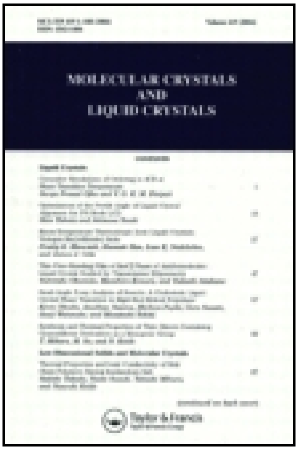

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Luminescence Properties and Assembled Structures of Dicyano(Diimine) Platinum(II) Complexes in Glassy Solution

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Luminescence Properties and Assembled Structures of Dicyano(Diimine)Platinum(II) Complexes in Glassy Solution

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Characteristic luminescence from the assembled species of $[Pt(CN)_2(L)]$ (L = 3,3'-biisoquinoline (*i*-biq) and 2,2'-bipyridine (bpy)) has been found in a dilute EtOH-MeOH (4:1 v/v) glassy solution at 77 K. For the *i*-biq complex, a broad emission band (λ_{max} = 680 nm) appears with increasing concentration in addition to a $^3\pi\pi^*$ emission band form the monomer complex (λ_{max} = 528 nm). The broad band is attributable to the emission from the ^{3}MLCT state of the assembled species with the Pt-Pt intermolecular interaction. In the case of the bpy complex, similar broad emission is also observed as well as the sharp $^3\pi\pi^*$ emission. However, the broad emission has an excimeric character. The π-π interaction between the π-conjugated ligands would be an important factor in the assemblage of the platinum complexes in the dilute system.

Keywords: platinum complexes; luminescence properties; self-assembly; metal-metal interaction; π-π interaction; biisoquinoline

INTRODUCTION

Square-planar platinum(II) complexes are often stacked in the solid state to display characteristic color and luminescence. The red forms of $[Pt(CN)_2(L)]$ (L = 3,3'-biisoquinoline(*i*-biq) and 2,2'-bipyridine (bpy), FIGURE 1) with Pt–Pt interactions have also intense emission in the visible region which is originated from a metal-to-ligand charge transfer

(MLCT) state, although the monomeric form emits structured $^3\pi\pi^*$(*i*-biq) luminescence in higher energy.[1],[2] Also in a dilute EtOH-MeOH (4:1 v/v) glassy solution, we have found concentration-dependent luminescence for the complexes. In order to elucidate the origin of the luminescence, the emission spectra and lifetimes of the complexes were investigated. We report here the self-assembly and the characteristic luminescence behavior of the diimine-platinum complexes in glassy solution.

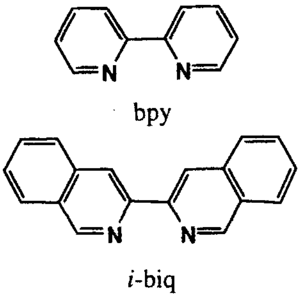

FIGURE 1 Structural formulas of the diimine ligands

EXPERIMENTAL SECTION

Materials [Pt(CN)$_2$(bpy)] was prepared according to the literature procedure.[3] The preparation of [Pt(CN)$_2$(*i*-biq)] was reported previously.[1]

Emission Spectroscopy Emission spectra were obtained on a Shimazu RF-5300PC spectrofluorimeter equipped with a liquid nitrogen dewer. Time-resolved measurements for the emission lifetimes were performed with a Hamamatsu C4780 emission-lifetime-measuring system.

RESULTS

FIGURE 2 shows the emission spectra of [Pt(CN)$_2$(*i*-biq)] in EtOH-MeOH (4:1 v/v) at different concentrations (λ_{ex} = 400 nm) and the excitation spectra observed at 533 and 680 nm at 77 K. The sharp structured spectrum with the maximum at 528 nm (τ = 1.5 ms) observed at the lowest concentration (4×10^{-7} mol dm^{-3}) is typical of the emission from the $^3\pi\pi^*$ state of the *i*-biq ligand as is the case for [Ru(*i*-biq)$_3$]$^{2+}$

