

## Redox-controlled Luminescence of a Cyclometalated Dinuclear Platinum Complex Bridged with Pyridine-2-thiolate Ions

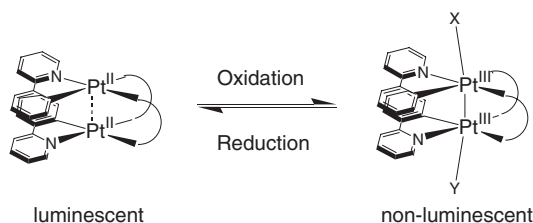
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A cyclometalated dinuclear platinum(II) complex bridged with pyridine-2-thiolate ions,  $[\text{Pt}_2(\text{ppy})_2(\text{pyt})_2]$  (Hppy = 2-phenylpyridine, Hpyt = pyridine-2-thiol) and its oxidized platinum(III) complex,  $[\text{Pt}_2\text{Cl}_2(\text{ppy})_2(\text{pyt})_2]$  have been synthesized and characterized. The divalent complex exhibits intense red luminescence both in solution and in the solid states. Corresponding to the short Pt...Pt distance (2.849(1) Å) for  $[\text{Pt}_2(\text{ppy})_2(\text{pyt})_2]$ , the reversible conversion between the divalent and trivalent complexes occurs easily with appearance and disappearance of the luminescence.

Recent progress in the development of the luminescent metal complexes is noteworthy. We also reported interesting luminescent properties of a dinuclear (2,2'-bipyridine)platinum(II) complex bridged with two pyridine-2-thiolate ions (pyt),  $[\text{Pt}_2(\text{pyt})_2(\text{bpy})_2]^{2+}$ .<sup>1</sup> The *anti* isomer with a head-to-tail configuration of two pyt's emits intense red luminescence originating from the Pt...Pt interaction and more interestingly, the *syn* isomer with a head-to-head configuration exhibits remarkable luminescence change by sensing particular organic vapors. By replacing the bpy ligand with 2-phenylpyridinate ion (ppy) known for the stronger ligand field, we can expect stronger Pt...Pt interaction that would significantly affect the luminescent properties.<sup>2</sup> In addition, much attention has been recently focused on mononuclear Pt(II) and Ir(III) complexes containing such cyclometalating ligands as promising light-emitting materials.<sup>3</sup> In this paper, we report a new cyclometalated dinuclear platinum(II) complexes,  $[\text{Pt}_2(\text{ppy})_2(\text{pyt})_2]$  (**Pt<sub>2</sub>(II-II)**) and its oxidized platinum(III) complex,  $[\text{Pt}_2\text{XY}(\text{ppy})_2(\text{pyt})_2]$  (**Pt<sub>2</sub>(III-III)XY**), which are easily interconverted following the redox-controlled luminescence change.



Scheme 1.

The divalent complex was synthesized by the reaction of an equimolar amount of  $(\text{Bu}_4\text{N})[\text{PtCl}_2(\text{ppy})]_4$  and Hpyt in acetonitrile by adding an EtOH solution of tri-*n*-butylamine as a reducing agent. After stirring the mixture for 1 day at room temperature, the red precipitate of **Pt<sub>2</sub>(II-II)** was purely produced as indicated by <sup>1</sup>H NMR spectrum.<sup>5</sup> When the reaction was performed without amine, the trivalent complex, **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>** was selectively precipitated.<sup>6</sup> Recrystallization of these products

from acetonitrile gave red plate and orange needle crystals, respectively. **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>** was also obtained by the recrystallization of **Pt<sub>2</sub>(II-II)** from chloroform.

