



Title	A Redox-Active Dinuclear Platinum Complex Exhibiting Multicolored Electrochromism and Luminescence
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Redox-active dinuclear platinum complex exhibiting multicolored electrochromism and luminescence

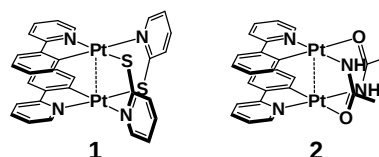
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Abstract: A redox series of cyclometalated platinum complexes based on a dinuclear motif linked by acetamidato (aam) bridging ligands, $[\text{Pt}_2(\mu\text{-aam})_2(\text{ppy})_2]$ (ppy^- = 2-phenylpyridinate ion), has been synthesized. The complexes in this series are easily oxidized and reduced by both electrochemical and chemical methods, and this is accompanied by multistep changes in their optical properties, that is, multiple color changes and luminescence. Isolation of the complexes and the structural determination of three oxidation states, +2, +2.33, and +3, have been achieved. The mixed-valent complex, with an average oxidation state of +2.33, forms a trimer based on the dinuclear motif. The mixed-valent complex has a characteristic color due to intervalence transitions in the platinum chain. In contrast, the divalent complex exhibits strong red phosphorescence originating from a triplet metal-metal-to-ligand charge transfer ($^3\text{MMLCT}$) state. This study demonstrates the unique chromic behavior of a redox-active and luminescent platinum complex.

Molecular-based display devices have attracted considerable attention owing to their mechanical flexibility and processability. In addition, the ability to tune their optoelectronic properties by making rational modifications of the active layer materials makes them attractive functional materials.^[1] Among these devices, organic light-emitting diodes (OLEDs) are the most widely developed devices using organic molecules^[2] and metal complexes.^[3] Recently, interest in electrochromic display devices (ECDs) has grown^[4,5] because of their applicability in smart windows and electronic paper. However, these display devices often have limited visibility. That is, images displayed by OLEDs can be difficult to see in direct sunlight, whereas ECDs cannot be used in the dark. Therefore, dual electrochromic/electroluminescent (EC/EL) display devices are desirable to exploit the advantages and overcome the disadvantages of these devices.^[6,7] However, the development of electrochromic luminescent materials (i.e., redox-controllable emitters) is still a challenging issue.

In this context, multinuclear Pt(II) complexes are promising candidates as redox-controllable emitters, owing to their outstanding luminescent properties and rich redox behavior that arises from electronic Pt...Pt interactions. Some of these complexes have already been used as triplet

Scheme 1. Dinuclear platinum complex motifs of **1** and **2**.



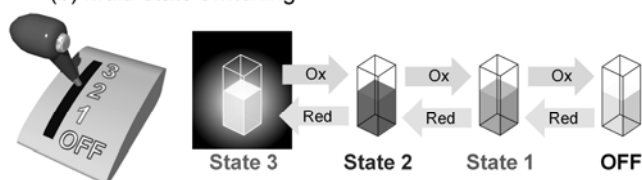
emitters in OLEDs.^[8] Using the above concepts, the authors^[9] and other research groups^[10] have reported cyclometalated dinuclear Pt(II) complexes that display redox-controllable luminescence. For example, a cyclometalated dinuclear Pt complex with a $[\text{Pt}_2(\mu\text{-pyt})_2(\text{ppy})_2]$ (pyt = 2-pyridinethiolate, ppy = 2-phenylpyridinate) motif (**1** in Scheme 1) showed redox-bistability of the luminescent Pt(II)-Pt(II) state and the non-luminescent Pt(III)-Pt(III) state.^[9a] These states were readily interconverted by oxidation and reduction and were accompanied by the appearance and disappearance of luminescence, as shown in Scheme 2a. However, so far, cyclometalated dinuclear Pt complexes with stable mixed-valent states, such as the Pt(II)-Pt(III) state, have not been found.^[9,10] In contrast, there have been numerous reports on dinuclear Pt complexes with ammine/amine ligands that form mixed-valent states, the so-called “platinum blues”.^[11] The intense coloration, which is due to charge-transfer bands of the mixed-valent states, is attractive for electrochromic dyes. Despite this, platinum blues have only been investigated with regard to their electronic, electric, and catalytic properties.^[11,12] In typical mixed-valent Pt complexes, mixed-valent states are stabilized by the formation of an extended Pt...Pt electronic system. Despite the fact that the electronic interactions between Pt centers are extremely important for the formation of a strong emitter and the stabilization of mixed-valence states, these two concepts have not been studied together.

