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Two-step Changes in Luminescence Color of Pt(II) Complex Bearing an Amide Moiety by Mechano- and Vapochromism

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A pincer Pt(II) complex with amide groups was investigated with respect to the change in their luminescence color in solid state. The Pt(II) complex exhibited mechanochromic behavior, changing from green to orange upon grinding. In addition, the orange luminescence changed to yellow via vapochromism.

Luminescent transition-metal complexes in solid state have attracted the attention of scientists because of their application in material sciences, such as in organic light-emitting diodes.[1] In solution state, luminescence properties depend on the chemical structure of the metal complex,[2] while in solid state, they also depend on the molecular orientation.[3] External stimuli such as mechanical pressure and exposure to volatile molecules affect the molecular orientation; therefore, they can change luminescence in solid state. For example, transition-metal complexes exhibit dramatic luminescence color changes through mechanochromism and vapochromism.[4] Since the chromisms are caused by changes in intermolecular interactions such as π–π stacking and metal–metal interactions, planar structures of pincer complexes are suitable for demonstrating interesting luminescence color changes. In previous work, we investigated luminescence properties of pincer complexes bearing hydrogen-bonding moieties.[5] The hydrogen-bonding capability of the N–H groups of the complexes with solvent molecules or a polymer matrix affected the intensity and color of the photoluminescence in solid state, suggesting that hydrogen bonding can control the molecular orientation and luminescence properties in solid state. Therefore, the purpose of this work was to investigate the strong luminescent pincer Pt(II) complexes with amide groups, with the aim of obtaining a novel mechano- and vapochromic complex via hydrogen bonding. Herein, we report the two-step changes in luminescence color of the Pt(II) complex bearing amide moieties induced by external stimuli.

Pincer Pt(II) complexes (Figure 1) were synthesized according to a method described in the literature;[5c] their photophysical properties are summarized in Table 1. The absorption spectra of the complexes in *N*,*N*-dimethylformamide (DMF) exhibited maxima at 398 (**1**) and 381 nm (**2** and **3**) (Figure S1).[6] The complexes **2** and **3** exhibited strong luminescence, with a maximum at 480 nm in DMF (Table 1). According to the literature,[7] the luminescence at about 480 nm is assigned to the phosphorescence from ligand-centered π–π^* transitions. The quantum yields of complexes **2** and **3** were 0.39 and 0.40, respectively. The luminescence decay time (τ) of complexes **2** and **3** was 1.59 µs, indicating phosphorescence. On the other hand, complex **1** exhibited a weak luminescence at 518 nm. Since an iridium complex with carbamoyl groups has weak luminescence,[8] weak luminescence in complex **1** is attributed to the the carbamoyl group. The complexes **2** and **3** exhibited strong luminescence in solid state.

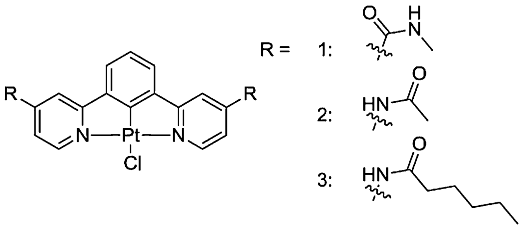

Figure 1. Structures of complexes **1**, **2**, and **3**.

Table 1. Photophysical properties of Pt(II) complexes

Complex	λ_{ex}/nm	λ_{em}/nm	Φ_{em}
1[a]	400	518	<0.01
2[a]	378	480	0.39
3[a]	378	480	0.40
3•DMF[b]	472	512	
3•Powder[c]	428	635	
3•MeOH[d]	434	574	

[a]The photoluminescence spectra were measured in 1.0×10^{-5} M solution in DMF at room temperature. The quantum yields were measured in degassed DMF at room temperature. [b]Crystals obtained by recrystallization from DMF. [c]Powder sample of complex **3** obtained by grinding. [d]Exposure of **3**•Powder to MeOH vapors.

Remarkably, complex **3** exhibited interesting luminescence properties in solid state, which is two-step changes in the photoluminescence by external stimuli (Figure 2). Thus, green luminescence was observed from the crystals obtained by recrystallization from DMF (**3**•DMF in Figure 2a) under UV light. Then, the green luminescent crystals changed to orange (**3**•Powder) when grinding in a ceramic mortar (Figure 2b). In addition, exposure of orange luminescent **3**•Powder to methanol vapors induced a change to yellow luminescence (**3**•MeOH in Figure 2c). The orange luminescence could be recovered from yellow luminescence by mechanical grinding or by heating at 200 °C (Figure 2). Figure 3 shows photoluminescence spectra of complex **3** in solution and in each of the three solid states. The

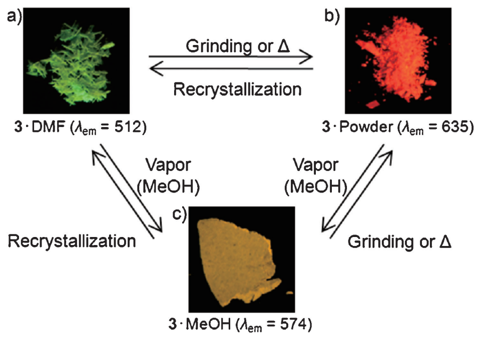

Figure 2. Two-step changes in the photoluminescence of complex **3** by external stimuli. The photographs were taken during irradiation with UV light (365 nm).