Figures 1 and 2 show the molecular structures of **Pt<sub>2</sub>(II-II)** and **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>**, respectively.<sup>7</sup> **Pt<sub>2</sub>(II-II)** takes a similar geometry to that found for the *anti* form of  $[\text{Pt}_2(\text{pyt})_2(\text{bpy})_2]^{2+}$ .<sup>1</sup> However, much shorter Pt...Pt distance (2.8491(4) Å) than that of the bpy complex (2.997(1) Å) is realized as expected. This is the shortest Pt<sup>II</sup>...Pt<sup>II</sup> distance among the dinuclear platinum complexes bridged with two ligands ever reported.<sup>8</sup> It suggests the strong Pt...Pt electronic interaction for **Pt<sub>2</sub>(II-II)**. It is interesting to note that the *anti* configuration is stereospecifically formed for the cyclometalated dinuclear complex. The strong Pt-C bonds also influence their *trans* positions preferring the *N*-coordination to the *S*-coordination of the pyt ligand where Pt-N distances at the *trans* positions definitely lengthen as usual.

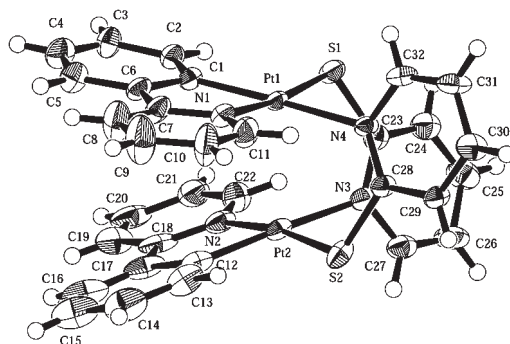


Figure 1. Molecular structure of **Pt<sub>2</sub>(II-II)**. Pt1-S1 = 2.284(2), Pt1-N1 = 2.037(7), Pt1-N4 = 2.142(7), Pt1-C1 = 1.986(8), Pt2-S2 = 2.284(2), Pt2-N2 = 2.037(7), Pt2-N3 = 2.144(7), Pt2-C12 = 1.983(9), Pt1...Pt2 = 2.8491(4) Å.

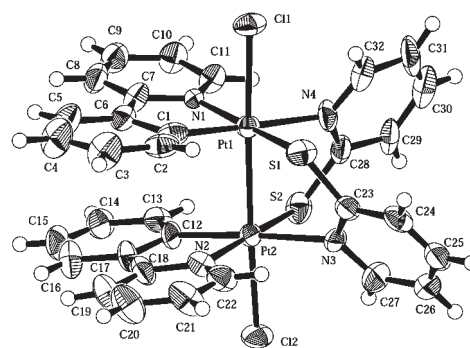
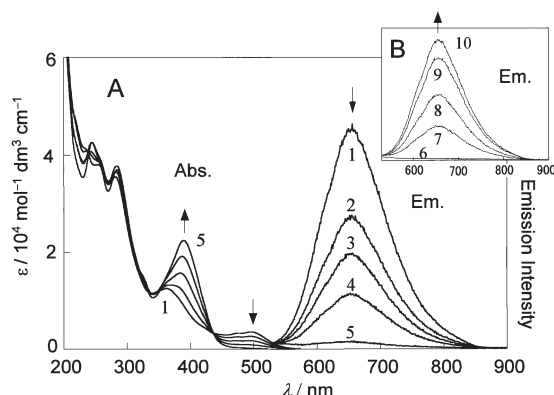


Figure 2. Molecular structure of **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>**. Pt1-Pt2 = 2.6150(8), Pt1-C11 = 2.482(4), Pt1-S1 = 2.310(4), Pt1-N1 = 2.09(1), Pt1-N4 = 2.19(2), Pt1-C1 = 2.01(2), Pt2-C12 = 2.442(4), Pt2-S2 = 2.302(5), Pt2-N2 = 2.08(1), Pt2-N3 = 2.20(1), Pt2-C12 = 2.03(2) Å.

