



Review

The luminescence properties of multinuclear platinum complexes [☆]Emma V. Puttock, Melissa T. Walden, J.A. Gareth Williams ^{*}

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ABSTRACT

Platinum(II) complexes featuring conjugated aromatic ligands are widely studied in the context of luminescence. Many such compounds have been discovered that display intense phosphorescence from triplet excited states, offering potential applicability to numerous areas of contemporary interest, including as phosphors for light-emitting devices and imaging agents in cell biology. Aside from the large number of mononuclear Pt(II) complexes that have been reported in the context of luminescence, there are several examples of multinuclear systems – ones that incorporate two or more Pt(II) ions or Pt(II) in combination with other platinum group metal ions. The introduction of a second metal ion can lead to very different luminescence properties compared to the mononuclear analogues. This review aims to provide an overview of some of the key features of multinuclear Pt(II) complexes and their luminescence. It proves to be convenient to subdivide the examples into three classes, according to whether or not there are significant intramolecular interfacial interactions between the square-planar units. In some cases (Class A), for example with aromatic bridging ligands, the units are rigidly held apart from one another and no such intramolecular interactions are possible. In some such complexes, however, the presence of a second metal ion can nevertheless lead to very different properties compared to mononuclear analogues. In particular, recent work has shown that large red shifts in absorption and emission can be accompanied by an increase in the phosphorescence radiative rate constant, offering a way to efficient red and near-infrared emitters. In Class B, on the other hand, the planar Pt(II) units are rigidly held in a conformation that facilitates interfacial interactions. In many cases they involve overlap of Pt 5d_{z²} and 6p_z orbitals, leading to the generation of low-energy ³MMLCT excited states similar to those seen in aggregates of mononuclear Pt(II) complexes. Finally, complexes in Class C – of which there are very many and we cover only a selection of examples – are those in which there is some flexibility in the linkers between the Pt(II) units. They may display dual emission both from excited states that resemble those of the isolated units, and from lower-energy excited states similar to aggregates or excimers, owing to the ability of the Pt(II) moieties to approach one another in the appropriate conformation.

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1. Introduction

The past 20 years has seen a huge increase in research into the luminescence properties of platinum(II) complexes and the synthesis of new complexes designed to display intense emission [1–6]. Prior to the 1990s, most studies had focused on complexes with diimine ligands such as bipyridine. Complexes such as Pt(bpy)Cl₂ were known to be luminescent in the solid state, but few were significantly so in solution. The development of cyclometallated complexes, for example those based on phenylpyridine (ppy) and related multidentate ligands, opened up more brightly luminescent systems with respectable quantum yields in deoxygenated solution at ambient temperature [2,4]. Owing to the high spin-orbit coupling (SOC) constant of platinum, intersystem crossing in low-molecular-weight Pt(II) complexes is typically much faster than fluorescence, and the triplet state T₁ is populated with high efficiency. Subsequent phosphorescence requires efficient SOC pathways to promote the formally forbidden T₁ → S₀ process [7]. High quantum yields are also favoured by a high degree of rigidity to disfavour non-radiative decay [8]. These principles have been reviewed elsewhere, illustrated by numerous examples of mononuclear complexes [1–6].

Much of the research in this field since 2000 has been driven by applications such as triplet phosphors for organic light-emitting diodes (OLEDs) [9–12]; probes and labels for biological imaging, including time-resolved emission microscopy [13–16]; triplet sensitizers for triplet-triplet annihilation upconversion [17,18]; and optical sensors for molecular oxygen which rely on quenching of long-lived excited states [19].

In this contribution, we focus on the luminescence properties of *multinuclear* platinum(II) complexes – those which feature two or more Pt atoms per molecule, or which contain Pt(II) and one (or more) other platinum group metal centres such as Ir(III) or Ru(II). Interest in such systems has begun to increase rapidly over the past few years, and the majority of the examples included here date since 2010, though not to the exclusion of pioneering earlier studies which underpin the recent work. We are not aware of any other reviews that deal specifically with this topic.

