

Luminescence Properties and Application of Versatile Coordination Compounds Based on Modified Platinum(II) Terpyridyl Complexes

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Abstract

A series of square-planar Platinum(II) terpyridyl modified by alkynyl, crown ether pendants, or supramolecular triblock copolymers have versatile luminescence behaviors. In this field, the utilization of the Platinum(II) terpyridyl coordination compounds have received great attention in the past few decades. This paper will summarize several relevant literatures about luminescence properties and application in responding pH, conformational change, microenvironmental change and detection of heparin quantification.

Keywords: coordination compounds, luminescence, Platinum(II), terpyridine ligands

Introduction

The study of Platinum(II) coordination compounds has a long history. A kind of lemon yellow crystal of $K[PtCl_3(C_2H_4)] \cdot H_2O$ was obtained occasionally in 1827 by W.C. Zeise, but published until 1831.^[1] Subsequently, G. Maguns' group reported the preparation and characterization of $[Pt(NH_3)_4][PtCl_4]$ in 1828, so-called Magnus' salt.^[2] Since then, great progress has been made in the extensive application of Platinum(II) complexes,^[3-7] especially the Platinum(II) terpyridyl complexes. The reason can be attributed to their useful physical and biological properties,^[8-9] as well as interesting luminescence behaviors^[10-11]. The preparation of such class of complexes was achieved by the reaction of the corresponding coordinated precursor compounds with organic alkynes or crown ether ligand under basic condition. In general, there are some characteristic peaks in H^1 NMR spectra of these complexes, and X-ray crystallography was employed to determine some of the structures.

Emission properties

Transition-metal complexes with triplet excited states show emission of phosphorescence. This is because those heavy metal centers make up larger spin-orbit coupling, which enhances the intersystem crossing.^[12] Like a previous report, the $[Pt(trpy)Cl]^+$, unlike the chloro-counterpart, was nonemissive in the solution state at room temperature,^[13] complexes except for **4**, **6**, and **7** were found to exhibit luminescence at room temperature in acetonitrile solution, but all of them show emission properties in 77 K butyronitrile glass. The excitation and emission wavelength for **1** in 77 K butyronitrile glass was about 350 nm and 550 nm respectively. The butyronitrile glass of complexes 1-5 upon excitation at $\lambda > 350$ nm show emissions at 510 - 580 nm. Meanwhile, there were several progression spacing of *ca.* 1300 cm^{-1} , which correspond to the aromatic vibrational mode of the terpyridine ligands. Furthermore, the electron-rich or electron-deficient substituents on the phenyl ring of the acetylide ligands

could impact on the emission energies of the complexes in solution. The order of emission energy is $5 > 2 > 1 > 3$, which is in accordance with the trend of electron-sequence from rich to poor. Sometimes, N-donor crown ether pendants of Platinum(II) terpyridyl complexes showed emission properties in dichloromethane solutions at room temperature.^[16] V. W. -W. Yam and coworkers found that complexes **1-6** show bright luminescence at 560 - 600 nm in solid state at room temperature, which have similar energies to the low-energy emission in 77 K glass. For example, the emission wavelengths were *ca.* 575 nm at 298 K and *ca.* 600 nm at 77 K, respectively. However, not all Platinum(II) terpyridyl complexes exhibit intense MLCT luminescence, as some kinds of complexes do not emit in acetonitrile solution or in the solid state (Figure 2),^[17-19] it's probably because that the substituents on acetylide ligands lead to the quenching of the emissive $^3\text{MLCT}$ excited state by reductive electron transfer and the lower-lying nonemissive $^3\text{LLCT}$ excited state. In light of extensive research on emissive spectrum of Platinum(II) terpyridyl complexes, more conjugated and more rigid arylsubstituted compounds have been designed and synthesized. More recently, reports about linear bimetallic alkynylplatinum(II) terpyridyl complexes in which two platinum(II) centers are linked by *p*-phenylene ethynylene oligomers, were synthesized.^[20] These complexes show multiple emission peaks and emission spectra in the range 625–765 nm. More interesting was that concentration-dependent emission spectra show the appearance of a broad low-energy emission band and a decrease of the high energy emission band when the concentration increases. Another kinds of Calix[4]arene-based Platinum(II) terpyridyl were also synthesized.^[21] Those derivatives will turn to be gelation from solution in DMSO/H₂O of

