

Aggregation induced phosphorescence of metal complexes: From principles to applications



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ABSTRACT

Metal complexes are the prototypes of phosphorescent materials, widely used in a range of optoelectronic and sensing applications. This review reports the most recent and tutorial results in the area of aggregation induced phosphorescence (AIP) of metal complexes, i.e. molecules that are weakly or non-phosphorescent in deaerated fluid solution and whose room temperature phosphorescence is switched on upon aggregation. The examples are divided into two main classes according to the AIP mechanism: (i) rigidification that causes a restriction of intramolecular motions as well as of structural distortion of the phosphorescent excited state and (ii) metallophilic interaction that brings about new electronic transitions compared to the isolated chromophores. The last section is devoted to a special class of molecules and supramolecular systems, in which metal complexation turns on phosphorescence of nearby organic chromophores, so that the metal complex is not directly involved in the phosphorescence process.

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1. Introduction

Phosphorescence, the spin-forbidden radiative decay of an electronically excited state, has been known for a long time. In 1941

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Lewis and his coworkers first suggested that the long-lived phosphorescence of fluorescein in rigid media derives from the lowest triplet state [1]. The first unequivocal demonstration of the fact that phosphorescence originates from a triplet state was made by Lewis and Calvin in 1945 [2]: they demonstrated that the phosphorescent state of fluorescein in a boric acid glass at room temperature is paramagnetic.

Although the first studies were devoted to organic molecules, phosphorescence is usually regarded as a property of metal complexes because the presence of a heavy metal atom increases the spin-orbit coupling and favors spin-forbidden radiative and non-radiative decays of electronically excited states. Indeed, phosphorescent metal complexes are widely used in technological applications, like organic light-emitting devices (OLED) [3], light-emitting electrochemical cells (LEC) [4], and luminescent sensors [5] of pressure and dioxygen, for example.

Recently, it has emerged a great interest on metal complexes that are weakly or non-phosphorescent in deaerated fluid solution and whose room temperature phosphorescence is switched on either by rigidification of the matrix (e.g. crystallization) or by aggregation and electronic interactions of the molecules among themselves. Some authors distinguish between “aggregation induced phosphorescence” (AIP), referred to a compound that is non-emissive as isolated molecule in solution and emissive in the aggregated form, and “aggregation induced phosphorescence enhancement” (AIPE), for a compound that is weakly emissive as monomer and more emissive as an aggregate. Since the underlying phenomenon is identical in the two cases and the distinction between a non-emissive and a weakly emissive compound is somehow arbitrary, we will describe examples of both classes and we will use the AIP acronym in this review. Many examples of this phenomenon has been studied in the past, for example in the case of metallophilic interactions in Au(I) or Pt(II) metal complexes, but they were not named as aggregation induced phosphorescent molecules, so that it is difficult to have a complete overview of the very vast area of this research. The present review is thus devoted to provide the reader with some basic concepts of photophysics of metal complexes, to discuss the designing principles to get AIP materials and to present recent and most relevant examples from a tutorial point of view.

Before presenting examples and their potential applications, it is worthwhile recalling a few elemental principles of electronic transitions in metal complexes with particular emphasis on phosphorescence and the parameters affecting its efficiency. Interested readers can refer to several books for a deeper discussion [6–9].

2. Photophysics of phosphorescent metal complexes

In order to simplify the picture and consider the effect of light excitation, schematic molecular orbital diagrams such as that shown in Fig. 1 for an octahedral complex may be used. Molecular

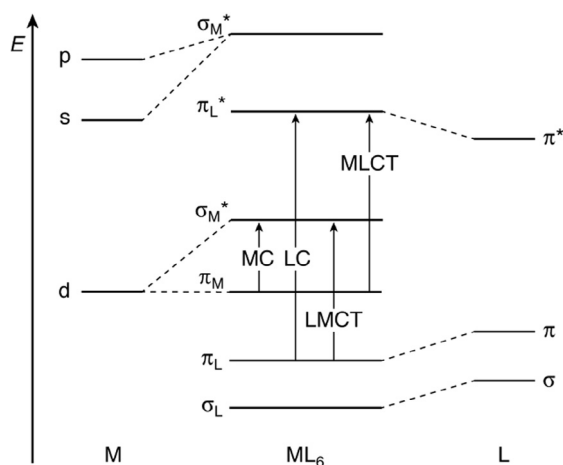


Fig. 1. Schematic molecular orbital diagram for an octahedral complex of a transition metal. The arrows indicate the four types of electronic transitions (only the lowest energy transitions are represented) based on localized MO configurations.