One of the ways in which Pt(II) complexes differ from those of other metals popular in the field of luminescence (*viz.*, the d⁶ metal ions Re(I), Ru(II), Os(II), Rh(III), Ir(III)) is that they are normally 4-coordinate square-planar as opposed to 6-coordinate pseudo-octahedral. Planarity opens up the possibility of face-to-face interactions between complexes, which often play an important role in the photophysics of Pt(II) complexes. In the case of mononuclear Pt(II) complexes, such interactions may occur in the ground state, leading to aggregates, or in the excited state, leading to excimers, or both. Aggregates and excimers may display different emission properties – normally red-shifted – from those of the isolated monomers (see Section 3.1 for further discussion), and indeed the combination of monomer and excimer/aggregate emission has been the subject of much interest with regard to white light generation in OLEDs using a single phosphor [20,21]. In a *multinuclear* complex incorporating two or more distinct Pt(II) units that are covalently bound, such interactions may be possible *within* the molecule – *i.e.*, intramolecular versus intermolecular. Of course, whether they do occur will depend upon the separation

and relative disposition of the units – whether they are linked in such a way that the necessary interactions can occur.

We have chosen to sub-divide the subject matter broadly according to whether or not such interactions occur in the complexes discussed, as illustrated schematically in Fig. 1. In the first section, we focus on systems with rigid linking units between the metal centres that do *not* offer the appropriate geometries for face-to-face interactions between the metal complex units (represented by case A in Fig. 1). The second section also deals with rigidly linked systems, but in this case, the rigid molecular conformation is one that *does* strongly favour ground and/or excited-state interactions between the metals and/or their aromatic ligands (case B). In these examples, aggregate-like or excimer-like emission predominates. Finally, in the third section, we describe a representative selection of examples that feature flexible linkers between the metal units (case C). Many of the complexes in this category feature dual emission from mononuclear and binuclear excited states, and the ratio between them may be influenced by a range of environmental factors such as temperature and polarity.

We should stress that our objective is not to produce an exhaustive survey of all luminescent multinuclear Pt(II) complexes reported to date, but rather to provide a survey of the different types of behaviour that may be observed, using a selection of representative examples. The discussion is confined to complexes featuring platinum in oxidation state +2, except for a few specific cases where conversion to +3 analogues occurs readily. Finally, it should be noted that we have restricted our coverage to complexes featuring at least one conjugated aromatic ligand. In such systems, crucial excited states are typically ones with a high degree of metal-to-ligand charge transfer (MLCT) character, owing to the presence of relatively low-energy π* orbitals on the aromatic ligand. Purely “inorganic” materials, such as the famous dinuclear complex known as “platinum POP” – [Pt₂(P₂O₅H₂)₄]⁴⁻ with bridging pyrophosphate ligands – and its relatives (e.g. with bridging phosphine ligands) are not discussed in detail here, but they have been extensively studied over many years [22–24]. Their photophysical and photochemical properties are dominated by metal-centred excited states, albeit unusual ones that involve molecular orbitals spanning both metal ions (see Section 3.1).

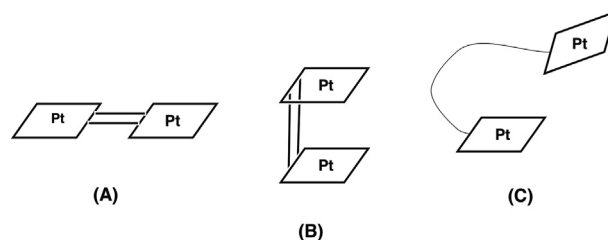


Fig. 1. Schematic illustration of the three subdivisions of binuclear complexes as used in this review. (A) Complexes featuring rigid bridges that hold the Pt units in such a way that they cannot come together through *intramolecular* face-to-face interactions. (B) Complexes in which the Pt units are rigidly held in a conformation that favours face-to-face interactions between them, either in the ground state and/or the excited state. (C) Complexes with flexible bridges where the Pt units may behave as essentially independent units or interact with each other.

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