varying compositions. Moreover, the DMSO/H₂O ratio of the solvent gives rise to strong luminescence enhancement. In the absence of H₂O, an emission band centered at 570 nm was observed. The band intensity dropped dramatically for higher proportions of H₂O. Simultaneously, a new emission band appeared at 660 nm, which originated from an excimer emission that is attributed to the formation of aggregate species. Furthermore, computational studies on the excited states of luminescent Platinum(II) alkynyl to provide an in-depth understanding of the nature of their emissive origin as well as the nonradiative processes.^[22] In spite of much research on the luminescence properties of Platinum(II) terpyridyl, we are still uncertain about what distance between two Platinum(II) terpyridyl molecules will induce luminescence quenching, and more experimental evidences and computational studies should be supplied.

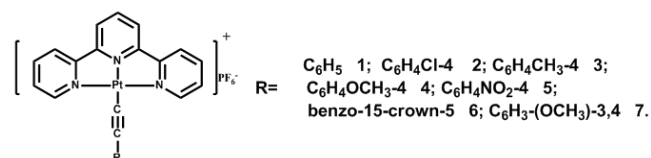


Figure 1 Structures of complexes **1-7**.^[17]

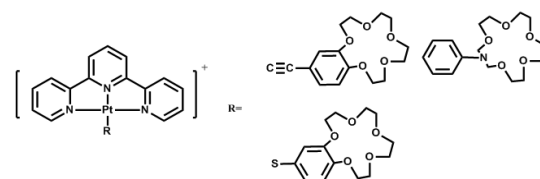


Figure 2 Structures of non-emissive complexes.^[17-19]

Application

In fact, most of transformed Platinum(II) terpyridyl complexes not only possess

luminescence properties, but also show potential application in detection of important biomolecules,^[23-27] conformational changes,^[25-26] enzymatic activities,^[27] pH sensor,^[30] molecular self-assembly of themselves,^[25] host-guest chemistry,^[28] and so on.

V. W. -W. Yam and coworkers prepared a series of dinuclear alkynyl Platinum(II) terpyridyl complexes, where the two Platinum(II) units were linked through a flexible bridge on terpyridyl rings (Figure 3).^[29] Those systems showed a high tendency toward spontaneous solution-state intramolecular self-association which was found to depend on bridge length and temperature. Another metallo-supramolecular triblock copolymers (PEO-PPO-PEO) linked between terpyridyl rings (Figure 4) were reported in 2011.^[30] As we know, the poly (ethylene oxide)-block-poly(propylene oxide) -blockpoly (ethylene oxide) (PEO-PPO-PEO) triblock copolymers undergoes conformational transition when the critical micelle concentration (CMC) or the critical micelle temperature (CMT) is reached.^[31] The triblock copolymers drive $[XPt(tpy)PEO-PPO-PEO(tpy)PtX](OTf)_2$ to the formation of spherical micelles at temperatures above the critical micelle temperature. As the temperature increased, the two complexes were found to aggregate with Pt...Pt and/or π - π interactions, and reveal the red-near-infrared (NIR) emission. Moreover, the NIR emission can be switched on and off by several cycles of heating and cooling. Therefore, those attractive Platinum(II) terpyridine complexes that were sensitive to temperature may be exploited for the design of sensitive luminescent temperature sensors for probing conformational and microenvironmental changes. Besides, a novel binuclear Platinum(II) alkynyl calix[4]crown-5 complex has been demonstrated to show selective luminescence chemosensing of Potassium ions in form of strong luminescence

