Accounts

Luminescent Platinum Complexes Having Sensing Functionalities

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Square-planar platinum(II) complexes often exhibit intense color and luminescence when they are stacked via self-assembly or bridging by ligands. The origin of the color and luminescence are the metal–metal electronic interactions, and thus, remarkable changes in color (i.e., chromism) are expected by controlling the Pt⋯Pt interactions. The molecular arrangement of the assembled complex systems is sensitive to environmental factors such as temperature, pressure, solvent, and vapor. This account focuses on the sensing functionalities of luminescent platinum(II) complexes with 2,2′-bipyridine or its derivatives toward their environment. Especially, luminescence changes that are induced by the vapor molecules will be examined from the viewpoint of chemical sensing. The vapochromic behavior and structural aspects of the mononuclear and dinuclear platinum(II) complexes are discussed.

Introduction

Platinum complexes are one of the most studied groups of transition-metal complexes since the 19th century before the beginning of the coordination chemistry. In addition to a variety of coordination structures, which depend on the oxidation states and the electronic structure of platinum, the assembled structures of platinum complexes have been investigated because of several interesting properties such as intense coloration, optical dichroism, electrical conductivity, and characteristic luminescence. With an increasing interest in metal complexes as luminescent materials, the characteristic luminescence properties of platinum complexes have attracted much more attention recently.

Platinum(II) complexes with a d^8 electronic structure adopt a square-planar four-coordinate geometry. They are often stacked in the solid state which causes intense color and luminescence based on metal–metal electronic interactions. Tetracyanoplatinum(II) salts, $M_2[Pt(CN)_4]\cdot nH_2O$ ($M = K$, Rb, etc.) have been studied for a long time as a prototype of linear-chain structure.[1,2] The luminescence occurs from metal-centered ($d \rightarrow p$) excited states mainly based on the transition from $5d_{z^2}$ to $6p_z$, or the corresponding band structure constructed with the overlapped atomic orbitals. Thus, the emission energy as well as the absorption energy depends on the Pt⋯Pt distance in the stack. For these quasi-one-dimensional systems, the control of the Pt⋯Pt interactions is limited to the changes in the counter ions except for the changes in physical factors such as temperature, pressure, and magnetic field. The introduction of various ligands having particular properties, such as aromaticity and the ability to hydrogen-bond, should make possible diverse arrangements and higher dimensional interactions, and these weak intermolecular interactions should be sensitive to environmental factors such as solvent and vapor. In other words, assembled platinum complexes are expected to exhibit sensing functionalities toward their environment. Based on this, we have been developing luminescent platinum complexes with aromatic ligands such as 2,2′-bipyridine (bpy). This account focuses on the ability of the platinum complexes to sense their environment.

Structural Classification of Luminescent Platinum(II) Complexes

Luminescent platinum(II) complexes are classified into three groups mainly: 1) mononuclear complexes, 2) dinuclear complexes with bridging ligands, and 3) linear chains comprised of stacked complex units.

Previously, most mononuclear platinum(II) complexes were known to be non-luminescent in solution at room temperature for several reasons, although they were emissive at low temperatures. The dd transition states that exist as the lowest or lower-lying excited states might induce fast nonradiative deactivation, and facile quenching of the excited state might occur by solvent molecules because the square-planar structures have open coordination sites. However, some complexes containing π-conjugated ligands were reported to be luminescent in solution at room temperature in the 1980's. For example, bis(8-quinolinolato)platinum(II) (**1**),[3] and cyclometalated complexes containing deprotonated carbons, such as bis(2-phenyl-κC^2-pyridinato-κN)platinum(II) (**2**) and bis[2-(2-thienyl-κC^3)pyridinato-κN]platinum(II) (**3**),[4] and dithiolato complexes with a triplet Pt–S to ligand charge-transfer state, $^3(Pt(d)/(S(p) \rightarrow \pi^*_{diimine})$, as the lowest excited state (e.g. [Pt(dpphen)(ecda)]

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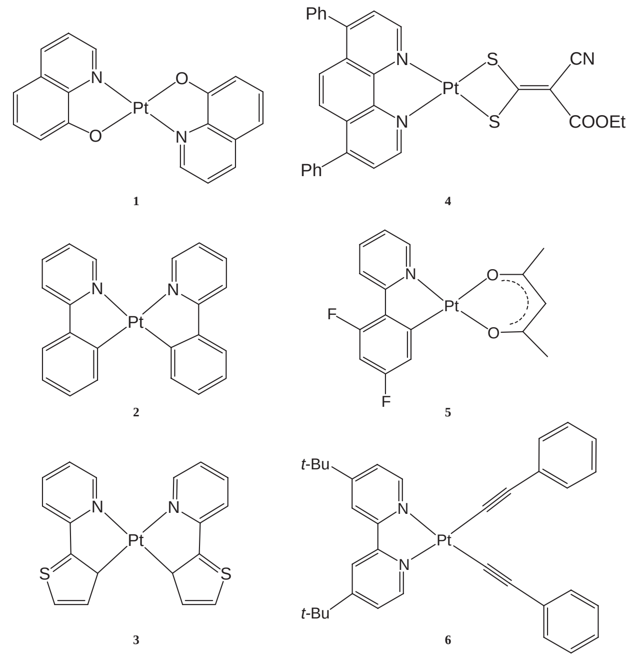