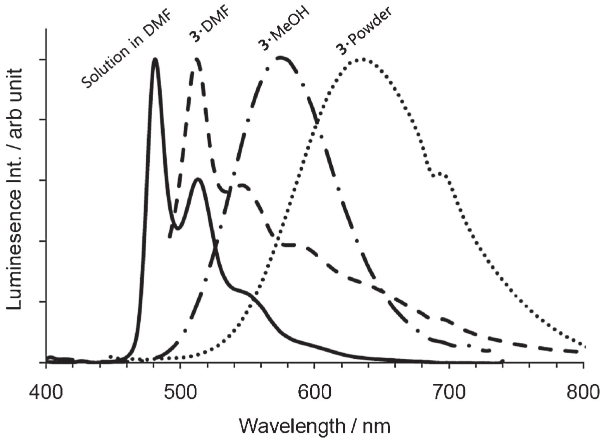

Figure 3. Photoluminescence spectra of complex **3** in solution state (1×10^{-5} M solution in DMF, $\lambda_{ex} = 378$ nm, $\lambda_{em} = 480$ nm, solid line), **3**•DMF ($\lambda_{ex} = 472$ nm, $\lambda_{em} = 512$ nm, broken line), **3**•MeOH ($\lambda_{ex} = 434$ nm, $\lambda_{em} = 574$ nm, dashed/dotted line), and solid after mechanical grinding ($\lambda_{ex} = 428$ nm, $\lambda_{em} = 635$ nm, dotted line).

maximum wavelength of green luminescent crystals (**3**•DMF) was 512 nm, whereas those of orange luminescent powder (**3**•Powder) and yellow luminescent solid (**3**•MeOH) were 635 and 574 nm, respectively.

To explore the differences in molecular orientation among **3**•DMF, **3**•Powder, and **3**•MeOH, these samples of complex **3** were further investigated by powder X-ray diffraction (XRD). The green luminescent crystals of **3**•DMF exhibited sharp diffraction at 5.90° (001) (Figure S2b).[6] In contrast, the ground **3**•Powder did not exhibit clear diffraction. This result indicates that the mechanical grinding scatters the regular arrangements of **3**•DMF. Interestingly, new sharp diffraction appeared at 4.94° (001) upon exposure of **3**•Powder to methanol vapors for several minutes. Since the diffraction pattern was similar to that of crystals of **3** possessing methanol molecules in the crystal lattice (Figure S2e),[6] vapors of methanol are likely to induce crystallization of **3** in powder state. Since the XRD pattern of **3**•DMF differs from that of **3**•MeOH, the arrangement of complex **3** in the solid state is assumed to be different. To elucidate this difference, **3**•DMF and **3**•MeOH were subjected to single-crystal X-ray diffraction studies.[9] Molecular structures of square-planar Pt(II) complex in **3**•DMF and **3**•MeOH are similar (Figure 4 and Table S2),[6,9,10] whereas their molecular orientations and hydrogen-bonding networks are different. The packing diagram of **3**•DMF is shown in Figure 4a. One of the N–H moieties in the amide groups interacts with the chloro ligand in the neighboring Pt(II) complex. Another N–H moiety has hydrogen-bonding interaction with the solvated DMF molecule (Figure 4a). In the case of **3**•MeOH, three types of hydrogen bonds are observed (Figure 4d). In addition to N–H···Cl and N–H···O (MeOH), one of the N–H moieties shows hydrogen-bonding interaction with the carbonyl group in the neighboring complex. The hydrogen-bonding network affects the Pt–Pt distance in the crystal. The packing diagram of **3**•DMF reveals a Pt–Pt distance of 4.854 Å (Figure 4b). On the other hand, the packing diagram of **3**•MeOH reveals a shorter Pt–Pt distance, of 3.385 Å (Figure 4c), than that of **3**•DMF. The shorter Pt–Pt distance indicates metal–metal interaction that induces excimer luminescence. Since the solvent molecules affect the distances between Pt and Pt in the solid state via