Scheme 2. Schematic representations of (a) two-state and (b) multistate redox-switching of colors and luminescence.

(a) Two-state switching



(b) Multi-state switching



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Herein, we report the first example of a redox-multistable Pt complex (Scheme 2b) that is switchable between luminescent, multicolored and colorless, nonluminescent states by electrochemical means. In this system, an acetamidato (aam) ligand was chosen as a sterically undemanding bridging ligand that can also form hydrogen bonds, which enhance the stabilization of mixed-valent states. The resulting cyclometalated dinuclear Pt motif, $[\text{Pt}_2(\mu\text{-aam})_2(\text{ppy})_2]$ (**2** in Scheme 1) was found to exhibit multistep redox states that were readily interconverted by electrochemical and chemical oxidation and reduction. Of the states, the structures of complexes with average formal oxidation numbers of +2, +2.33, and +3 were successfully elucidated crystallographically.

The Pt complex with the aam-bridged dinuclear motif **2** was obtained as a deep blue solid (the color is indicative of the formation of a typical “platinum blue”) by a one-pot, two-step process from $[\text{Pt}_2(\mu\text{-Cl})_2(\text{ppy})_2]$ in acetonitrile (Scheme S1). The complex was isolated and characterized as a tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAR^{F_4}) salt successfully. Its UV-visible absorption spectrum in DMF showed an intense absorption band with a maximum at 700 nm ($\epsilon = 1.29 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure S5), which, based on the literature,^[13] is assignable to an intervalence charge transfer band. Elemental analysis and electrospray-ionization mass spectroscopy (ESI-MS) indicate the formation of an unprecedented “trimer-of-dimer” structure with an average Pt valence of +2.33, $\mathbf{2(+2.33)}_3$. Here, “dimer” signifies the dinuclear platinum complex motif. Furthermore, this unique “trimer-of-dimer” structure was found for $\mathbf{2(+2.33)}_3$ by X-ray crystallography.

Figure 1a shows the molecular structure of a “trimer-of-dimer” in the crystal $[\mathbf{2(+2.33)}_3(\text{acetonyl})_2] \cdot 2\text{H}_2\text{O}$, which was crystallized by the diffusion of hexane into an acetone solution of $\mathbf{2(+2.33)}_3$.^[14] It has an interesting bowed structure composed of three dinuclear $[\text{Pt}_2(\mu\text{-aam})_2(\text{ppy})_2]$ units. The two terminal axial positions of the trimer-of-dimer are occupied by acetonyl ligands (i.e., deprotonated acetone) derived from the solvent.^[15] Two aam ligands bridge two Pt(ppy) units in a head-to-tail manner, adopting *anti*-configurations due to the strong *trans* influence of the carbanion of the ppy ligand. The “trimer-of-dimer” structure of $\mathbf{2(+2.33)}_3$ formed because of Pt–Pt interactions, π – π interactions of the ppy ligands, and inter-dimer hydrogen bonding between the aam ligands (Figure 2, pale-blue broken lines). In the Pt chains, the Pt–Pt distances of both ends (Pt1–Pt2 = 2.6668(7) and Pt5–Pt6 = 2.6676(5) Å) are significantly shorter than the other Pt–Pt distances (2.8201(6)–2.8860(5) Å). By comparison with the structures of other cyclometalated Pt dimers (Table S1), the formal oxidation states of the six Pt ions in $\mathbf{2(+2.33)}_3$ can be assigned to be approximately Pt(III)–Pt(II)–Pt(II)–Pt(II)–Pt(II)–Pt(III). This is a novel “platinum blue” complex composed of three dinuclear units;^[16] in contrast, most “platinum blues” are composed of either two or four dinuclear units.^[11–13,15]

As shown in Figure 2a, CV measurements of **2** clearly show four redox couples at $E_{1/2} = -0.180, 0.556, 0.719$, and 1.122 V vs. NHE.^[17] Given the experimental rest potential of a solution containing $\mathbf{2(+2.33)}_3$ of $E = 0.229 \text{ V}$, the redox couple at $E_{1/2} = -$

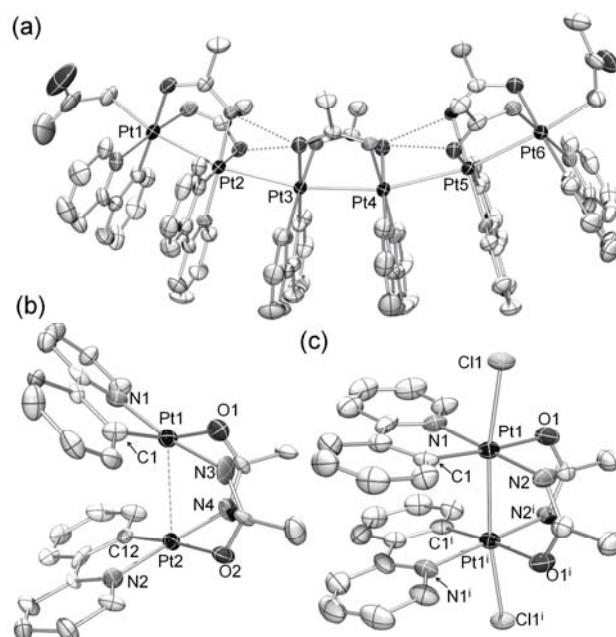


Figure 1. The molecular structures of (a) $[\mathbf{2(+2.33)}_3(\text{acetonyl})_2]$, (b) **2(+2)**, and (c) **2(+3)Cl**, showing the atom labelling scheme. Thermal ellipsoids are displayed at the 50% probability level. H atoms have been omitted for clarity. Hydrogen bonds are displayed as gray dotted lines. Pt–Pt distances: for $[\mathbf{2(+2.33)}_3(\text{acetonyl})_2]$, Pt1–Pt2 = 2.6668(7) Å, Pt2–Pt3 = 2.8740(7) Å, Pt3–Pt4 = 2.8201(6) Å, Pt4–Pt5 = 2.8860(5) Å, Pt5–Pt6 = 2.6676(5) Å; for **2(+2)** Pt1–Pt2 = 2.987(2) Å; for **2(+3)Cl**, Pt1–Pt2 = 2.5940(7) Å.

0.180 V can be assigned to reduction of the Pt(+2.33) state into the divalent state, Pt(+2). On the other hand, considering the assembled structure of **2**, the three redox couples observed in the anodic side are reasonably assigned to the stepwise oxidation of the Pt(+2.33) state to Pt(+2.5), Pt(+2.67), and finally the trivalent state Pt(+3). This multistep redox behavior of **2** is distinctly different to that of **1**, which showed only one redox couple at $E_{1/2} = 0.495 \text{ V}$, assigned to a Pt(III)/Pt(II) couple (Figure S4).^[9b]

Corresponding to the redox behavior, **2** exhibited remarkable multicolored electrochromic behavior. Colorful changes from blue to pink, yellow, and orange were observed by spectroelectrochemical measurements and were dependent on the applied voltage, as shown in Figures 2b and S6. Upon the oxidation of the blue solution of $\mathbf{2(+2.33)}_3$ at 0.84 V, the absorption band around 698 nm decreased and new absorption bands at 495 nm and 710 nm appeared (Figure 2b(iii)). These absorption bands disappeared during further oxidation at 1.34 V (Figure 2b(iv)), indicating the formation of the trivalent state: a dinuclear Pt(III) complex.^[9,10] On the other hand, the reduction of $\mathbf{2(+2.33)}_3$ at -0.51 V afforded a broad absorption band around 505 nm (Figure 2b(i)). This band is characteristic of that of a ¹MMLCT (metal-metal-to-ligand charge transfer) transition ($d\sigma^*(\text{Pt} \cdots \text{Pt}) \rightarrow \pi^*(\text{ppy})$) that arises from the strong electronic interactions between Pt(II) centers (Scheme S2). Interestingly, the absorption band of $\mathbf{2(+2.33)}_3$ was almost recovered by electrolysis at the rest potential (0.229 V) for both oxidized (Figure S6b) and reduced species (Figure S6d).

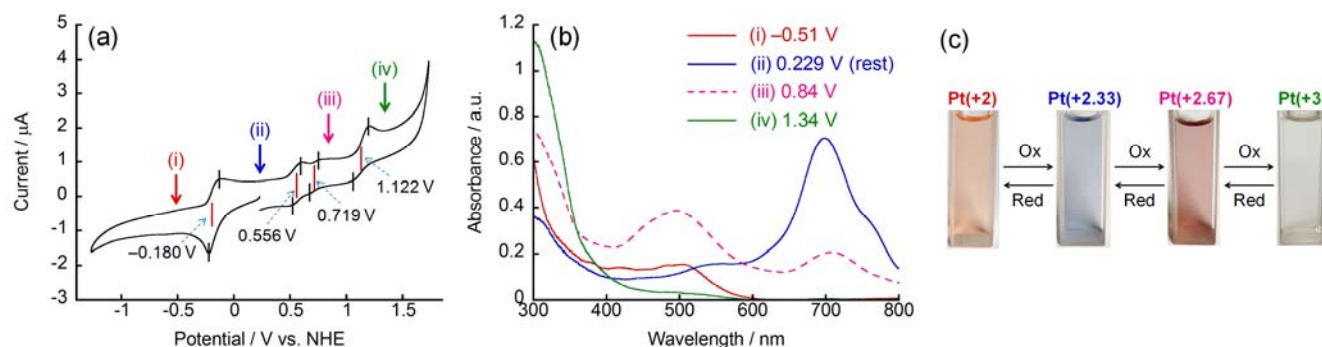


Figure 2. (a) Cyclic voltammogram of $[2(+2.33)_3](\text{BARF}_4)_2$ (0.5 mM) in a solution of dry DMF containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) under N₂ atmosphere, recorded at a scan rate of 5 mV/s ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$). (b) Controlled-potential UV-visible absorption spectra of $[2(+2.33)_3](\text{BARF}_4)_2$ (0.1 mM) in a dry DMF solution containing 0.1 M TBAPF₆ under N₂ atmosphere using an optically transparent thin layer electrode (OTTLE) cell. The applied potentials were referenced to NHE. (c) Photographs of DMF solutions of **2** in each oxidation state.

The above electrochemical results encouraged us to isolate the complexes with other oxidation states, and complexes with both divalent and trivalent states were successfully obtained, by chemical reduction and oxidation, as the discrete dinuclear complexes $[\text{Pt}_2(\mu\text{-aam})_2(\text{ppy})_2]$ (**2(+2)**) and $[\text{Pt}_2\text{Cl}_2(\mu\text{-aam})_2(\text{ppy})_2]$ (**2(+3)Cl**), respectively (Scheme 3). Both **2(+2)** and **2(+3)Cl** exhibited essentially the same UV-visible absorption spectra as those obtained by the electrochemical reduction or oxidation of **2(+2.33)**₃, respectively (Figure S7), confirming that the electrochemical reduction and oxidation products of **2(+2.33)**₃, shown in Figure 2b, were the divalent and trivalent forms, respectively. Time-dependent density-functional theory (TD-DFT) calculations also support this conclusion (Figures S8 and 9).

Crystal structures of **2(+2)** and **2(+3)Cl** are shown in Figures 1b and 1c, respectively.^[14] Both structures retain the aam-bridged dinuclear motif, which indicates the stability of this dinuclear framework toward multielectron oxidation/reduction. However, the different Pt–Pt distances clearly indicate the different electronic characters of the three states. The Pt–Pt distance for **2(+2)** (2.987(2) Å) is similar to those of other cyclometalated dinuclear Pt(II) complexes (2.8–3.0 Å, see Table S1) that have Pt^{II}...Pt^{II} electronic interactions. In contrast, the shortest Pt–Pt distance found for **2(+3)Cl** (2.594(7) Å) indicates that **2(+3)Cl** has a Pt–Pt single bond, comparable to those reported for other dinuclear Pt(III) complexes (2.5–2.6 Å, see Table S1).

It is noteworthy that only the divalent complex **2(+2)** produces an intense red emission in the solid state (Figure 3). The spectrum of **2(+2)** shows a structureless, broad emission band centered at 643 nm at room temperature with a quantum efficiency (Φ) of 0.14 and an emission lifetime (τ) of 1.39 μs. On

the basis of these data, the broad emission of **2(+2)** is attributed to a transition from the ³MMLCT state (Figure S13).

The absorption and emission spectra clearly indicate that optical properties of divalent and trivalent states of **2** are very similar to those of **1** (Table S2). This means the bridging ligands do not affect the lower electronic states significantly, yet are essential for stabilizing the mixed-valent states. The differences between **2** and **1** can be attributed to the assembling properties of the dimer motifs. As shown in the crystal structure (Figure 1a), the aam ligand in **2** acts as a good bridging ligand to form the assembled structure. However, the 2-pyridinethiolato (pyt) ligand in **1** is bulky, hindering the assembly of the trimer (Scheme 4). Actually, the steric hindrance due to the pyt ligand can be seen clearly in a related dinuclear Pt(II) complex, $[\text{Pt}_2(\mu\text{-pyt})_2(\text{bpy})_2]^{2+}$ (bpy = 2,2'-bipyridine), which can form two geometrical isomers; a *syn*-isomer with a head-to-head configuration of the two pyt bridging ligands and *anti*-isomer with a head-to-tail configuration (Scheme S4). Only the *syn*-isomer can form a dimer-of-dimer structure by the avoidance of the steric hindrance of the pyridine ring.^[18] Also, the well-known platinum blues containing a pyridonato bridge adopt this head-to-head configuration of the bridging ligands so as to form a similar dimer-of-dimer structure.^[11,19] In the case of cyclometalated complexes **1** and **2**, however, the head-to-tail configuration is the only molecular framework that can form (Scheme 1). Therefore, for the complex **1** including the pyt ligands, it is clearly difficult to form even in the "dimer-of-dimer".

In conclusion, we succeeded in preparing a redox-

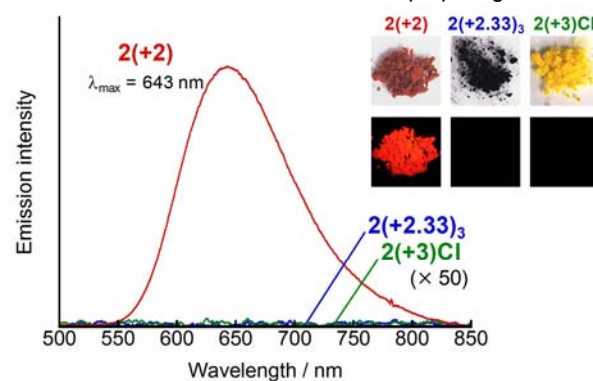
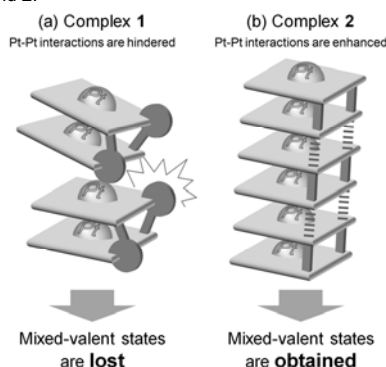


Figure 3. Emission spectra of **2(+2)** (red line), $[2(+2.33)_3](\text{BARF}_4)_2$ (blue line), and **2(+3)Cl** (green line) at room temperature in the solid state ($\lambda_{\text{ex}} = 400$ nm). inset: Photographs of powders of **2(+2)**, $[2(+2.33)_3](\text{BARF}_4)_2$, and **2(+3)Cl** under bright field (top) and UV light (bottom), respectively.

Scheme 3. Redox reactions of **2(+2.33)**₃.

Scheme 4. Schematic illustration of the difference in steric effects between complexes **1** and **2**.



multistable system that exhibits both emissive multicolor electrochromism and luminescence. This was achieved by using a cyclometalated dinuclear Pt complex bridged by the aam ligand. A unique bowed “trimer-of-dimer” structure with an average oxidation state of +2.33 was identified by X-ray crystallographic studies, as well as the structure of the red-luminescent dinuclear Pt(II) and non-luminescent dinuclear Pt(III) complexes. Our investigation provides significant information for the development of new luminophores capable of multistep switching by electrochemical oxidation and reduction. Further application of such redox-multistable systems is now in progress.

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Keywords: multiredox system • dinuclear Pt complex • luminescence • mixed-valence state • electrochromism

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