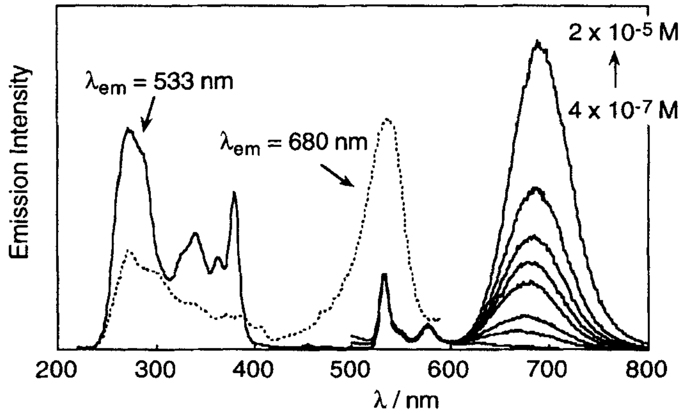

FIGURE 2 Emission spectra at different concentrations (λ_{ex} = 400 nm) and excitation spectra (λ_{em} = 533 and 680 nm) of $[Pt(CN)_2(i\text{-biq})]$ in EtOH-MeOH (4:1 v/v) at 77K.

and $[PtCl_2(i\text{-biq})]$.[4],[1] At higher concentration, however, a broad band has evolved at a range of 600-800 nm in addition to the $^3\pi\pi^*$ emission band. These emission spectra shown in FIGURE 2 are normalized at the peak of the sharp $^3\pi\pi^*$ emission. Thus the relative intensity of the broad band to the sharp one increases with concentration. The broad emission has the lifetime of 1.7 μs, *ca.* 10^{-3} of that for the $^3\pi\pi^*$ emission. The excitation spectra observed at 533 nm is very similar to the absorption spectrum of the complex in solution at room temperature, while that observed at 680 nm is completely different. At the constant concentration of 2×10^{-5} mol dm^{-3}, the appearance of the broad emission band was inhibited by adding DMF. These results strongly suggest that the broad emission band originates from the assembled species such as dimer or oligomer, whereas the sharp and structured emission spectrum is due to the monomeric complex. It is interesting to note that there appears a very strong peak at the visible region (*ca.* 540 nm) in the excitation spectrum. In fact, the sample solution turned to violet in color when it was frozen. This would be ascribed to the occurrence of the Pt–Pt interactions.

As shown in FIGURE 3, the concentration-dependent emission

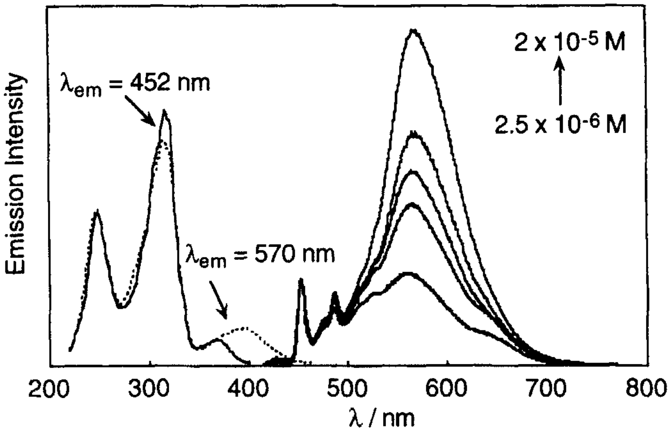

FIGURE 3 Emission spectra at different concentrations (λ_{ex} = 400 nm) and excitation spectra (λ_{em} = 452 and 570 nm) of [Pt(CN)$_2$(bpy)] in EtOH-MeOH (4:1 v/v) at 77K.

spectra were observed also for [Pt(CN)$_2$(bpy)]. The relative intensity of the broad band at 570 nm increased with concentration compared with the sharp $^3\pi\pi^*$ (bpy) band at 452 nm. The emission lifetime of the broad band was obtained as a comparable value (1.8 μs) to that for [Pt(CN)$_2$(*i*-biq)]. However, the features of the excitation spectra are quite different. The excitaion spectrum observed at 570 nm is similar to that observed at 452 nm except for the band around 350–450 nm which shifts depending on the monitor wavelength. The absence of an intense band in the visible region for [Pt(CN)$_2$(bpy)] indicates low ability of the self-assembly of this complex compared with [Pt(CN)$_2$(*i*-biq)]. Consistently, the broad emission band shifts with the excitation wavelength (400–500 nm). Thus the broad emission could have an excimeric character.