orbitals of metal complexes are classified as centered either on the metal or on the ligand according to their predominant contributions. As a consequence, electronic transitions are defined as follows: *metal-centered* (MC) transitions when an electron is transferred between two metal-centered orbitals, e.g. from π_M orbitals to σ_M^* orbitals; *ligand-centered* (LC) transitions when the involved orbitals are ligand-centered, e.g. $\pi_L \rightarrow \pi_L^*$; *ligand-to-metal charge-transfer* (LMCT) transitions e.g. of type $\pi_L \rightarrow \pi_M^*$; *metal-to-ligand charge-transfer* (MLCT) transitions e.g. of type $\pi_M \rightarrow \pi_L^*$. Fig. 1 is just a schematic representation and represents the lowest energy electronic transitions: for example, LMCT can originate from $\sigma_L \rightarrow \sigma_M^*$ transitions. The relative energy ordering of the resulting excited electronic configurations depends on the nature of metal and ligands. Low energy metal-centered transitions are expected for the first row transition metals, low energy ligand-to-metal charge-transfer transitions are expected when at least one of the ligands is easy to oxidize and the metal is easy to reduce, low energy metal-to-ligand charge-transfer transitions are expected when the metal is easy to oxidize and a ligand is easy to reduce, and low energy ligand centered transitions are expected for aromatic ligands with extended π and π^* orbitals.

If the ground electronic configuration is closed-shell, the ground electronic state is a singlet, usually denoted by S_0 . When an electron is promoted from one of the low-energy occupied molecular orbitals to a high-energy unoccupied orbital, singlet and triplet excited states occur in pairs (S_1 and T_1 , S_2 and T_2 , etc.). Thus, the lowest excited state is a triplet state (T_1), i.e. a state having a different multiplicity from that of the ground state. This is always the case for organic molecules, but, for some transition metal complexes, the ground-electronic configuration contains degenerate orbitals which are not completely filled and, as a consequence of the Hund rule, the ground state has a multiplicity higher than one and intraconfigurational electronic transitions can occur (see e.g., Cr(III) complexes) [6,10].

In the present review, most of the examples will deal with metal complexes featuring a closed-shell configuration and thus the ground state is a singlet (S_0) and the lowest excited states are singlet (S_1) and triplet states (T_1). The phosphorescence quantum yield (Φ_{ph}), i.e. the ratio between the number of emitted photons and the number of absorbed photons, is the product of the efficiency of population of T_1 (η_{isc}) by inter system crossing from upper lying excited states (e.g., S_1) and the intrinsic efficiency of phosphorescence (η_{ph}), i.e. the percentage of T_1 deactivating by phosphorescence:

$$\Phi_{ph} = \eta_{isc} \times \eta_{ph} \quad (1)$$

To maximize the phosphorescence quantum yield, we need to maximize η_{isc} and η_{ph} , both processes are spin-forbidden. The spin selection rules of radiative and non-radiative processes are valid to the extent to which spin and orbital function can be separated rigorously. Departures from this approximation are due to spin-orbit coupling, which mix electronic states of different multiplicity and increases as the atomic number of the atoms involved increases (for an atomic species, spin-orbit coupling is proportional to the fourth power of atomic number, Z^4). This is the reason why most of the phosphorescent materials are based on metal complexes. The spin-orbit coupling is particularly high for metals belonging to the second and third transition series. The efficiency of the $S_1 \rightarrow T_1$ intersystem crossing is usually close to unity and the quantum yield of fluorescence is close to zero. In addition, rate constants of both the $T_1 \rightarrow S_0$ phosphorescence and the $T_1 \rightarrow S_0$ intersystem crossing are much greater than in organic molecules. As an example, the different amount of spin-orbit coupling is one of the reasons why in a rigid matrix at 77 K (where bimolecular deactivation processes cannot occur) the lifetime of the lowest spin

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