**Table 1.** Emission spectral data for **Pt<sub>2</sub>(II-II)**

	298 K			77 K	
	$\lambda_{\max}/\text{nm}^a$	$\tau/\text{ns}^b$	$\phi^c$	$\lambda_{\max}/\text{nm}^a$	$\tau/\mu\text{s}^b$
neat crystals	641	87	—	643	3.1
solution <sup>d</sup>	648	94	0.005	616	4.8

<sup>a</sup> $\lambda_{\text{ex}} = 500 \text{ nm}$ . <sup>b</sup> $\lambda_{\text{ex}} = 337 \text{ nm}$ . <sup>c</sup>in DMF,  $\lambda_{\text{ex}} = 370 \text{ nm}$ . <sup>d</sup>in EtOH/MeOH (4/1 v/v).



**Figure 3.** Absorption and emission spectral changes of **Pt<sub>2</sub>(II-II)** in  $\text{CH}_3\text{CN}$  ( $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) at room temperature by the addition of HCl in 1) 0, 2) 0.5, 3) 1.0, 4) 1.5, and 5) 2.0 molar ratios (A), followed by the addition of  $\text{NEt}_3$  in 6) 0, 7) 0.25, 8) 0.5, 9) 1.0 and 10) 2.0 molar ratios (B). For emission spectra,  $\lambda_{\text{ex}} = 300 \text{ nm}$ .

Thus the thiolate ions occupy the *trans* positions to the N atoms of ppy. As a result, the only one configuration shown in Figure 1 should be produced as the most stable configuration. The preferential geometry of the *anti* configuration is also found for **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>** which includes the two  $\text{Cl}^-$  ions at the axial positions (Figure 2). The shorter Pt–Pt distance (2.615(1) Å) than that of **Pt<sub>2</sub>(II-II)** clearly indicates the formation of the single bond between the Pt(III) ions.<sup>9</sup>

**Pt<sub>2</sub>(II-II)** exhibits intense red luminescence both in solution and in the solid states which is assignable to the emission from the <sup>3</sup>MMLCT state arising from the Pt...Pt interaction.<sup>1</sup> As summarized in Table 1, both neat crystals and solution show similar luminescence indicating that the dinuclear framework is rigid and the Pt...Pt interaction is kept in any states.

Figure 3a shows luminescence spectral changes of an acetonitrile solution of **Pt<sub>2</sub>(II-II)** by the addition of HCl as well as the absorption spectral changes. The emission intensity decreased with increasing concentration of HCl. The absorption spectral changes indicate the facile oxidative addition occurred for **Pt<sub>2</sub>(II-II)**.<sup>10</sup> After the luminescence disappeared, the addition of  $\text{NEt}_3$  to the solution revived the emission intensity as shown in the Figure 3b.<sup>11</sup> Thus the dinuclear system with the strong Pt...Pt interaction exhibits the reversible change in the luminescence intensity by the control of the redox states (Scheme 1). The oxidation potential of **Pt<sub>2</sub>(II-II)** in  $\text{CH}_3\text{CN}$  was estimated at +0.58 V ( $E_p$ ) vs NHE as the two-electron oxidation though the process is irreversible as is usual for (diimine)Pt(II) complexes.

By the combination of the redox behavior and the photo excitation of **Pt<sub>2</sub>(II-II)**, a promising photocatalytic system would

be constructed. The preliminary experiments indicated that the photoinduced decomposition of  $[\text{Co}(\text{acac})_3]$  (Hacac = acetyl-acetone) occurred in the presence of **Pt<sub>2</sub>(II-II)**. The studies are now in progress.

