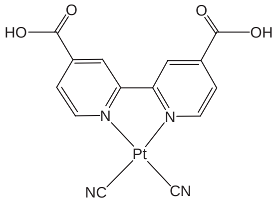
Outstanding Vapochromism and pH-dependent Coloration of Dicyano(4,4′-dicarboxy-2,2′-bipyridine)platinum(II) with a Three-dimensional Network Structure

Masako Kato,* Shinobu Kishi,[†] Yuki Wakamatsu, Yoshiko Sugi, Yoko Osamura, Tamami Koshiyama, and Miki Hasegawa[†]
Division of Material Science, Graduate School of Humanities and Sciences, Nara Women's University, Nara 630-8506
[†]*Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama-Gakuin University,*
5-10-1 Fuchinobe, Sagamihara 229-8558

(Received July 6, 2005; CL-050876)

Dicyano(4,4′-dicarboxy-2,2′-bipyridine)platinum(II) forms pH-dependent polymorphs of various colors and displays outstanding vapochromism followed by luminescence changes upon exposure to certain organic vapors. The high sensitivity of the complex to vapor and pH is related to its three-dimensional network structure, which includes large cavities formed by hydrogen bonds and Pt···Pt interactions.

Assembled metal complex systems involving platinum(II) and Au(I) ions, which often exhibit characteristic coloration and luminescence, have attracted much attention recently as potential sensing materials.[1] A variety of chromic behaviors such as thermochromism, solvatochromism, and vapochromism have been reported for assembled metal complexes in connection with metal–metal interactions.[2] The design and control of such assembled structures are thus essential in the development of sophisticated chromic systems. We report here a platinum(II) complex, [Pt(CN)$_2$(dcbpy)] (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) bearing carboxy and cyano groups, which are good supramolecular synthons (Scheme 1).[3] The complex exhibits remarkable pH-dependent multicolored polymorphism and vapochromic behavior upon exposure to certain volatile organic compounds.



[Pt(CN)$_2$(dcbpy)]

Scheme 1.

[Pt(CN)$_2$(dcbpy)] was synthesized by refluxing a mixture of Pt(CN)$_2$·xH$_2$O and dcbpy in 28% aqueous ammonia for a few days. A purple precipitate was subsequently obtained from the yellowish reaction solution upon addition of hydrochloric acid. The complex was soluble in basic water through dissociation of carboxy groups but was insoluble at acidic pH. The precipitate was recrystallized by the addition of hydrochloric or carboxylic acid to a pale-yellow aqueous ammonia solution. Various [Pt(CN)$_2$(dcbpy)] polymorphs, each with distinctive coloration, were produced depending on the pH of recrystallization. The color of the precipitate changed from yellow to red, blue, and purple with decreasing pH. A colorless precipitate (white form) was also obtained by recrystallization from a hot solution of 2 M HCl and DMF.[4]

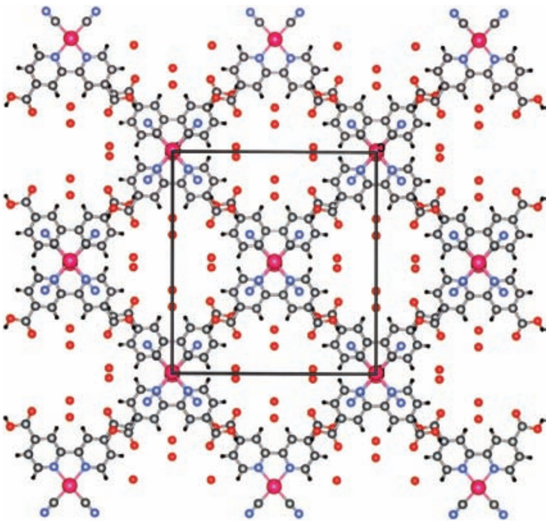


Figure 1. Packing structure of red form of [Pt(CN)$_2$(dcbpy)]·4H$_2$O. Pt···Pt = 3.2358(1) Å at 173 K.

