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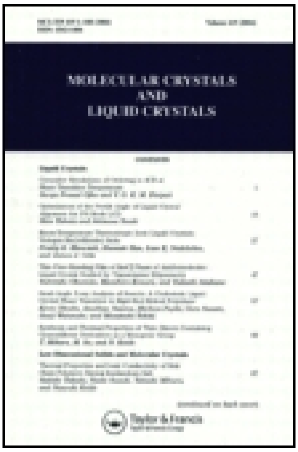

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Vapochromism and Crystal Structures of Luminescent Dicyano(2,2′-Bipyridine)Platinum(II)

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Vapochromism and Crystal Structures of Luminescent Dicyano(2,2′-Bipyridine)Platinum(II)

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Vapochromic behavior of the crystal of dicyano(2,2'-bipyridine)platinum(II), $[Pt(CN)_2(bpy)]$, has been investigated structurally and emission spectroscopically. Red Form with an infinite Pt···Pt chain transforms to Yellow Form reversibly by taking up water vapor. The crystal structure of Yellow Form ($[Pt(CN)_2(bpy)]\cdot H_2O$) was determined by X-ray analysis: the square-planar complexes form the inclined stack with short and long Pt···Pt distances (3.3279(3) and 4.6814(3) Å). The crystal water makes hydrogen bonds with CN^- ligands connecting the stacks. The transformation is accompanied by the sensitive luminescence change as well as the color change, which reflects the change of the Pt···Pt electronic interactions. The sensitive vapochromism for this system is attributable to the slight deformation of the stacking structure induced by water molecules.

Keywords: platinum complex; luminescence spectrum; vapochromism; metal-metal interaction; crystal structure

INTRODUCTION

Dimorphism of dicyano(2,2'-bipyridine)platinum(II), $[Pt(CN)_2(bpy)]$ is known for a long time[1]: Red Form transforms to Yellow Form by taking up water molecules reversibly (eq. 1). Interestingly, the

$$\underset{\text{Red Form}}{[\mathrm{Pt(CN)_2(bpy)}]} \xrightleftharpoons{\mathrm{H_2O}} \underset{\text{Yellow Form}}{[\mathrm{Pt(CN)_2(bpy)}]\cdot \mathrm{H_2O}} \qquad (1)$$

transformation occurs depending on the vapor pressure of water in the atmosphere. The correct crystal structure of Red Form was determined recently[2]. It has a stacked structure of the complex units with the Pt···Pt distance of 3.34 Å at room temperature. As a result of the Pt···Pt electronic interaction, Red Form emits intense red luminescence which is originated from the metal-metal-to-ligand charge transfer state (MMLCT). For this system, we found a good correlation that the emission spectrum shifts to lower energy with shorter Pt···Pt distance[3]. On the other hand, the structure of Yellow Form has never been known because it usually crystallizes only as fine needles. As a similar system, both crystal structures of red and yellow forms for [PtCl$_2$(bpy)] have already been determined[4]: The red form for [PtCl$_2$(bpy)] has the same crystal structure as the corresponding form of [Pt(CN)$_2$(bpy)], while the yellow form has a π–π stack with no Pt···Pt interactions. However, the crystal structure of Yellow Form for [Pt(CN)$_2$(bpy)] should be different from that of [PtCl$_2$(bpy)] because the latter system does not contain crystal water nor show the vapochromic behavior.

In this paper, we have finally done the X-ray analysis of Yellow Form of [Pt(CN)$_2$(bpy)]. On the basis of the structural change and luminescence spectral change between Red and Yellow Forms, the mechanism of the vapochromic behavior of [Pt(CN)$_2$(bpy)] has been elucidated.

EXPERIMENTAL

Materials

[Pt(CN)$_2$(bpy)] was prepared according to the literature procedure[5]. Recrystallization from DMF/water (1:1 v/v) gave yellow plates of Yellow Form, whereas Red Form crystallized from DMF solution.