DISCUSSION

[Pt(CN)$_2$(*i*-biq)] containing an extended π-system shows the unique emission properties by assembling in the glassy solution even at a very

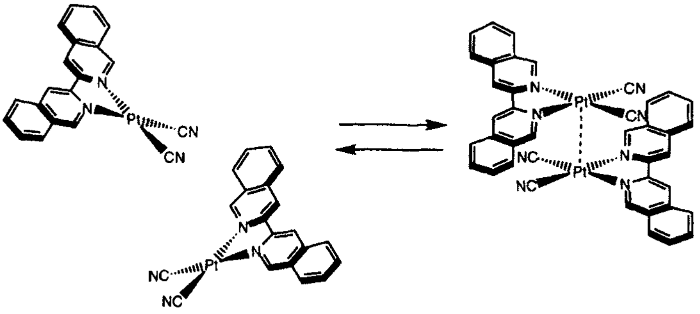

FIGURE 4 Assemblage of [Pt(CN)$_2$(*i*-biq)] in a dilute glassy solution.

low concentration as shown schematically in FIGURE 4. Compared with those for [Pt(CN)$_2$(bpy)], which forms no definite assembled species but occurs the excimeric interaction, it is concluded that the π–π interaction between the α–diimine ligands would play an important role of the assemblage of the platinum complexes. In fact, the stacking structure of [Pt(CN)$_2$(*i*-biq)] found in the crystal is different from that found in the [Pt(CN)$_2$(bpy)] crystal regarding the π–π interactions though the Pt···Pt distances are similar to each other at room temperature. We reported that the different π–π interactions for the [Pt(CN)$_2$(*i*-biq)] and [Pt(CN)$_2$(bpy)] crystals caused completely different emission behavior and structural change at lower temperatures.[2] Additional ligands would also affect the self-assembly of the platinum complexes because the effect of the ligand field strength affects the formation of linear chain structures and strength of Pt–Pt interactions in the crystal state. Also in the glassy solution, for [PtCl$_2$(*i*-biq)] containing Cl$^-$ with much weaker ligand-field strength instead of CN$^-$, we could not detect any sign of assembly in the emission spectrum under the same conditions. These facts also support our conclusion that the broad emission spectrum appearing in the glassy solution of [Pt(CN)$_2$(*i*-biq)] is due to the assembled species with Pt–Pt interactions of the complex units. Similar emission behavior based on the self-assembly of [PtCl(tpy)]$^+$ (tpy = 2,2':6',2''-terpyridine) was reported by Bailey *et al.*, but it seems very complicated because of the generation of several types of the assembled species.[5] The complex could be in the intermediate position between [Pt(CN)$_2$(*i*-biq)] and [Pt(CN)$_2$(bpy)] in the character of the intermolecular interactions.

It is interesting to note that the broad emission band of [Pt(CN)$_2$(*i*-biq)] appears at longer wavelength compared with the emission of the crystal (λ_{max} = 630 nm at room temperature), while the excimeric emission for [Pt(CN)$_2$(bpy)] represents at shorter wavelength than that of the crystal (λ_{max} = 610 nm at room temperature). It is known that the transition energy between HOMO and LUMO of Pt–Pt interactive systems decreases with increasing Pt–Pt interaction.[6] Thus the lower emission energy in the glassy solution of [Pt(CN)$_2$(*i*-biq)] suggests of that the assembled species with stronger Pt–Pt interaction than that in the crystal are formed in the glassy solution. It is reasonable taking the flexibility of the assembled species in the glassy solution into account: Two or a few complex units could be assembled taking more favorable arrangement than that in the crystal with a rigid three-dimensional array.

In conclusion, from the characteristic emission, we have found the tight assemblage of [Pt(CN)$_2$(*i*-biq)] and soft excimeric interaction of [Pt(CN)$_2$(bpy)] in the dilute glassy solution.

Acknowledgments

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