The crystal structure of the red form ([Pt(CN)$_2$(dcbpy)]·4H$_2$O) was determined by X-ray analysis.[5] The complex has a fully planar molecular structure on the crystallographic mirror plane. The carboxy groups at the 4,4′-positions form hydrogen bonds with the cyano ligands of the adjacent complexes to form a mesh sheet (Figure 1). The sheets are stacked in parallel at a short Pt···Pt distance of ca. 3.3 Å at room temperature. This value is typical for the linear chain structure of Pt(II) complexes with Pt···Pt interactions.[6] The stacking pattern for the red form of [Pt(CN)$_2$(dcbpy)] is essentially the same as that found for the red form of [Pt(CN)$_2$(bpy)] (bpy = 2,2′-bipyridine).[6b] However, it is noteworthy that the network structure constructed by hydrogen bonds for [Pt(CN)$_2$(dcbpy)] generates large cavities in the crystal. Four water molecules per complex are included in the cavities as supported also by thermogravimetry, differential thermal analysis, and elemental analysis.

The colorful polymorphs can be readily converted depending on the media. For example, the white form in DMF transforms to the red and then purple forms with increasing ratio of water in DMF. Conversely, the purple form becomes red immediately upon addition to DMF or ethanol. It is also noteworthy that the complex exhibits vapochromic behavior in the solid state. On exposure to acetic acid and ethanol vapor, the purple solid became red in a few minutes,[7] and the color reverted in the air. The outstanding diversity in color in the solid state is attributable to changes in the Pt···Pt interactions, as supported by the emission properties of these polymorphs. Figure 2 shows the

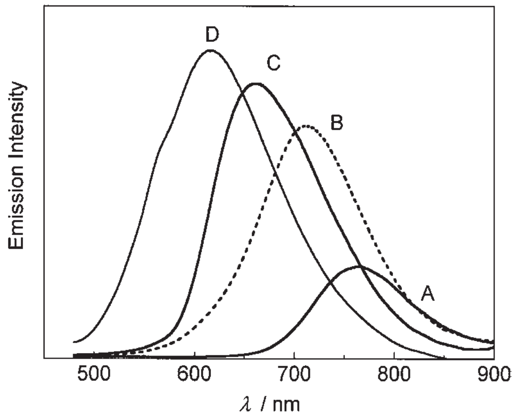


Figure 2. Changes in emission spectra for purple form of [Pt(CN)$_2$(dcbpy)] upon exposure to DMF. (A) 0 min, (B) 30 min, (C) 120 min, (D) overnight. $\lambda_{ex} = 400$ nm.

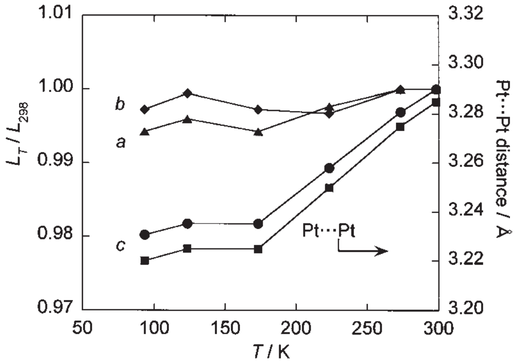


Figure 3. Ratio of cell dimensions (*a*, *b*, and *c*) relative to those at 298 K and the Pt···Pt distance for red form of [Pt(CN)$_2$(dcbpy)] plotted as a function of temperature.

luminescence spectral changes for the purple form upon exposure to DMF vapor. The change from the purple to the yellow form is accompanied by a large spectral shift from 764 to 614 nm at the maximum. All of these spectra have the lifetimes of 50–200 ns at room temperature and are assignable to emission from the ^{3}MMLCT state generated by the Pt···Pt interactions based on comparison with the luminescence spectra for [Pt(CN)$_2$(bpy)] and related linear-chain (polypyridine)platinum(II) complexes.[8] With increasing strength of Pt···Pt interactions, the ^{3}MMLCT emission state shifts to lower energy. Thus, these luminescence spectra indicate that the Pt···Pt interactions become weaker upon exposure to DMF.

As a direct indication of the relation between luminescence energy and Pt···Pt interaction, thermochromism accompanied by changes in Pt···Pt distances was observed for the red form. The red form with emission maximum at $\lambda_{max} = 678$ nm becomes dark blue at 77 K, exhibiting a red-shifted spectrum ($\lambda_{max} = 727$ nm). A corresponding anisotropic shrink along the Pt···Pt chain (*c* axis) can be seen in Figure 3. A similar correlation between emission energy and Pt···Pt distance has also been observed for the red form of [Pt(CN)$_2$(bpy)] and [PtCl$_2$(bpy)].[9,10]

