

Vapor-induced structural regeneration of a vapochromic platinum complex

Atsushi KOBAYASHI¹, Tsubasa YONEMURA¹, Masako KATO*¹, Yusuke WAKABAYASHI², Hiroshi SAWA²

¹Division of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan
²KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

One-dimensional (1-D) stacking Pt-diimine complexes have well studied for several decades because of their characteristic luminescence based on the Pt...Pt interaction[1,2]. In recent years, the "vapochromism", which is a color change induced by exposure to a volatile solvent vapor, has attracted much attention because vapochromic materials have the potential applicable to chemical sensors. Our group have designed and synthesized a luminescent Pt-diimine complex, [Pt(CN)₂(4,4'-*dc bpy*)] (4,4'-*dc bpy*: 4,4'-dicarboxy-2,2'-bipyridine) and reported the vapochromism sensing the various volatile organic solvent vapors such as CH₃OH, CH₃CN and so on [3]. Although this complex has vapor-accessible 1-D pores with the diameter of 0.6 nm (see Fig. 1.), the origin of vapochromism is under discussion yet. In this report, we discuss the vapochromism on the basis of powder X-ray diffraction (PXRD).

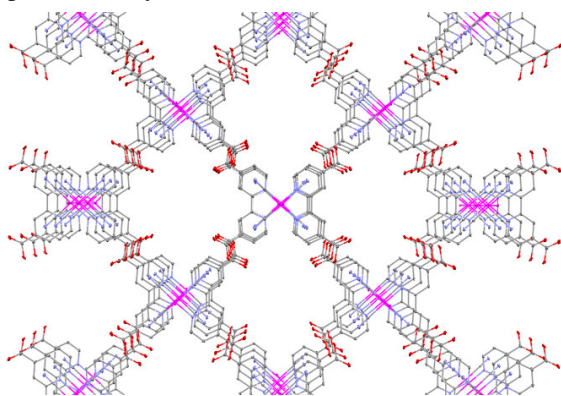


Fig. 1. Crystal structure of [Pt(CN)₂(4,4'-*dc bpy*)].

Result and Discussion

To detect the vapor-induced structural change, PXRD patterns were measured under exposure to some organic solvent vapors. Fig. 2 shows the PXRD patterns and emission spectra in vacuum and DMF (*N,N*-dimethylformamide) vapor. Observed PXRD pattern before vacuum was identical to the structure with vapor-accessible 1-D pores. On the other hand, the pattern under vacuum consisted of broad and poor peaks, suggesting that the crystal structure with 1-D pores was partly broken by the removal of crystal water. Surprisingly, after exposure to the DMF vapor for 1 day, observed PXRD pattern was almost the same with the pattern before vacuum. It is proved that the crystal structure with 1-D pores was regenerated on exposure to DMF vapor. The emission peak also shifted from 647 nm to 710 nm and

returned to 640 nm. It is well known that the emission of Pt-diimine complex with 1-D stacking structure is originated from the ³MLCT (Metal-to-Ligand Charge Transfer) state and the emission energy is mainly dominated by the Pt-Pt distance in 1-D stacking column. In the case of [Pt(CN)₂(4,4'-*dc bpy*)], observed red and blue shifts in vacuum and exposure to DMF vapor, respectively, suggest the structural change accompanying with shortening and elongation of the Pt-Pt distance. This vapor induced structural regeneration was confirmed also in the case of the exposure to EtOH and CH₃CN vapors.

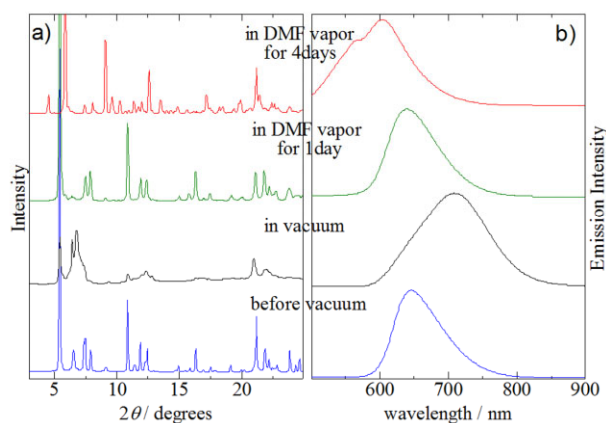


Fig. 2. a) Powder X-ray diffraction patterns. b) Emission spectra of [Pt(CN)₂(4,4'-*dc bpy*)].

Further exposure to DMF vapor, a quite different pattern and new emission peak at 560 nm were observed, suggesting that another structural phase transition occurred. Considering that such phase transition could not be observed in the exposure to EtOH vapor, this vapor-induced phase transition may be related to both the absorbed amount of vapor and hydrogen bonding ability of vapor molecules.

Summary

Powder X-ray diffraction study on vapochromic Pt complex [Pt(CN)₂(4,4'-*dc bpy*)] indicates that the vapochromism originates from the structural flexibility which enables the structural breakdown and regeneration.

References

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* mkato@sci.hokudai.ac.jp