X-ray crystallography

The X-ray diffraction data of Yellow Form were collected on a Rigaku AFC-7R four-circle diffractometer[6]. The structure was solved by Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Two hydrogen atoms for water were found by the differential Fourier synthesis and other

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hydrogen atoms were located on the calculated positions and treated with the riding model. The structure was converged nicely[6]. All calculations were performed using teXsan[7].

Emission Spectroscopy

Emission spectra were obtained on a Shimadzu RF-5300PC spectrofluorimeter. Time-resolved measurements for the emission lifetimes were performed with a Hamamatsu C4780 emission-lifetime-measuring system.

RESULTS AND DISCUSSION

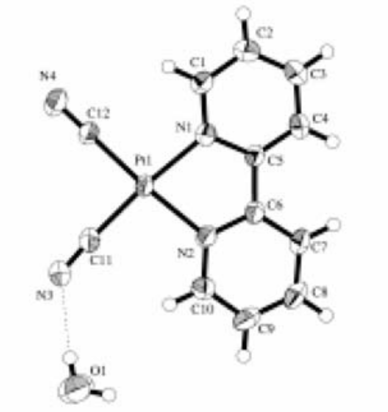

FIGURE 1 ORTEP drawing of Yellow Form ([Pt(CN)$_2$(bpy)]·H_2O)

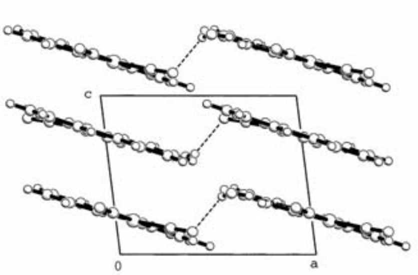

FIGURE 2 Packing diagram of Yellow Form ([Pt(CN)$_2$(bpy)]·H_2O)

Figure 1 shows the molecular structure of [Pt(CN)$_2$(bpy)]·H_2O for Yellow Form. The geometry of the complex is similar to that found in Red Form. The water molecule is located near the complex making the hydrogen bond with the CN$^-$ ligand. As shown in Figure 2, the complexes form the inclined stacks in the crystal. The stacks are connected with water molecules through hydrogen bonds. The stacking structure is quite different from that of the yellow form for [PtCl$_2$(bpy)] constructed with a π–π stacking. It is rather recognized as the deformed structure of the infinite chain structure for Red Form of [Pt(CN)$_2$(bpy)]. In Figure 3, the stacking structures of Red and Yellow Forms are compared. It is clear that the stack for Yellow Form is much more zigzag than that for Red

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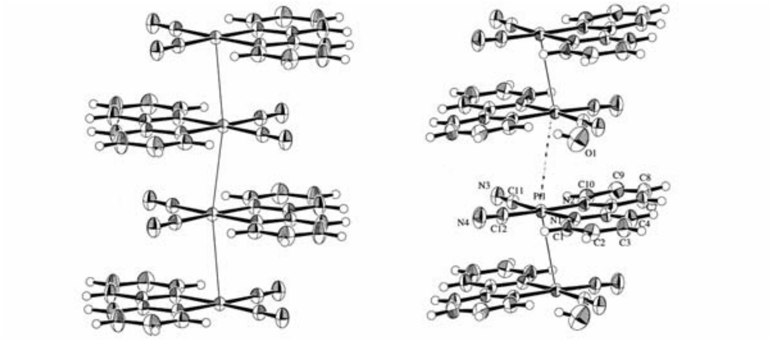

FIGURE 3 Comparison of the stacking structures for Red and Yellow Forms of $[Pt(CN)_2(bpy)]$. Left: Red Form (Pt···Pt = 3.3388(1), Pt···Pt···Pt = 168.59(4)°), right: Yellow Form (Pt···Pt = 3.3279(3), 4.6814(3) Å, Pt···Pt···Pt = 132.89(1)°).

Form. There are short and long Pt···Pt distances in the stack. The distances suggest that Yellow Form has a dimer structure in view of the Pt···Pt interaction.