Chart 1.

where dpphen = 4,7-diphenyl-1,10-phenanthroline, ecda = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2′-dithiolate (**4**))[5] are luminescent in solution at room temperature though the emission quantum yields for the complexes except for complex **3** are not so high. The number of highly luminescent platinum(II) complexes has been increasing recently due to an interest in developing phosphorescent materials for organic light-emitting devices (OLED), and for cyclometalated platinum(II) complexes such as [Pt(46dfppy)(acac)] (H46dfppy = 2-(4′,6′-difluorophenyl)pyridine, Hacac = acetylacetone, **5**) and platinum(II) complexes with acetylide ligands (e.g. [Pt(dbbpy)-(C≡CPh)] where dbbpy = 4,4′-di(*tert*-butyl)-2,2′-bipyridine, **6**), high quantum yields ($\phi > 0.1$) are attained, even in solution at room temperature (Chart 1).[6,7] Ligands that have a strong σ-donor ability should raise the energy of the dd state, which causes nonradiative decay, and thus, improve the radiative efficiency of the platinum complexes as a result of an increase in the energy gap between the dd state and the luminescence state such as $^3\pi\pi^*$ (triplet ligand-centered state) and ^{3}dπ^* (triplet metal-to-ligand charge-transfer states, ^{3}MLCT).

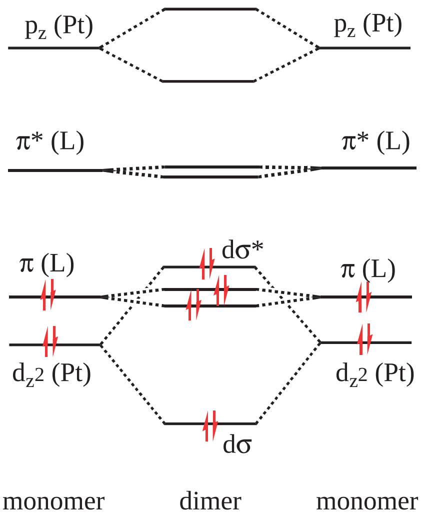


Fig. 1. Schematic MO diagram for platinum(II) complexes.

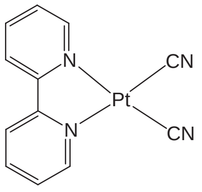
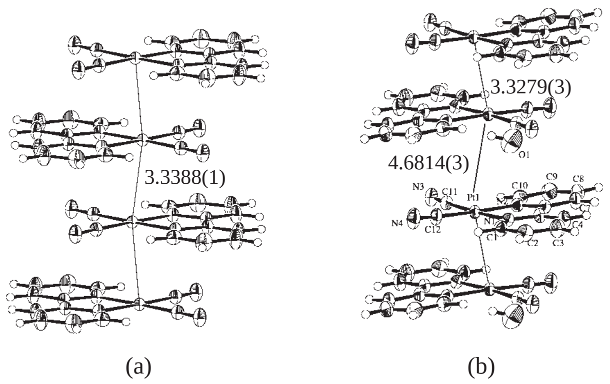


Chart 2.

The luminescence state in dinuclear complex systems and linear chain systems are based on the metal–metal interactions as mentioned in the introductory section. These systems are special in that the luminescence occurs when mononuclear platinum units are assembled. It is in contrast to luminescent mononuclear complexes because their luminescence is often quenched in assemblages like many luminescent organic molecules. Figure 1 shows a schematic MO diagram for platinum(II) complexes with appropriate π-conjugated ligands such as 2,2′-bipyridine. When square-planar platinum(II) complexes are closely stacked, electronic interactions between the platinum ions occur. Overlap of the d_{z^2} orbitals of the platinum ions generates a particularly large splitting between dσ and dσ^*, and as a result, the dσ^* orbital becomes the HOMO for the stacked dimer. In this case, the charge-transfer transition from dσ^* to the π^* orbital of the ligand occurs in the visible region as the lowest energy transition although it is the $\pi\pi^*$ transition of the ligands for the monomeric complexes. The charge-transfer states based on the metal–metal interactions are called, in particular, the metal–metal to ligand charge-transfer (MMLCT) states.[8] Thus, in addition to the lowest singlet MMLCT state giving rise to characteristic color, the luminescence state would be a triplet MMLCT excited state for dinuclear complexes and linear-chain complexes with Pt···Pt interactions. Because the radiative rate of the ^{3}MMLCT state is generally fast compared to that for the $^3\pi\pi^*$ state, at least at temperatures higher than 77 K, intense luminescence is expected for assembled systems with Pt···Pt interactions. In addition, the luminescence is sensitive to subtle changes in the Pt···Pt interactions. In other words, sensing functionalities occur with assembled systems.

