



## Review

# Theories of phosphorescence in organo-transition metal complexes – From relativistic effects to simple models and design principles for organic light-emitting diodes



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## ABSTRACT

We review theories of phosphorescence in cyclometalated complexes. We focus primarily on pseudo-octahedrally coordinated  $t_{2g}^6$  metals (e.g., [Os(II)(bpy)<sub>3</sub>]<sup>2+</sup>, Ir(III)(ppy)<sub>3</sub> and Ir(III)(ptz)<sub>3</sub>) as, for reasons that are explored in detail, these show particularly strong phosphorescence. We discuss both first principles approaches and semi-empirical models, e.g., ligand field theory. We show that together these provide a clear understanding of the photophysics and in particular the lowest energy triplet excitation, T<sub>1</sub>. In order to build a good model relativistic effects need to be included. The role of spin-orbit coupling is well-known, but scalar relativistic effects are also large – and are therefore also introduced and discussed. No expertise in special relativity or relativistic quantum mechanics is assumed and a pedagogical introduction to these subjects is given. Once both scalar relativistic effects and spin-orbit coupling are included, time dependent density functional theory (TDDFT) provides quantitatively accurate predictions of the radiative decay rates of the substates of T<sub>1</sub> in phosphorescent organotransition-metal complexes. We describe the pseudo-angular momentum model, and show that it reproduces the key experimental findings. For example, this model provides a simple explanation of the relative radiative rates of the substates of T<sub>1</sub>, which differ by orders of magnitude. Special emphasis is placed on materials with potential applications as active materials in organic light-emitting diodes (OLEDs) and principles for the design of new complexes are identified on the basis of the insights provided by the theories reviewed. We discuss the remaining theoretical challenges, which include deepening our understanding of solvent effects and, vitally, understanding and predicting non-radiative decay rates.

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## 1. Introduction

There has been long-standing fundamental interest in low-energy excitations of phosphorescent organo-transition metal complexes [1–4], some examples of which are given in Fig. 1. This interest initially stemmed from the discovery that the emission properties of these complexes can be very different from typical organic molecules, particularly at low temperatures [5–27]. However, interest in the field has grown significantly as the number of potential applications for such complexes have increased. These include dye-sensitised solar cells [28–34], non-linear optics [34], photocatalysis [4,34–37], biological imaging [38–40], chemical and biological sensing [34,38,41–43], photodynamic therapy [34], light-emitting electro-chemical cells [44–47] and OLEDs [2,33,48–55].

For many of these applications a detailed understanding of the lowest energy triplet excitation, T<sub>1</sub>, would greatly facilitate the design of better materials. For example, in OLED applications the active organometallic complex is embedded in a host matrix, which transports the charge to the complex. When an excitation is formed on the complex it rapidly decays to the T<sub>1</sub> state. In phosphorescent organo-transition metal complexes strong spin-orbit coupling (SOC) enables fast intersystem crossing. This is estimated to occur in tens to hundreds of femtoseconds [56]. In contrast the lifetimes of the T<sub>1</sub> states, which are discussed in detail below, range from microseconds to milliseconds, i.e., many orders of magnitude slower than the intersystem crossing. Thus, even the generation of singlet excitations rapidly leads to the occupation of T<sub>1</sub> – a process known as triplet harvesting, cf. Fig. 2. Therefore, the design of an active material for an OLED, in large part, amounts to controlling the key properties of T<sub>1</sub> such as its zero field splitting (ZFS), and the radiative and non-radiative decay rates of its three substates. Of course, this is far easier to write than to achieve via the chemical modification of a complex.

In non-relativistic quantum mechanics the conservation of spin dictates that a triplet state may not decay radiatively to a singlet state. However, in relativistic quantum mechanics such processes are allowed due to SOC. Therefore, a proper description

of phosphorescence will necessarily involve relativistic effects. In order to keep this review as self-contained as possible, in Section 2 we provide a brief introduction to relativity and its role in chemistry. The topics covered here are not intended to be exhaustive, but rather to give the necessary introduction for non-specialists wanting to read the remainder of the review. Experts may wish to skip over this section. More comprehensive discussions of these subjects can be found elsewhere, for example in the excellent monograph by Dyall and Fægri [57].

Two major approaches have been taken to modelling the phosphorescence in organo-transition metal complexes: phenomenological or semi-empirical approaches, such as ligand field theory, and first principles approaches, primarily based on (relativistic) (time dependent) density functional theory.

Semi-empirical theories have fallen somewhat out of fashion in the theoretical chemistry community since the rise of computational chemistry. However, they have continued to be developed, particularly in the context of strongly correlated electron materials [58]. For example, models involving strong SOC have recently gathered much attention from the solid-state physics community in the context of the iridates [59,60]. In Section 5 we give a modern reformulation of some semi-empirical models of phosphorescent organo-transition metal complexes. This allows us to place several different models in a unified context and explain the consistency of their key predictions. In particular we stress that many of the key properties of the complexes we discuss are unavoidable consequences of their (approximate) (pseudo)trigonal and pseudo-octahedral symmetries. These models also explain why (pseudo)trigonal pseudo-octahedral  $t_{2g}^6$  complexes are often strongly phosphorescent.

While the semi-empirical theories described in Section 5 provide a powerful unified framework for understanding phosphorescence in organo-transition metal complexes, first principles approaches have the advantage of making more specific predictions for individual complexes. Therefore, in Section 6, we review first principles calculations for phosphorescent organo-transition metal complexes, which have mainly been based on relativistic

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