The transformation between Red and Yellow Forms is accompanied by the sensitive luminescence change as well as the color change, which reflects the change of the Pt···Pt electronic interactions. Figure 4 shows the emission spectral change of Red Form in the

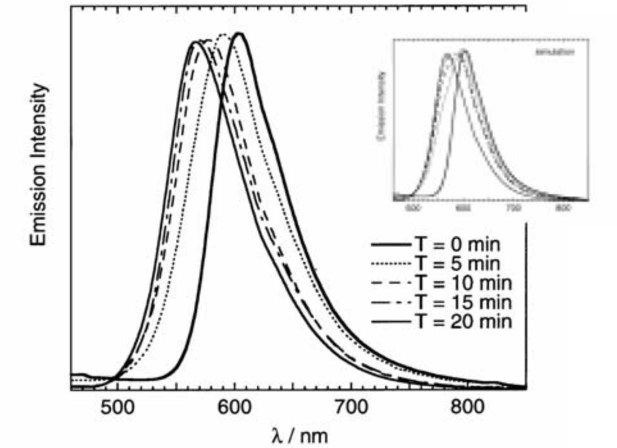

FIGURE 4 Emission spectral change of Red Form in the presence of water vapor at room temperature. Inset: simulation spectra made of those for Red and Yellow Forms.

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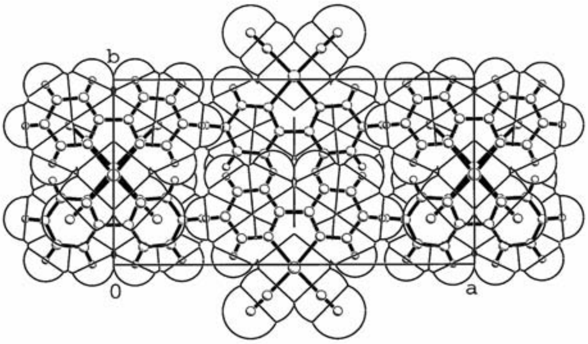

FIGURE 5 Packing Structure of Red Form of [Pt(CN)$_2$(bpy)] with van der Waals spheres viewed down *c* axis.

presence of water vapor at room temperature. The spectrum with the maximum of 602 nm gradually shifts to the shorter wavelength and reaches to the spectrum with the maximum of 566 nm. The final spectrum is consistent with that for Yellow Form. Thus the transformation from Red Form to Yellow Form induced by taking up of water molecules was confirmed specrtroscopically. The origin of the luminescence for Yellow Form is assigned to the ^{3}MMLCT state which is essentially the same state as that for Red Form on the basis of the similarity of the spectral profiles and emission lifetimes (τ = 56 and 109 ns for Yellow and Red Forms, respectively). In fact, the yellow form for [PtCl$_2$(bpy)] exhibits only weak luminescence at room temperature because it has no Pt···Pt interactions and the lowest excitation state is dd state[8]. The assignment of the luminescence is quite reasonable also from the viewpoint of the crystal structure: Yellow Form of [Pt(CN)$_2$(bpy)] has the short Pt···Pt distance enough to interact electronically. However, the interaction is restricted within the dimer unit and the inclined stack would reduce the orbital overlap between Pt atoms. As a result, the ^{3}MMLCT emission state for Yellow Form shifts to the higher energy than that for Red Form. Similar behavior has been observed for the crystal of [Pt(CN)$_2$(*i*-biq)] (*i*-biq = 3,3'-biisoquinoline): the Pt···Pt interaction decreases with the inclination of the complex planes in the stack even if the Pt···Pt distance dose not vary[3].

Furthermore, the crystal packing structure of Red Form of [Pt(CN)$_2$(bpy)] suggests the easiness of the uptake of water molecules. As shown in Figure 5, the arrangement of the linear chain stacks in Red Form is well-ordered and there are cavities among the stacks. It could be channels for water molecules. However, as the channels are narrow for water molecules, the structural deformation must be induced. In conclusion, the sensitive vapochromic behavior for the [Pt(CN)$_2$(bpy)] crystal is attributable to the slight deformation of the stacking structure with Pt···Pt chain induced by water molecules.

Acknowledgments
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