Temperature Dependence of the Emission Spectra for Linear-Chain Systems

(2,2′-Bipyridine)dicyanoplatinum(II), [Pt(CN)$_2$(bpy)] (**7**) (Chart 2) is a typical example of (α-diimine)platinum(II) complexes which form linear-chain structures. As shown in Fig. 2a, the red form of [Pt(CN)$_2$(bpy)] has a stacking structure, in which the complex units have a Pt···Pt distance of 3.35 Å at room temperature.[9,10] The crystal exhibits intense red luminescence even at room temperature, as shown in Fig. 3, although no emission is observed for the monomeric form in dilute solutions.[11] The luminescence is due to an emission from ^{3}MMLCT [dσ^*(Pt) → π^*(bpy)] state as mentioned in the previous section. Gliemann et al. reported that the emis-



(a) (b)

Fig. 2. Stacking structures of [Pt(CN)2(bpy)]. (a) Red form (Pt···Pt = 3.3388(1) Å, Pt···Pt···Pt = 168.59(4)° at 293 K), (b) yellow form (Pt···Pt = 3.3279(3), 4.6814(3) Å, Pt···Pt···Pt = 132.89(1)° at 293 K).[16]

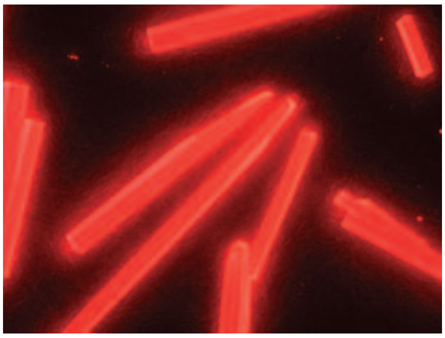


Fig. 3. Luminescence image for the red form of [Pt(CN)2(bpy)].

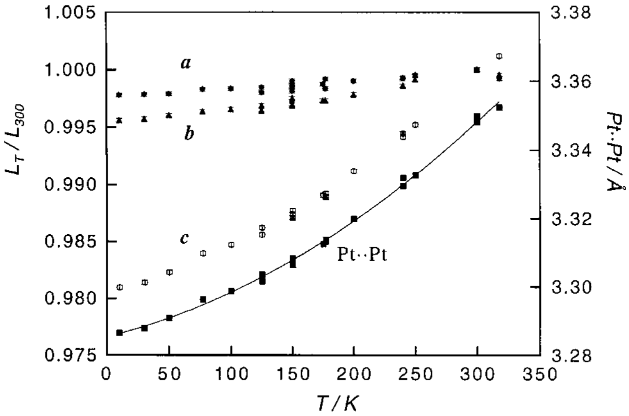


Fig. 4. Ratio of cell length (***a***, ***b***, and ***c***) relative to that at room temperature (300 K) and the Pt···Pt distance for the red form of [Pt(CN)2(bpy)] plotted as a function of temperature.[10]

sion maximum shifted to longer wavelengths when the temperature was lowered,[12] and we have clarified the relationship between the emission energy and the Pt···Pt distance for the red form of [Pt(CN)2(bpy)]:[10] with decreasing temperature, the unit cell of the [Pt(CN)2(bpy)] crystal shrinks anisotropically along the Pt···Pt chain (Fig. 4) which causes the ^{3}MLCT emission spectrum to shift to longer wavelengths (Fig. 5). The shift to lower energy as the Pt···Pt distance decreases is consistent with an increase in the energy of the HOMO (dσ^*(Pt) orbital) (cf. Fig. 1). A linear relationship between the emission maxima and R^{-3} has been found, where R denotes the Pt···Pt distance in the stack as shown in Fig. 6. A similar correlation was found empirically for (tetracyano)platinum(II) salts with ^{3}(dσ^* $\rightarrow$ pσ) emission and interpreted in terms of exciton interactions.[2,13] Connick et al. also reported a similar correlation between the emission energy and the Pt···Pt distance for the red form of [PtCl2(bpy)].[14] It is interesting to note that this correlation is obtained also for these ^{3}MMLCT emission systems as in the case of the systems with metal-centered emission states, and thus the red forms of these bpy complexes are considered to be mainly controlled by one-dimensional linear-chain interactions.

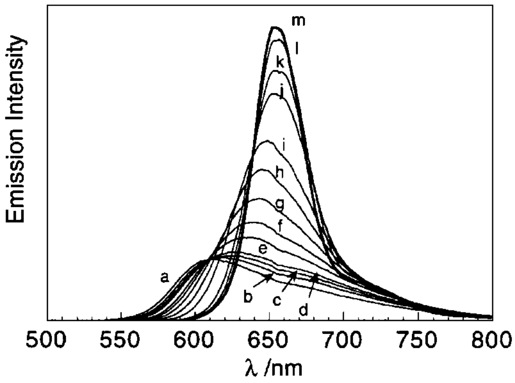


Fig. 5. Emission spectra of the red form of [Pt(CN)2(bpy)] at different temperatures: (a) 292, (b) 260, (c) 240, (d) 220, (e) 180, (f) 160, (g) 140, (h) 120, (i) 100, (j) 60, (k) 45, (l) 30, (m) 15 K. $\lambda_{ex} = 514.5$ nm.[10]

