Systematic structural variations in transition metal dipyrrin complexes: Effects on luminescence

A library of variably substituted dipyrrins has been synthesized, and the luminescence spectra of the N-H dipyrrins 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 \([\text{Li}(I), \text{Cu}(I), \text{Zn}(II)]\) to \(\text{Mn}(II)\), 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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References: