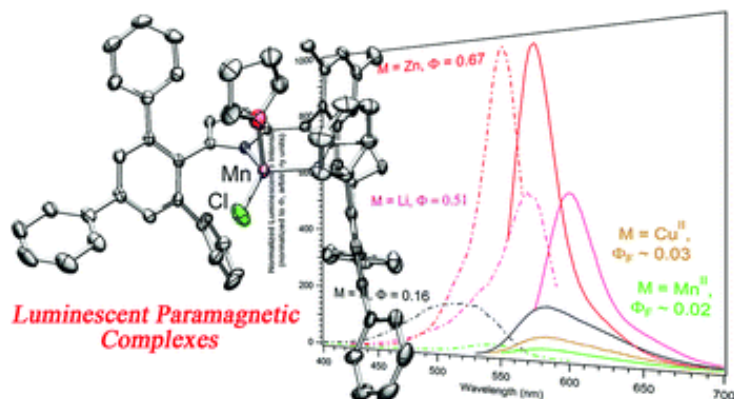


## Systematic structural variations in transition metal dipyrriin complexes: Effects on luminescence

A library of variably substituted dipyrriins has been synthesized, and the luminescence spectra of the N-H dipyrriins as well as their heteroleptic metal chelates have been obtained. Herein we report a number of trends in the luminescence wavelength and intensity induced by these structural changes. Such variations include **a)** changing the bulk and/or rotational freedom of the 2- and 10-substituents that flank the metal binding site; **b)** varying the size and electronic characteristics of the *meso* aryl group; **c)** di- or tetra-halogenation of the pyrrole backbone; and **d)** changing the identity of the metal ion itself, ranging from diamagnetic ions [Li(I), Cu(I), Zn(II)] to Mn(II), with  $S = 5/2$ . While many trends adhere to expectations -- such as increased luminescence quantum yield upon restriction of rotation of the *meso* aryl group increasing quantum yield, and quenching of fluorescence upon the introduction of heavy halogens (Br, I) to the luminophore itself -- other structural variations cause unexpected changes in the luminescence behavior. Such unexpected results include the appreciable fluorescence and phosphorescence from some paramagnetic species, which are typically non-luminescent.



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