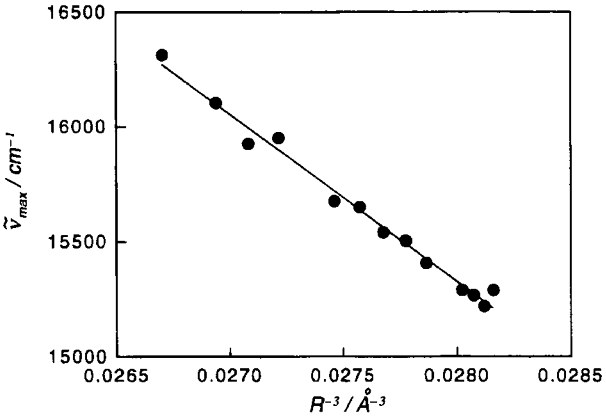


Fig. 6. Plot of emission peak energy vs R^{-3} for the red form of [Pt(CN)2(bpy)], where R is the Pt···Pt distance. The data are fitted with the following equation: $\tilde{\nu}_{max}$ (cm^{-1}) = $35.7(7) \times 10^3 - 7.3(3) \times 10^5 R^{-3}$.[10]

Vapochromic Behavior and the Crystal Structures of (2,2′-Bipyridine)dicyanoplatinum(II)

In addition to the red form, [Pt(CN)2(bpy)] has a yellow form which is a monohydrate. The two forms are produced depending on the solvent. Interestingly, the transformation between the red and yellow forms is induced by water vapor in the atmosphere. The phenomenon was reported many years ago;[15] however, the structural origin of the color change was not known until we finally determined the crystal structure of the yellow form.[16]

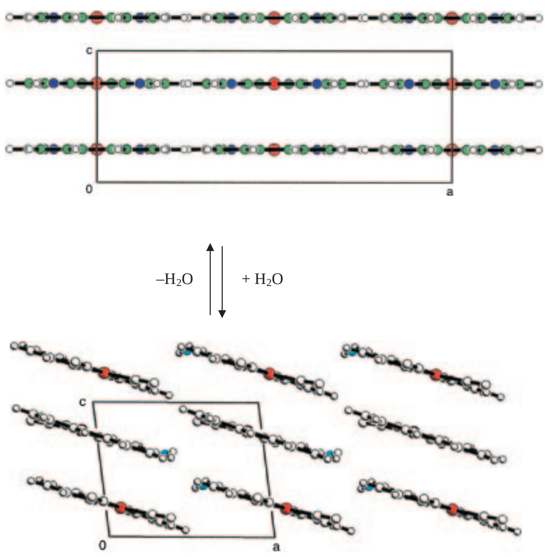


Fig. 7. Structural transformation between the red (top) and yellow (bottom) forms of [Pt(CN)$_2$(bpy)] induced by water vapor. The oxygen atoms for included water molecules are colored light-blue in the lower diagram.

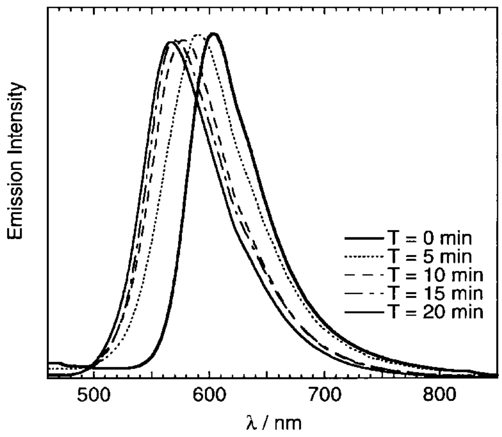


Fig. 8. Emission spectral changes of the red form in the presence of water vapor at room temperature.[16]

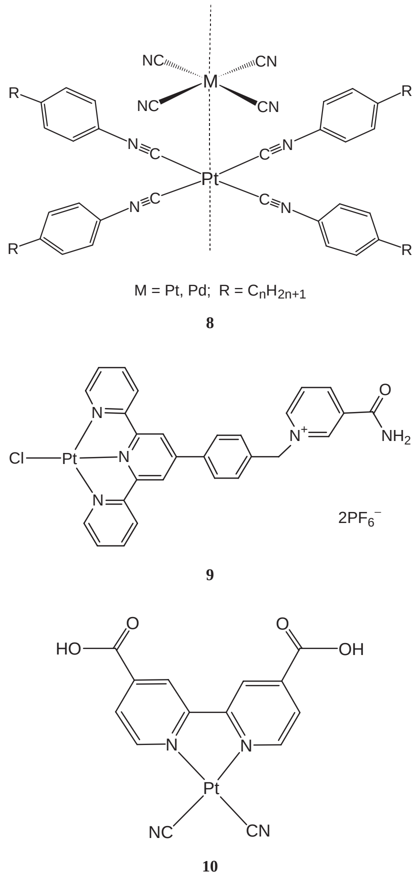


Chart 3.

Figure 7 shows the packing structures of the both forms. The complexes in the red form are stacked horizontally while in the yellow form they are stacked on an incline with water molecules hydrogen bonded to the stack. As a result, the yellow form has a more zigzag structure than that of the red form and has two different Pt···Pt distances as shown in Fig. 2b. Inclined stacks often occur with planar compounds that are likely to form the π–π stacking. The slant in the coordination planes would reduce the orbital overlap between the d_{z^2} orbitals and weaken the Pt···Pt interaction even if the stack keeps the same Pt···Pt distance as in the horizontal stack. Therefore, the color is sensitive to slight changes in the stacking structures caused by water molecules.

