of Mn^{II} tetraphenylporphyrin, which showed weak NIR phosphorescence ($\lambda_{\text{p}} = 840$ nm, $\Phi_{\text{p}} = 3 \times 10^{-4}$) in methylcyclohexane glass at 77 K,⁶³ and one report of discrete molecular manganese species exhibiting solid-state phosphorescence.⁶⁴

To ascertain whether phosphorescence could be enhanced to a greater degree, the halogenated variants (^{BrAr}L)H and (^IArL)H, respectively, were examined. 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 (^{BrAr}L)Li(THF) and (^IArL)Li(THF)_{1.5} displayed measurable phosphorescence in solution at room temperature, albeit with significantly lower quantum yields than for fluorescence emission (Figure S23-S24). We can attribute the quenching of fluorescence upon introduction of halogens to two phenomena: the enhancement of spin-orbit coupling, and the dipyrin deplanarization upon halogenation.⁴⁹ Upon complexation of the (^IArL) to Mn^{II}, phosphorescence was totally quenched, and the only observable emission was by fluorescence, albeit quite weakly ($\Phi_{\text{f}} = 0.02$, Fig. S22).

In conclusion, complexes of the fluorescent dipyrin ligand (^{Ar}L) are shown to also display appreciable fluorescence in the orange portion of the visible spectrum ($\lambda = 567$ -605 nm), even in the presence of heavy atoms (Br or I) or paramagnetic transition metal ions (Mn^{II} or Cu^{II}). Quantum yields of up to 0.67 were observed for the Zn^{II} complex. Room-temperature phosphorescence was observed from the halogenated dipyrin lithium salts, as well as for the non-halogenated Mn complex (^{Ar}L)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 dipyrin complexes, and may have potential applications in metal sensing, biological fluorescence labeling, or as hybrid optical/MRI imaging agents.

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Conflicts of interest

There are no conflicts to declare.

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