Several systems displaying similar vapochromic behavior have been reported for linear-chain platinum(II) complexes. Vapochromism for [Pt(CN)$_2$(bpy)] occurs between yellow and red forms upon exposure to water vapor. We previously found that the penetration of water molecules into small channels of the red form induces a slight inclination of the stacking structure, resulting in transformation to the yellow form due to weakening of the Pt···Pt interactions.[11] Mann et al. reported a series of double salts, [Pt(aryl isonitrile)$_4$][M(CN)$_4$] (aryl isonitrile = *p*-CN-C$_6$H$_4$C$_n$H$_{2n+1}$, $n = 6$, 10, 12, and 14, M = Pt and Pd) that respond to various volatile organic compounds through luminescence spectral changes.[2a] Eisenberg et al. recently reported on the basis of the structural change of the same single crystal that the vapochromism of [Pt(Nttpy)Cl](PF$_6$)$_2$ (Nttpy = 4′-(*p*-nicotinamide-*N*-methylphenyl)-2,2′:6′,2″-terpyridine) is induced by a change in intermolecular contacts and Pt···Pt interaction.[2c] These examples suggest that systems exhibiting large vapochromic changes involve ligands having extended structures and/or bulky substituents, which form suitable cavities in the crystal lattices. [Pt(CN)$_2$(dcbpy)] is a very good system from this point of view, even though the molecular structure is relatively simple. It is considered that the hydrogen-bonded network structure allows for sensitive changes of Pt···Pt interactions depending on the molecules trapped in the cavities.

In summary, [Pt(CN)$_2$(dcbpy)] which can form a three-dimensional network structure with large cavities was shown to exhibit remarkable multicolored polymorphism. The range of color is the most pronounced reported to date for linear-chain platinum(II) complexes. It is thus expected that the design of network structures will improve the selective sensing functionalities of such complexes.

This work was supported by a Grant-in-Aid for Scientific Research in priority area 434 (No. 17036040) from MEXT, a Grant-in-Aid for Scientific Research (No. 15350034) from JSPS.

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4 IR (KBr, cm^{-1}): white form, 1709 (ν_{CO}), 2161, 2151 (ν_{CN}); yellow form, 1717 (ν_{CO}), 2151 (ν_{CN}); red form, 1717 (ν_{CO}), 2149 (ν_{CN}); blue form, 1733 (ν_{CO}), 2150, 2139 (ν_{CN}); purple form, 1725 (ν_{CO}), 2149 (ν_{CN}). All forms gave essentially the same ^{1}H NMR spectra in solution: ^{1}H NMR (400 MHz, 26% ND$_3$ in D$_2$O): δ 8.06 (d, 2H), 8.74 (s, 2H), 9.13 (d, 2H). The ^{1}H NMR spectrum for the white form indicated that it included dimethylamine (δ 2.28 (s, 6H)), which was a decomposition product of DMF. Anal. purple form ([Pt(CN)$_2$(dcbpy)]•2H$_2$O), Calcd for C$_{14}$H$_{12}$N$_4$O$_6$Pt: C, 31.89; H, 2.29; N, 10.62%. Found: C, 31.80; H, 2.07; N, 10.79%. red form ([Pt(CN)$_2$(dcbpy)]•4H$_2$O), Calcd for C$_{14}$H$_{16}$N$_4$O$_8$Pt: C, 29.85; H, 2.86; N, 9.94%. Found: C, 29.35; H, 2.45; N, 9.55%. white form ([Pt(CN)$_2$(dcbpy)]•NH(CH$_3$)$_2$), Calc. for C$_{16}$H$_{16}$N$_5$O$_4$Pt: C, 35.83; H, 2.82; N, 13.26%. Found: C, 35.84; H, 3.03; N, 13.26%.

5 Crystal data for red form: [Pt(CN)$_2$(dcbpy)]•4H$_2$O, Formula = C$_{14}$H$_{16}$N$_4$O$_8$Pt, $M_r = 563.39$, orthorhombic, $a = 17.2496(7)$ Å, $b = 18.5822(7)$ Å, $c = 6.4537(2)$ Å, $V = 2068.6(1)$ Å^3, $T = 173$ K, space group = *Cmcm* (No. 63), $Z = 4$, μ(Mo Kα) = 6.8 mm^{-1}, $D_{calcd} = 1.809$ g cm^{-3}, 7948 reflections measured, 1337 unique ($R_{int} = 0.031$). The final R_1 and $wR(F^2)$ were 0.031 ($F^2 > 2\sigma(F^2)$) and 0.100 (all data), respectively. Full crystallographic details have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-280733.

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