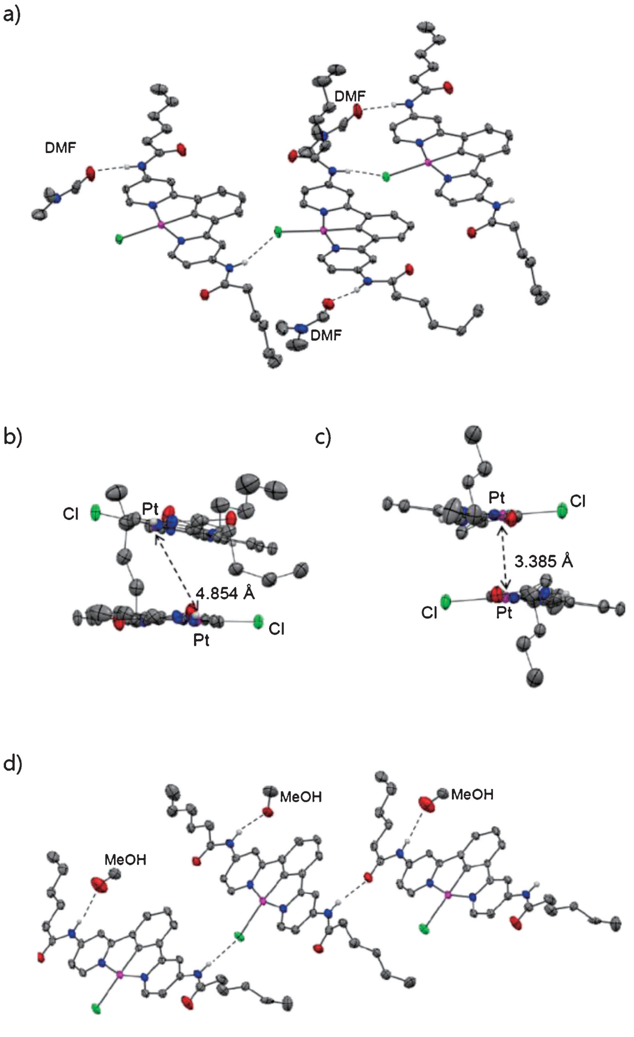

Figure 4. Packing diagrams of complex **3**•DMF; a) top view, b) side view and **3**•MeOH, c) side view, and d) top view. Element colors are as follows: Pt: violet, Cl: green, N: blue, C: dark gray, and H: white gray.

hydrogen bonding, the hydrogen-bonding interaction is likely to play an important role in determining luminescence color.

To confirm the effect of Pt–Pt interaction on luminescence properties, luminescence spectra were measured under various concentrations in DMF (Figure S3).[6] Although green luminescence ($\lambda_{em} = 480$ nm) was observed in a dilute solution of complex **3**, luminescence at a long wavelength ($\lambda_{em} = 651$ nm) was observed at a high concentration (10 mM). Since a high concentration promotes metal–metal interactions, luminescence at 651 nm is presumably caused by excimer formation through metal–metal interactions.[11] These results support the assumption that the luminescence at a long wavelength in **3**•Powder is associated with the metal–metal interactions. In addition to mechanical grinding, heating induced a change in the luminescence color of **3**•DMF to orange. Thermogravimetric analysis of **3**•DMF at temperatures ranging from 50 to 500 °C showed a decrease in weight at around 150 °C (Figure S4).[6] From the amount of weight loss, it was estimated that one DMF molecule was eliminated from **3**•DMF for each Pt complex through heating. The molar ratio was consistent with the crystal structure. The loss of the solvent molecules upon heating caused the same effect as grinding, which induced formation of an amorphous and orange luminescent solid. The formation of the amorphous solid by loss of DMF indicates that the hydrogen-bonding capacity of the amide groups with DMF plays a crucial role in keeping the solid crystalline and maintaining its green luminescence. In contrast to complex **3**, complex **2** exhibits similar luminescence color in **2**•Powder and **2**•MeOH (Figure S5).[3,4,6]

In conclusion, Pt(II) complex **3** bearing the hexanoylamide group exhibited interesting two-step luminescence color changes from green to yellow and orange, in the solid state. This is a rare example of the combination of vapochromism and mechanochromism. The luminescence color was strongly affected by the Pt–Pt distance in molecular packing, depending on the hydrogen-bonding network. Therefore, the hydrogen-bonding capability of luminescent material is expected to be a key factor for tuning luminescence color in solid state.

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9. Crystal data for **3**•DMF: 2($C_{28}H_{33}N_4O_2PtCl$•DMF), $M_r = 1552.53$, triclinic, $P\bar{1}$ (#2), $a = 14.409(3)$, $b = 14.824(3)$, $c = 15.720(3)$ Å, $\alpha = 68.155(2)$, $\beta = 83.331(2)$, $\gamma = 84.179(2)°$, $V = 3089.4(10)$ Å^3, $Z = 2$, $D_{calcd} = 1.669$ g cm^{-3}, observed reflections 13496 ($I > 2\sigma(I)$), $R_1 = 0.0202$, $wR_2 = 0.0538$, $S = 1.042$. For **3**•MeOH: 2($C_{28}H_{33}N_4O_2PtCl$•MeOH), $M_r = 1464.38$, triclinic, $P\bar{1}$ (#2), $a = 12.726(2)$, $b = 14.062(2)$, $c = 18.434(3)$ Å, $\alpha = 71.007(2)$, $\beta = 87.466(2)$, $\gamma = 65.605(2)°$, $V = 2825.1(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.721$ g cm^{-3}, observed reflections 12318 ($I > 2\sigma(I)$), $R_1 = 0.0270$, $wR_2 = 0.0626$, $S = 1.026$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-842935 (**3**•2DMF) and CCDC-842936 (**3**•2MeOH). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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