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Review

Luminescence platinum(II) terpyridyl complexes—From fundamental studies to sensory functions

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Contents

Abstract

Different types of luminescent platinum(II) terpyridyl complexes, $[Pt(trpy)X]^{+/2+}$ (X = anionic or neutral ligand), have been designed, synthesized and characterized. Their electronic absorption and luminescence behaviour has been investigated. Through systematic variation of the ligands, their electronic absorption properties and emission origin have also been elucidated. By the judicious design and choice of the ancillary ligand $X^{0/-}$, some of these complexes could be employed as potential chemosensors as well as biomolecule labeling agents.

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1. Introduction

Square planar platinum(II) complexes with coordinate-unsaturation have received a great deal of interest due to their capability to exhibit metal···metal interactions. One of the widely studied complexes is the dinuclear platinum(II) complex, $[Pt_2(POP)_4]^{4-}$, which exhibits rich luminescence and photochemistry associated with the presence of Pt···Pt interaction as a result of the close separation between the two anions of 2.925 Å [1]. Since the first report on the preparation and characterization of the so-called Magnus' salt, $[Pt(NH_3)_4][PtCl_4]$, in 1828, extensive optical investigations of such complexes have been made due to the surprising green colour associated with the presence of the Pt···Pt interaction, when compared to the colourless $[Pt(NH_3)_4]^{2+}$ and the pink $[PtCl_4]^{2-}$ ions [2]. Recently, numerous double salts of platinum(II)–platinum(II), $[Pt(CNR)_4][Pt(CN)_4]$, have been shown to exhibit interesting vapochromic and vapoluminescence behaviour, which is presumably attributed to the change of Pt···Pt interaction upon sorption of guest vapor [3–5]. The platinum(II) polypyridyl system has also aroused a growing interest in the past few decades owing to its rich photoluminescence and polymorphism

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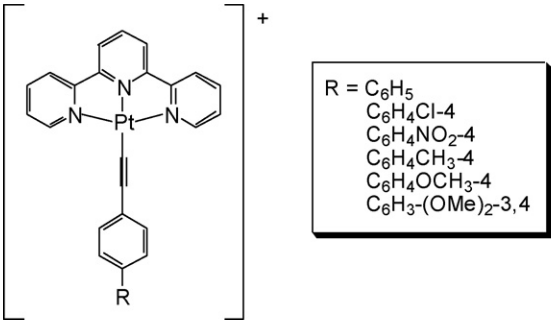
behaviour [6–24], with some of the intriguing spectroscopic features ascribed to the occurrence of Pt···Pt and/or π–π interactions. For instance, two crystal forms of $[Pt(bpy)Cl_2]$, the red form and the yellow form, have been isolated with identical chemical behaviour and they can be inter-converted into each other. The variation in such optical properties was attributed to the different Pt···Pt separation of 3.45 and 4.44 Å, respectively, in the red and yellow form as revealed by X-ray crystallography [6–8].

The platinum(II) terpyridyl system, $[Pt(trpy)X]^{+/2+}$ (trpy = 2,2′:6′,2″-terpyridine; X = anionic or neutral ligand), is another representative class of the platinum(II) polypyridyl system. The synthesis of the chloroplatinum(II) terpyridyl complex, $[Pt(trpy)Cl]Cl·2H_2O$, was first reported by Morgan and Burstall [25]. Apart from the subsequent structural and mechanistic investigation [26,27], the complex was found to bind calf thymus DNA through an intercalative interaction involving the planar terpyridyl moiety and the formation of covalent bond with the bases, as reported by Lippard and co-workers [28,29]. Later on, the same group and others reported a variety of the related thiolate analogues, $[Pt(trpy)(SR)]^+$, as well as other mononuclear and dinuclear platinum(II) terpyridyl complexes that exhibit metallointercalation and cytotoxicity behaviour [28–35]. The potential of these complexes as antitumor drugs has also been explored.