enhancement.^[32] Therefore, Platinum(II) terpyridine complexes may have interesting applications in designing luminescence chemosensors. If the $[Pt(tpy)Cl]^+$ was modified by various kinds of groups both on the side of metal and terpyridine, then they would become latent applying in pH and the polarity of solution media.^[33] A system of supramolecular diblock copolymers based on Platinum(II) terpyridyl present pH- and solvent-responsive micellization properties. This properties could induce drastic UV-vis and emission spectral changes *via* modulation of Pt...Pt and π - π stacking interactions, while those two interactions were affected by the pH and polarity of solution. Such qualities of amphiphilic Platinum(II) terpyridyl based diblock copolymers may be exploited for probing conformational and microenvironmental changes. In addition, Platinum(II) terpyridyl can be used as a probe in detection heparin in view of alkynylplatinum(II) terpyridine complex possess rich positive charge, and heparin is believed to have the highest negative charge densities amongst the biological macromolecules, so heparin macromolecule can induce self-assembly of the platinum(II) complexes with luminescence spectral changes in NIR region.^[34] Upon addition of heparin in buffer solution to a water-soluble platinum(II) complex, growth of a low-energy NIR emission band was observed. This emission was due to triplet MMLCT (³MMLCT). The changed emission indicate that the complex molecule of **14** were close proximity, and induce the self-assembly of **14**. This is because that the positively charged platinum(II) complex and the multiple negatively charged heparin got close each other through electrostatic attraction. Linear relationships could be obtained for the concentration range from 0 to 8.7 μ M for heparin measurements via luminescence enhancement method. So platinum(II) complex

was a label-free sensing nearinfrared (NIR) probe in detection heparin quantification, avoiding the problems of autofluorescence and light scattering arising from the biological environment. However, we cannot deny the limit of detection range, and cannot underestimate the involvement of hydrogen bonding interactions between complex **14** and heparin. Meanwhile, the determination of heparin will be disturbed by other negatively charged polydispersed polysaccharide biological macromolecules due to the presence of numerous sulfate and carboxylate groups, such as chondroitin 4-sulfate (ChS) or hyaluronic acid (HA) and so on. Furthermore, Platinum is a kind of heavy, precious and toxic metal, so it cannot be used widely in clinical application. It is believed that more better methods will be developed and less toxic metal or non-metal coordination compounds should be replaced in the future.

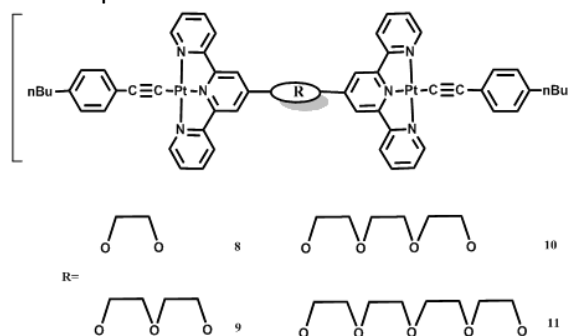


Figure 3 Structures of the dinuclear alkyne Platinum(II) terpyridyl complexes 8-11.^[28]

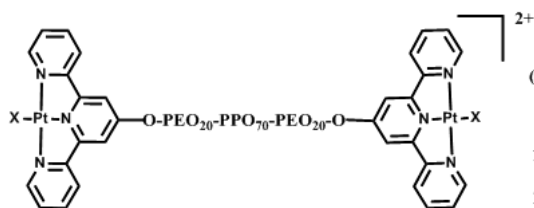


Figure 4 Chemical structures of complexes 12 and 13.^[29]

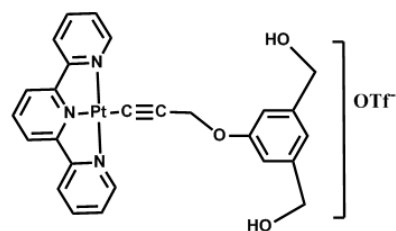
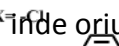
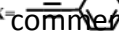


Figure 5 Chemical structure of complex 14.^[34]

Conclusions

In summary, the luminescent nature of Platinum(II) terpyridine complexes can be assigned to a $[d\pi(\text{Pt}) \rightarrow \pi^*(\text{trpy})]$ $^3\text{MLCT}$ excited state and some mixing of a $[\pi(\text{C}\equiv\text{CR}) \rightarrow \pi^*(\text{trpy})]$ $^3\text{LLCT}$ state. Some non-emissive cases also exist, which may be ascribed to the quenching of the emissive state by photoninduced electron transfer (PET). In spite of this, more and more attention are focused on the promising application of Platinum(II) terpyridine complexes, and diversified pendants modification on Platinum(II) or multiple branches on the ring of terpyridine will be explored. In general, from our point of view, the application of Platinum(II) terpyridyl complexes may be extended to the area of catalytic oxidation, dye-sensitized solar cells, organic light-emitting devices, optical materials, and so on.

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