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## References and Notes

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- <sup>1</sup>H NMR(dms-*d*<sub>6</sub>,  $\delta$ ) for **Pt<sub>2</sub>(II-II)**: 6.32 (t, 2H), 6.64 (t, 2H), 6.89 (t, 2H), 7.03 (d, 2H), 7.10 (t, 2H), 7.18 (d, 2H), 7.28 (t, 2H), 7.39 (t, 4H), 7.60 (d, 2H), 7.73 (t, 2H), 8.50 (d, 2H). Anal. Found: C, 41.88; H, 2.68; N, 6.15%. Calcd for  $\text{Pt}_2\text{C}_{32}\text{H}_{24}\text{N}_4\text{S}_2$ : C, 41.83; H, 2.63; N, 6.10%.
- <sup>1</sup>H NMR(dms-*d*<sub>6</sub>,  $\delta$ ) for **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>**: 6.42 (t, 2H), 6.77 (d, 4H), 7.09 (t, 2H), 7.18 (d, 2H), 7.39 (t, 2H), 7.46 (d, 2H), 7.55 (t, 2H), 7.64 (d, 2H), 7.78 (t, 2H), 7.99 (d, 2H), 9.30 (d, 2H). Anal. Found: C, 38.61; H, 2.49; N, 5.60%. Calcd for  $\text{Pt}_2\text{C}_{32}\text{H}_{24}\text{N}_4\text{S}_2\text{Cl}_2$ : C, 38.33; H, 2.44; N, 5.66%.
- Crystal data for **Pt<sub>2</sub>(II-II)**.  $\text{Pt}_2\text{C}_{32}\text{H}_{24}\text{N}_4\text{S}_2$ ,  $M = 918.87$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 12.508(1)$ ,  $b = 16.528(1)$ ,  $c = 14.406(1)$  Å,  $\beta = 108.221(3)^\circ$ ,  $V = 2829.0(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 173 \text{ K}$ ,  $D_{\text{calcd}} = 2.157 \text{ g cm}^{-3}$ ,  $D_m = 2.160 \text{ g cm}^{-3}$  at 298 K,  $\mu(\text{Mo K}\alpha) = 100.17 \text{ cm}^{-1}$ . The final  $R$  indices:  $R(F) = 0.066$  based on 4434 reflections ( $I > 2\sigma(I)$ ),  $wR(F^2) = 0.172$  based on 6373 observed reflections (all data) and 363 parameters,  $\text{GOF} = 1.08$ . For **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>·1.5CH<sub>3</sub>CN**,  $\text{Pt}_2\text{C}_{35}\text{H}_{28.5}\text{N}_{5.5}\text{S}_2\text{Cl}_2$ ,  $M = 1051.35$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 9.573(5)$ ,  $b = 14.296(7)$ ,  $c = 25.68(1)$  Å,  $\beta = 97.877(6)^\circ$ ,  $V = 3481(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 173 \text{ K}$ ,  $D_{\text{calcd}} = 2.006 \text{ g cm}^{-3}$ ,  $D_m = 2.013 \text{ g cm}^{-3}$  at 298 K,  $\mu(\text{Mo K}\alpha) = 100.41 \text{ cm}^{-1}$ . The final  $R$  indices:  $R(F) = 0.088$  based on 4558 reflections ( $I > 2\sigma(I)$ ),  $wR(F^2) = 0.210$  based on 7847 observed reflections (all data) and 380 parameters,  $\text{GOF} = 1.12$ . Full crystallographic details excluding structure factor tables have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-248008 and 248009. Copies of the data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; deposit@ccdc.cam.ac.uk).
- The shortest Pt<sup>II</sup>...Pt<sup>II</sup> distance (2.680(2) Å) was reported for  $[\text{Pt}_2(4\text{-mpyt})_4]$  which was constructed with four bridging ligands, 4-methylpyridine-2-thiolate ions (4-mpyt).<sup>9</sup>
- K. Umakoshi, I. Kinoshita, A. Ichimura, and S. Ooi, *Inorg. Chem.*, **26**, 3551 (1987).
- In fact, **Pt<sub>2</sub>(III-III)Cl<sub>2</sub>** was isolated from the solution. In the presence of HBr, **Pt<sub>2</sub>(III-III)Br<sub>2</sub>** was obtained instead.
- Correspondingly, the absorption spectrum reverted to that for **Pt<sub>2</sub>(II-II)**. By the addition of the excess of  $\text{NEt}_3$ , the recovery of **Pt<sub>2</sub>(II-II)** was completed, which was also confirmed by means of <sup>1</sup>H NMR spectroscopy.