The transformation between the red and yellow forms is accompanied by a change in the luminescence, which reflects the change in the Pt···Pt electronic interactions. Figure 8 shows the emission spectral changes of the red form in the presence of water vapor at room temperature. The peak maximum gradually shifts from 602 to 566 nm, which is consistent with that for the yellow form. The origin of the luminescence for the yellow form assigned to the ^{3}MMLCT state which is slightly higher in energy but essentially the same state as that for the red form based on the similarities in the spectral profiles and emission lifetimes ($\tau = 56$ and 109 ns for the yellow and red forms, respectively). The emission properties of the yellow form for [Pt(CN)$_2$(bpy)] are quite different to the yellow form for [PtCl$_2$(bpy)] which does not exhibit any vapochromic behavior. The latter yellow form exhibits only weak luminescence at room temperature because it has no Pt···Pt interactions in the stack, and the lowest excitation state is assigned to the dd state.[17]

Outstanding Vapochromism of Dicyano-(4,4′-dicarboxy-2,2′-bipyridine)platinum(II)

As shown in the previous section, a remarkable change in luminescence occurs by a slight change in the stacking structure of the platinum complexes. Thus, the design and control of the assembled structures are essential in the development of sophisticated chromic systems using linear-chain type platinum complexes. Several systems displaying vapochromic behavior have been developed using bulky ligands. For example, 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, **8**) and related complexes that respond to various volatile organic compounds through luminescence spectral changes (Chart 3).[18] Eisenberg et al.

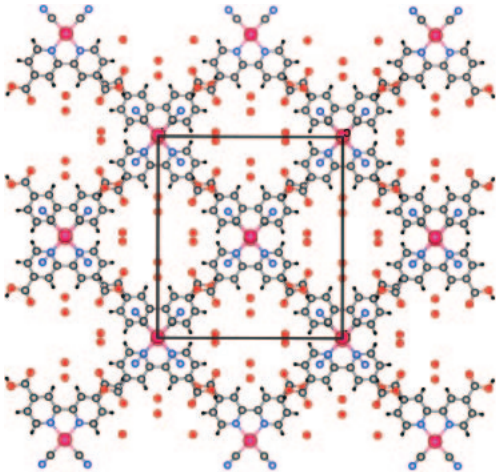


Fig. 9. Packing diagram of the red form of [Pt(CN)$_2$(dcbpy)].[20]

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, **9**) is induced by a change in intermolecular contacts and Pt···Pt interaction.[19] These examples suggest that systems exhibiting large vapochromic changes involve ligands that have extended structures and/or bulky substituents, which form suitable cavities in the crystal lattices.

In this context, [Pt(CN)$_2$(dcbpy)] (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine, **10**) is a very good system for vapochromism, even though its molecular structure is relatively simple.[20] It bears carboxy and cyano groups, which are known as good supramolecular synthons, and the complexes can form a mesh structure with a large cavity through hydrogen bonding. As shown in Fig. 9, the tetrahydrate of [Pt(CN)$_2$(dcbpy)] (red form) has a three-dimensional network structure. In the red form, the mesh sheets are stacked in parallel with 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.[21] 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)]. However, it is noteworthy that the network structure constructed by hydrogen bonding for [Pt(CN)$_2$(dcbpy)] has large cavities in the crystal. In this case, four water molecules per complex are included in the cavities. Depending on the media for crystallization, colorful polymorphs of [Pt(CN)$_2$(dcbpy)] are produced, and those can be readily converted on exposure to various vapors. For example, the purple form, which is obtained from an aqueous solution at low pH ($2 < \mathrm{pH}$), becomes red in minutes upon exposure to acetic acid and ethanol vapor, and the color reverts back on standing in air. Figure 10 shows the luminescence spectral changes for the purple form upon exposure to various vapors. The diversity in luminescence changes as well as the color change in the solid state is the most pronounced reported to date for linear-chain platinum(II) complexes. Each form of the complex has a luminescence lifetime of 50–200 ns at room temperature and the luminescence is assigned 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.[22] Thus, the color changes are attributed to the changes in the Pt···Pt interactions, as supported by the emission properties of these polymorphs. With an increase in the strength of the Pt···Pt interactions, the ^{3}MMLCT emission state shifts to lower energy. Figure 11 shows a plot of the emission energies against the dielectric constant of guest substances, and when the complex is exposed to vapors of polar molecules, the Pt···Pt interactions become weaker. The three-dimensional network structure likely amplifies the changes in the local structure that are induced by vapor molecules penetrating into the crystal lattice. The mechanistic studies are now in progress.

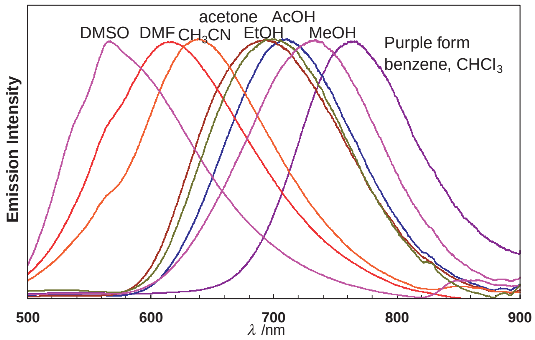


Fig. 10. Luminescence spectral changes for the purple form of [Pt(CN)$_2$(dcbpy)] upon exposure to various vapors.