The chloroplatinum(II) terpyridyl complex, $[Pt(trpy)Cl]^+$, was reported to exhibit very strong luminescence in the solid state and in low-temperature glass [17,18]. Moreover, the solid-state colours and luminescence energies were dependent on the nature of the counter anions, including PF_6^-, ClO_4^-, Cl^- and $CF_3SO_3^-$, which was attributed to the variations of stacking arrangement that gave rise to different Pt···Pt and π–π interactions [18]. Although, a low-lying triplet $[d\pi(Pt) \rightarrow \pi^*(trpy)]$ metal-to-ligand charge-transfer (^{3}MLCT) excited state is anticipated to show luminescence, no detectable emission was observed in its solution state at room temperature due to the quenching of the ^{3}MLCT state by the thermally accessible ^{3}d–d excited state via non-radiative decay [9]. The introduction of various substituents on the 4′-position of the terpyridine ligand on $[Pt(4'\text{-R-trpy})Cl]^+$ greatly enhances their luminescence properties by rendering the ^{3}MLCT excited state lower-lying than the non-emissive ^{3}d–d excited state or through the incorporation of intra-ligand character into the excited state [17,22–24].

In this review, we describe efforts that mainly focus on the studies of numerous platinum(II) terpyridyl complexes, $[Pt(trpy)X]^{+/2+}$, with various anionic or neutral ancillary ligand X, including alkynyl, thiolato and phosphino groups, prepared by this laboratory. Through the systematic variation of different substituents on the ligand $X^{-/0}$ or functionalization of such ligands, a fundamental understanding of the origin of their photophysical properties has been elucidated. Some of the complexes have also been shown to serve as chemosensors as well as biomolecule labeling agents.

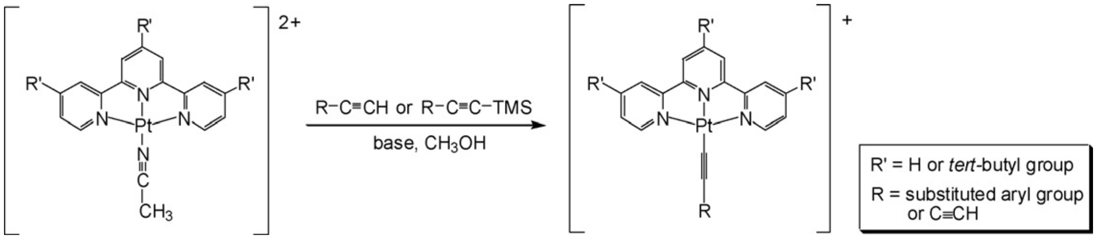


Scheme 1.

2. Mononuclear platinum(II) terpyridyl alkynyl complexes

2.1. Syntheses and characterization

Subsequent to the first report on the synthesis and preliminary photophysical studies of platinum(II) diimine bisalkynyl complexes, $[Pt(N\wedge N)(C\equiv CR)_2]$ (N∧N = diimine ligand) by Che and co-workers [12], numerous studies on their chemical, photophysical and electroluminescence properties by different research groups have appeared [14,36–42]. Despite numerous reports on the photophysical studies of the platinum(II) terpyridyl system [15–24], related work on the platinum(II) terpyridyl alkynyl system did not appear until 2001 when we reported the first successful synthesis of a series of platinum(II) terpyridyl alkynyl complexes, $[Pt(trpy)(C\equiv CR)]^+$ [43] (Scheme 1), which represents a continuation of our efforts on transition metal alkynyl complexes [44–50]. Later on, several laboratories showed their research interests in this novel class of complexes [51–57]. The preparation of such class of complexes was achieved by the reaction of the acetonitrile-coordinated precursor complex, $[Pt(N\wedge N\wedge N)(MeCN)]^{2+}$, with various organic alkynes under basic condition (Scheme 2). Triethylamine or sodium hydroxide was employed to deprotonate the acetylenic proton of the terminal alkynes, which



Scheme 2.

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