



Review

Luminescent cyclometalated-pentafluorophenyl Pt^{II}, Pt^{IV} and heteropolynuclear complexes

Jesús R. Berenguer, Elena Lalinde, M. Teresa Moreno^{*}

Departamento de Química-Centro de Síntesis Química de La Rioja (CISQ), Universidad de La Rioja, 26006 Logroño, Spain

ARTICLE INFO

Article history:

Received 11 January 2018

Received in revised form 2 April 2018

Accepted 5 April 2018

Keywords:

Cyclometalating ligands

Luminescence

Platinum

Polynuclear complexes

Chromic behaviour

ABSTRACT

Platinum complexes bearing cyclometalating ligands possess impressive photophysical properties that make these compounds desirable for optoelectronic and photonic applications. This review is focused on the structural aspects and photoluminescence properties of cycloplatinated pentafluorophenyl (C₆F₅) compounds. The C₆F₅ group is a strong field ligand that confers a high stability to the complexes and improves their photoluminescence properties, contributing, on occasions, to the self-assembly by formation of secondary *o*-F...M interactions. In the review, the complexes are classified according to the oxidation state of platinum in mononuclear Pt^{II}-C₆F₅ and Pt^{IV}-C₆F₅ complexes, and their synthesis and properties are discussed. Some anionic and neutral Pt^{II}-C₆F₅ synthons are able to react with closed or subclosed shell ions to form a rich variety of highly emissive heteropolymetallic complexes. The properties of the latter are mainly determined by the heterometal, the cyclometalating group and the auxiliary ligands and, also, by diverse additional interactions (Pt...M, M...F, π ... π), which are responsible for their intriguing multi stimulus-responsive activity (thermochromism, vapochromism, vapoluminescence or mechanochromism).

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Abbreviations: Br-Hpbt, 2-(4-bromophenyl)benzothiazole; CC, cluster-centered; cyclen, 1,4,7,10-tetraazacyclododecane; Hbzq, 7,8-benzo[h]quinoline; Hdfppy, 2-(2,4-difluorophenyl)pyridine; HE, high energy; HOMO, highest occupied molecular orbital; Hpbt, 2-phenylbenzothiazole; Hppy, 2-phenylpyridine; Hpq, 2-phenylquinoline; Hthpy, 2-(2-thienyl)pyridine; hqH, 8-hydroxyquinoline; hqH', 2-methyl-8-hydroxyquinoline; LC, ligand centered; LE, low energy; LLCT, ligand-to-ligand charge transfer; LUMO, lowest unoccupied molecular orbital; MLCT, metal-to-ligand charge transfer; MLLCT, metal-to-ligand-ligand charge transfer; MMLCT, metal-metal-to-ligand charge transfer; 2-Np, 2-naphthyl; OLED, organic light emitting diodes; PMMA, polymethylmethacrylate; PPETS, 2-(diphenylphosphino)ethyltriethoxysilane; pyPh₂, 2,6-diphenylpyridine; PXRD, powder X-ray diffraction; Spy, 2-pyridinethiolate; TD-DFT, time-dependent density functional theory; TEOS, tetraethoxysilane; thf, tetrahydrofuran; tht, tetrahydrothiophene.

* Corresponding author.

E-mail address: teresa.moreno@unirioja.es (M.T. Moreno).

1. Introduction

Cyclometalated Pt^{II} complexes have attracted a great interest in the last decades mainly due to their rich and tunable photophysical properties, with a wide range of applicability as dopants in OLEDs [1], photocatalysis [2], biological labelling reagents [3], optical sensors [4], nonlinear optical materials [5], solid-state light emitting electrochemical cells [6] and photodynamic therapy [3c,7]. This behaviour can be explained by the efficient singlet-triplet intersystem crossing (ISC) induced by the heavy atom Pt and by the strong field ligand of the cyclometalating groups. In these complexes, the strong σ -donation of the carbon atom of the cyclometalating group and the acceptor π^* orbitals of the heteroatomic ring destabilize the unoccupied $d_{x^2-y^2}$ orbital of the Pt^{II} ion, which increases the energy of the ³dd states to a level high enough to suppress the thermal population. As a consequence, these complexes display highly efficient triplet-state phosphorescence which, in the most of the cases, is attributed to ³LC ($\pi\pi^*$) or admixtures ³LC/³MLCT or ³LLCT/³MLCT states [1f,8]. A wide range of luminescent color tunability has been described by modification of the cyclometalating group and coligands.

Moreover, the square planar Pt^{II} complexes exhibit a strong tendency to self-assembly through non-covalent Pt...Pt and $\pi\cdots\pi$ interactions with characteristic luminescent changes [9]. The assembly-induced luminescence of Pt^{II} complexes is thus ascribed to emission from a new low lying emissive state, such as metal-metal-to-ligand charge transfer (³MMLCT) or ³ $\pi\pi^*$ excimeric emission, arising from aggregation through stacking of aromatic groups, red shifted in relation to the monomer, and very sensitive to mechanical [4a,9a,10] and chemical [4a,9a,b,10a,11] stimuli (grinding, concentration, vapors or temperature).