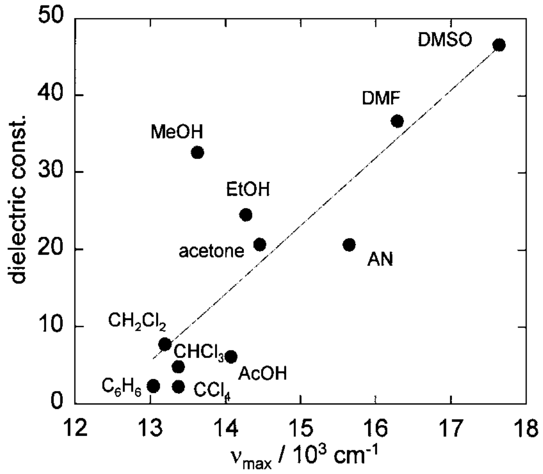
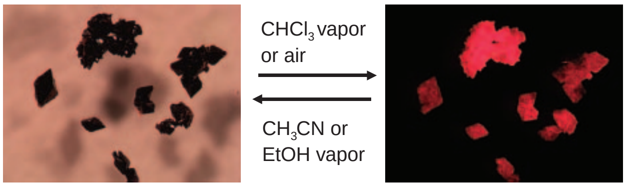


Fig. 11. Plot of the emission energies for [Pt(CN)$_2$(dcbpy)] in the solid state against the dielectric constant of vapors.

Vapor-Induced Luminescence Switching of a Dinuclear (Bipyridine)platinum(II) Complexes Bridged by Pyridine-2-thiolate Ions

Dinuclear complexes linked by the bridging ligands form a rigid and discrete framework, and thus, the characteristic luminescence based on the Pt···Pt interactions are also observed in solution.[23–25] However, they should not be useful for sensing because the Pt···Pt interaction should not change. On the contrary, a crystalline sample of a platinum(II) dinuclear complex bridged by the pyridinethiolate ions, *syn*-[Pt$_2$(pyt)$_2$(bpy)$_2$]-(PF$_6$)$_2$ (Hpyt = pyridine-2-thiol) exhibits remarkable luminescence changes in the presence of organic vapors such as acetonitrile or ethanol.[26] The dark-red form is a vapor-inclusion form and the light-red form is the vapor-released form. As



(a) (b)

Fig. 12. Vapochromic change in crystals of the *syn*-isomer between (a) dark-red form and (b) light-red form.[26]

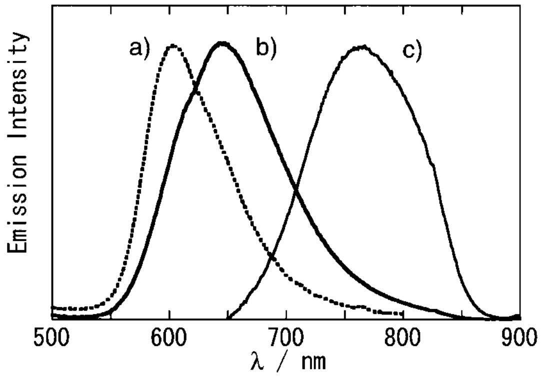
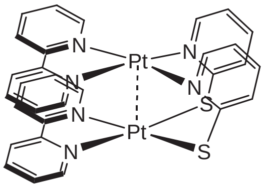


Fig. 13. Luminescence spectra at room temperature for a) the *anti*-isomer, b) the light-red form of the *syn*-isomer, and c) the dark-red form of the *syn*-isomer.[26]



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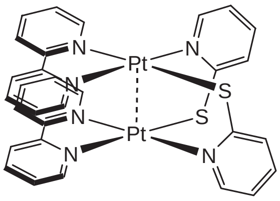

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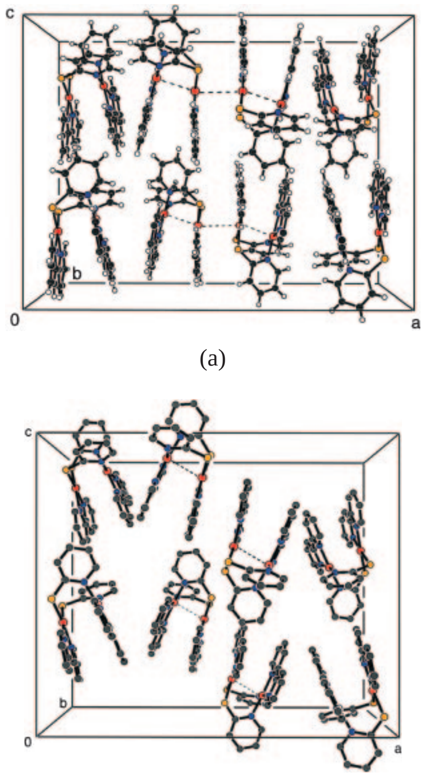
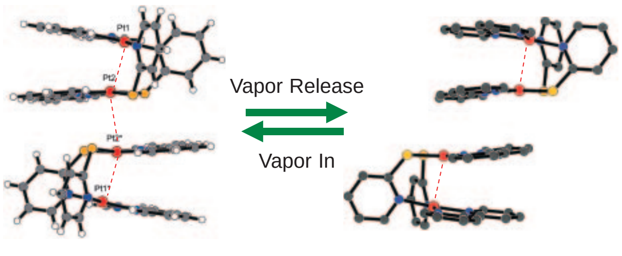
Chart 4.



(a)

(b)

Fig. 14. Crystal structure of (a) the dark-red form, and (b) the light-red form of the *syn*-isomer. The PF_6^- ions and acetonitrile molecules are omitted for clarity.



(a) (b)

Fig. 15. Arrangements of two *syn*-$[Pt_2(pyt)_2(bpy)_2]^{2+}$ for (a) the dark-red form, and (b) the light-red form, and the dd/$\pi\pi$ interconversion between them induced by acetonitrile vapor.

shown in Fig. 12, the conversion from the light-red form exhibiting red luminescence to the "dark" dark-red form occurs immediately on exposure to acetonitrile vapor. The corresponding luminescence spectral change shown in Fig. 13 indicates that the large red shift occurs simultaneously with the conversion from the light-red form to the dark-red form. Such vapor-induced luminescence switching is characteristic of the *syn*-isomer, *syn*-$[Pt_2(pyt)_2(bpy)_2]^{2+}$ (**11**) which is one of two geometrical isomers having a head-to-head configuration of two bridging pyridine-2-thiolate ions (Chart 4). Crystals of the *anti*-isomer (**12**) exhibit no vapochromic behavior although they have an intense orange luminescence (Fig. 13a).

The vapochromic behavior for the dinuclear complex system has been clarified with a single-crystal to single-crystal transformation. Figure 14a shows the crystal structure of the dark-red form *syn*-$[Pt_2(pyt)_2(bpy)_2](PF_6)_2 \cdot CH_3CN$ with the counter anions omitted for clarity. In the crystal, the dinuclear complexes were found to be arranged facing the N_2S_2 coordination plane (head-to-head arrangement). Figure 15a shows the tetranuclear motif. The Pt⋯Pt distance between the dinuclear complexes is 3.434(2) Å, suggesting that electronic interaction could occur between the dinuclear complexes. The acetonitrile molecules are also not shown because of the intense disorder, however, they are in the channel separate from the tetranuclear units. When the single crystal of the dark-red form was kept at 0 °C under nitrogen gas stream, the crystal turned to the light-red form while maintaining its single crystallinity, and the resulting packing structure is shown in Fig. 14b. In the

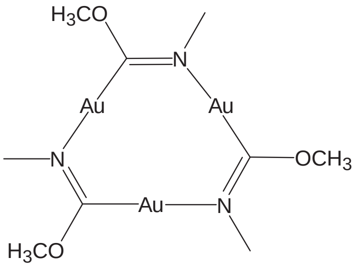


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Chart 5.

crystal, the dinuclear complexes are shifted along the *c* axis drastically to form a $\pi\pi$-stacked arrangement instead and the Pt atoms between the dinuclear complexes become separated from each other (Fig. 15b). Basically, it appears that the acetonitrile molecules fill in the cavities to support the tetranuclear motif in the crystal, and the slip occurred upon the release of the acetonitrile molecules. In conclusion, the vapochromic dinuclear complex undergoes a dynamic dd/$\pi\pi$ interconversion that is induced by vapor molecules (Fig. 15), and the head-to-head arrangement of two *syn* isomers is essential for the vapochromism.

Concluding Remarks

The sensing functionalities of luminescent platinum(II) complexes shown in this account are colorful and quite attractive. In each case, the color change is ultimately based on the Pt$\cdots$Pt interaction which is a well-known phenomenon. However, it is also clear that sophisticated molecular and crystal design is indispensable for effective sensing. Therefore, it is important to explore much various complex systems and develop new complex materials. The number of interesting assembled metal complex systems has increased year after year. Luminescent trinuclear platinum(II) complexes have also been reported.[27] Besides platinum(II) complexes, much attention has been given to assembled systems involving gold(I) and copper(I) complexes.[28] Especially, trimer complexes with a triangular framework, such as $[\mathrm{Au(CH_3N{=}COCH_3)}]_3$ (**13**) (Chart 5), are reported to exhibit interesting luminescence behavior such as vapochromism, solvatochromism, and solvent-stimulated photoemission.[29] Mixed-metal complexes would be also effective to control the luminescence properties.[30] Although mechanistic studies are still necessary for many of the reported systems, great progress hereafter is expected in this field.

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References

1 T. W. Thomas, A. E. Underhill, *Chem. Soc. Rev.* **1972**, *1*, 99.

2 G. Gliemann, H. Yersin, *Struct. Bonding* **1985**, *62*, 87.

3 R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, *Inorg. Chem.* **1986**, *25*, 3858.

4 a) M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet, A. von Zelewsky, *Chem. Phys. Lett.* **1985**, *122*, 375. b) D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. von Zelewsky, *J. Am. Chem. Soc.* **1987**, *109*, 7720.