In this topic, much scarcer is the knowledge on the optical properties of d⁶ Pt^{IV} complexes containing cyclometalating ligands [12]. Since pioneering studies by von Zelewsky and Balzani on bis(cyclometalated) Pt^{IV} derivatives [13], a few examples of luminescent mono-[12i-l], bis-[12a-e] and tris-[12f-h] (cyclometalated) Pt^{IV} complexes have been reported in the last decade. Recently, some heterobimetallic Pt^{IV}-Re^{VII} derivatives containing a discrete oxide bridge have been published as the first luminescent heterobimetallic Pt^{IV} complexes [14]. Notwithstanding, luminescent Pt^{IV} complexes are attractive because their octahedral environment offers a greater variety of ligand combination than the square planar does on Pt^{II}. Furthermore, the octahedral geometry leads to more rigid systems, favouring high quantum yields and also preventing the typical quenching deactivation of the luminescence by intermolecular interactions. Perhaps, one of the major disadvantage to obtain luminescent Pt^{IV} derivatives is the relative ease of these to undergo photochemical reduction [15]. In fact, in the platinum chemistry the formation of C—C or C—X (halide, O, N, P...) bonds usually implies oxidative/reductive reactions mediated by Pt^{II}/Pt^{IV} species [16].

Of current interest are heteropolynuclear platinum complexes and self-assembled architectures [17] generated from Pt^{II} precursors and closed- or pseudo-closed-shell (d^{10} , $d^{10}s^2$) ions. They show interesting structures and bonding features involving supported and/or unsupported metallophilic interactions and/or donor-acceptor bonds, associated in general, with interesting photochemical and photophysical properties [9b,18]. Many studies have shown that their efficient luminescence depend on the nature of the metals, the co-ligands, the strength of the Pt—M, M—M and ligand–ligand interactions and the secondary contacts. Interestingly, some of these systems are sensitive in the solid state to external stimuli, giving rise to vapoluminescent, vapochromic, thermochromic or mechanochromic systems, with extensive applications as photofunctionals materials [4a,9b,11c,19]. Cycloplatinated units have also been employed to form interesting heterometallic

complexes [18a,20], however, the number of studies on their emissive properties is rather scarce [9b,18a,19a,21], and, therefore the role of the Pt—M bonds on the optical properties of the final aggregates is not yet clear. In these systems, the donor-acceptor bond is not fully understood, because X-ray data and theoretical calculations reveal that the interaction is highly sensitive to the nature of the Pt fragment and the acidic heterometal [17g-i,21c,22]. Generally, the lone pair of the filled dz^2 orbital in the Pt^{II}, which lies perpendicular to the molecular plane, is mainly responsible for the establishment of closed-shell metal-metal electronic overlap. However, in some bimetallic complexes the acidic metal center establishes also additional interactions with the Pt-C(aryl) bonds, being these complexes models of intermediate species in aryl-ligand interchange processes [17g,i].

As it has been said before, the role of the ancillary ligands becomes important for determination of photophysical properties of cyclometalated complexes. In particular, it is desirable that the ancillary ligands also have a high intrinsic ligand-field able to avoid or reduce the quenching. As such, the C₆F₅ group, with its negative sp^2 -C donor atom also exerts strong ligand-field, what help to raise the energy of non-emissive d-d transitions above the emissive states, favouring their photoluminescence properties. In addition, in pentafluorophenyl complexes the presence of *ortho*-fluorine atoms and its high group electronegativity [23], usually lead to robust Pt^{II,IV}—C bonds, thus avoiding reductive/elimination processes (particularly on Pt^{IV}) [24]. Therefore, the aim of the present review is to highlight those contributions of light-emitting heteroleptic platinum compounds bearing bidentate cyclometalating C[^]N ligands and the C₆F₅ group as one of the ancillary ligands. The contribution is focused on emissive systems and thus, although there have been a number of interesting papers on cycloplatinated-C₆F₅ complexes related to other organometallic topics, these are out of the scope of the present review [25].

This review begins with mononuclear Pt^{II} complexes bearing C[^]N/C₆F₅ groups, followed by related cyclometalated Pt^{IV} derivatives. The last part is confined to structural and emissive properties of heteropolynuclear Pt^{II}-cyclometalated-C₆F₅ derivatives. This type of emissive systems have demonstrated to display interesting photophysical properties including multi-emissions, aggregation induced emissions (AIE), thermochromism, vapochromism, vapoluminescence or mechanochromism.

2. Mononuclear Pt^{II} complexes

A variety of alkyl or aryl heteroleptic platinum(II) complexes with cyclometalating (C[^]N) ligands have been described in the literature [25h,26], whose formation usually requires a selective intramolecular N[^]C—X (X = H, halide) bond activation process [16c,25h,27]. Among the platinum substrates used for cycloplatinated, common starting materials are labile species *cis*-[PtX₂S₂] (X = Cl, R; S = SME₂, NCMe, DMSO and so forth) and dimeric complexes [PtR₂(μ -SME₂)₂] (R = Me, aryl), because they enable the required initial N-coordination of the HC[^]N ligand. A number of neutral alkyl and aryl cycloplatinated complexes [Pt(C[^]N)XS] (X = Cl, R; S = labile solvent) [26] have been prepared. However, cyclometalation of potential H-C[^]N ligands by [*cis*-PtR₂S₂] are very rare [26g,28], probably due to the higher thermal stability of perfluoro organyl R^F-platinum bonds. Cyclometalation also encompasses less conventional reactions such as rollover [26i,29], as well as recent examples where C—H activation is preceded by reductive elimination [16g,30]. In this section we discuss the synthesis and recent developments for cycloplatinated pentafluorophenyl derivatives.

The first reported example, by Forniés and coworkers, namely the monoanionic complex (NBu₄)[Pt(bzq)(C₆F₅)₂] [31] **1**, with two

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