5 J. A. Zuleta, M. S. Burberry, R. Eisenberg, *Coord. Chem. Rev.* **1990**, *97*, 47.

6 a) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055. b) K. P. Balashev, M. V. Puzyk, V. S. Kotlyar, M. V. Kulikova, *Coord. Chem. Rev.* **1997**, *159*, 109.

7 a) C.-W. Chan, L.-K. Cheng, C.-M. Che, *Coord. Chem. Rev.* **1994**, *132*, 87. b) W. B. Connick, D. Geiger, R. Eisenberg, *Inorg. Chem.* **1999**, *38*, 3264. c) Q.-Z. Yang, I.-Z. Wu, Z.-X. Wu, I.-P. Zhang, C.-H. Tung, *Inorg. Chem.* **2002**, *41*, 5653. d) F. Hua, S. Kinayyigit, J. R. Cable, F. N. Castellano, *Inorg. Chem.* **2005**, *44*, 471. e) I. E. Pomestchenko, C. R. Luman, M. Hissler, R. Ziessel, F. N. Castellano, *Inorg. Chem.* **2003**, *42*, 1394.

8 J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4591.

9 W. B. Connick, L. M. Henling, R. E. Marsh, *Acta Crystallogr., Sect. B* **1996**, *52*, 817.

10 M. Kato, C. Kosuge, K. Morii, J. S. Ahn, H. Kitagawa, T. Mitani, M. Matsushita, T. Kato, S. Yano, M. Kimura, *Inorg. Chem.* **1999**, *38*, 1638.

11 C.-M. Che, L.-Y. He, C.-K. Poon, T. C. W. Mak, *Inorg. Chem.* **1989**, *28*, 3081.

12 J. Biedermann, M. Wallfahrer, G. Gliemann, *J. Lumin.* **1987**, *37*, 323.

13 P. Day, *J. Am. Chem. Soc.* **1975**, *97*, 1588.

14 W. B. Connick, L. M. Henling, R. E. Marsh, H. B. Gray, *Inorg. Chem.* **1996**, *35*, 6261.

15 E. Bielli, P. M. Gidney, R. D. Gillard, B. T. Heaton, *J. Chem. Soc., Dalton Trans.* **1974**, 2133.

16 S. Kishi, M. Kato, *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 303.

17 V. M. Miskowski, V. H. Houlding, C.-M. Che, Y. Wang, *Inorg. Chem.* **1993**, *32*, 2518.

18 a) C. L. Exstrom, J. R. Sowa, Jr., C. A. Daws, D. Janzen, K. R. Mann, *Chem. Mater.* **1995**, *7*, 15. b) C. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton, K. R. Mann, *J. Am. Chem. Soc.* **1998**, *120*, 7783. c) C. E. Buss, K. R. Mann, *J. Am. Chem. Soc.* **2002**, *124*, 1031.

19 T. J. Wadas, Q.-M. Wang, Y.-J. Kim, C. Flashenreim, T. M. Blanton, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 16841.

20 M. Kato, S. Kishi, Y. Wakamatsu, Y. Sugi, Y. Osamura, T. Koshiyama, M. Hasegawa, *Chem. Lett.* **2005**, *34*, 1368.

21 W. B. Connick, R. E. Marsh, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1997**, *36*, 913.

22 V. H. Houlding, V. M. Miskowski, *Coord. Chem. Rev.* **1991**, *111*, 145.

23 D. M. Roundhill, H. B. Gray, C.-M. Che, *Acc. Chem. Res.* **1989**, *22*, 55.

24 H.-K. Yip, C.-M. Che, Z.-Y. Zhou, T. C. W. Mak, *J. Chem. Soc., Chem. Commun.* **1992**, 1369.

25 T. Koshiyama, A. Omura, M. Kato, *Chem. Lett.* **2004**, *33*, 1386.

26 M. Kato, A. Omura, A. Toshikawa, S. Kishi, Y. Sugimoto, *Angew. Chem., Int. Ed.* **2002**, *41*, 3183.

27 W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* **2004**, *126*, 7639.

28 a) M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling, R. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 1329. b) V. W. W. Yam, K. K. W. Lo, *Chem. Soc. Rev.* **1999**, *28*, 323. c) Y.-A. Lee, R. Eisenberg, *J. Am. Chem. Soc.* **2003**, *125*, 7778. d) E. Cariati, J. Bourassa, P. C. Ford, *Chem. Commun.*

1998, 1623.

29 a) J. C. Vickery, M. M. Olmstead, E. Y. Fung, A. L. Balch, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179. b) A. Hayashi, M. M. Olmstead, S. Attar, A. L. Balch, *J. Am. Chem. Soc.* **2002**, *124*, 5791. c) M. M. Olmstead, F. Jiang, S. Attar, A. L. Balch, *J. Am. Chem. Soc.* **2001**, *123*, 3260. d) H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072.

30 a) V. W.-W. Yam, K.-L. Yu, K. M. C. Wong, K.-K. Cheung, *Organometallics* **2001**, *20*, 721. b) V. J. Catalano, B. L. Bennett, H. M. Kar, *J. Am. Chem. Soc.* **1999**, *121*, 10235. c) V. J. Catalano, B. L. Bennett, R. L. Yson, B. C. Noll, *J. Am. Chem. Soc.* **2000**, *122*, 10056.

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