

Pyrazolato- and 3,5-Dimethylpyrazolato-Bridged Dinuclear Platinum(II), Palladium(II), and Their Mixed-Metal Complexes of 2,2′-Bipyrimidine. Syntheses, Structures, and Luminescent Properties

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The pyrazolato (pz)- and 3,5-dimethylpyrazolato (Me_2pz)-bridged dinuclear platinum(II) and palladium(II) complexes of 2,2′-bipyrimidine (bpym), $[Pt_2(bpym)_2(\mu\text{-}pz')_2](PF_6)_2$ (pz′ = pz (**1a**) and Me_2pz (**1b**)) and $[Pd_2(bpym)_2(\mu\text{-}pz')_2](PF_6)_2$ (pz′ = pz (**2a**) and Me_2pz (**2b**)), have been synthesized and structurally characterized. The Pd–Pt complex, $[PdPt(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**4b**), has also been synthesized and characterized by ^{1}H NMR spectroscopy. Among these Pt_2, Pd_2, and PdPt complexes, only **1a** and **1b** exhibit greenish blue and yellow-green luminescence, respectively, in the solid state at ambient temperature. The emissions of **1a** and **1b** in the solid state are tentatively assigned as the emission from the ^{3}LC/MLCT and ^{3}MMLCT excited states, respectively.

Platinum(II) complexes containing α-diimine, terpyridine, acetylide, or related ligands have attracted much attention in view of their luminescent properties and potential application to materials.[1–17] Remarkable features of these complexes are that metal–metal interactions are expected in the solid state and in concentrated solutions. Furthermore the intramolecular metal–metal interactions between (π-type ligand)platinum units are also expected by constructing dinuclear complexes with face-to-face association of coordination planes. Their emissive states are attributed to a variety of low energy excited states depending on the nature of π-type ligands and the extent of intermolecular metal–metal interactions.

We have recently found that the heteropolynuclear complex of 3,5-dimethylpyrazolate, $[Pt_2Ag_4(Me_2pz)_8]$ (Me_2pzH: 3,5-dimethylpyrazole) exhibits cluster-centered bright sky-blue luminescence and the emission energy can be controlled by the change of incorporated group 11 elements.[18,19] Our preliminary examination of the luminescent properties of Pd analog, $[Pd_2Ag_4(Me_2pz)_8]$, revealed that the Pd_2Ag_4 complex exhibits orange luminescence, indicating that the replacement of Pt atoms by Pd atoms results in the decrease of emission energy of Pd_2Ag_4 complex. It is thus interesting to compare luminescent properties of Pt_2, Pd_2, and PdPt complexes containing α-diimine ligands, though Pd_2 and PdPt complexes did not show luminescence at least at an ambient temperature. Herein we report the syntheses, structures, and luminescent properties of pyrazolato- and 3,5-dimethylpyrazolato-bridged dinuclear platinum(II), palladium(II), and their mixed-metal complexes of 2,2′-bipyrimidine.

Results and Discussion

Synthesis and Characterization. The reaction of $[Pt(bpym)Cl_2]$ (bpym: 2,2′-bipyrimidine) with pyrazole (pzH) and 3,5-dimethylpyrazole (Me_2pzH) in a 1:1 ratio at 85 °C in water and an addition of NH_4PF_6 into the solution afforded pyrazolato-bridged dinuclear platinum(II) complexes, $[Pt_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (**1a**) and $[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**1b**), respectively. The palladium analogs, $[Pd_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (**2a**) and $[Pd_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**2b**), were obtained similarly by the reaction of $[Pd(bpym)Cl_2]$ with pzH or Me_2pzH at an ambient temperature (Scheme 1). The ^{1}H NMR spectra of **2a** and **2b** closely resemble those of **1a** and **1b**, respectively, and the signals of **2a** and **2b** appear in higher field than those of **1a** and **1b** (Table 1). As is described below, **1a** and **1b** exhibit greenish blue and yellow-green luminescence, respectively, in the solid state at an ambient temperature upon exposure to UV radiation. However, the palladium analogs, **2a** and **2b**, do not exhibit luminescence at ambient temperature even in the solid state. It is thus interesting to study the luminescent properties of the mixed-metal complex, which contains both of Pt(II) and Pd(II) ions in the molecule. Because Pt(II) ion is more inert than Pd(II) ion, we adopted a strategy that the bridging ligands were introduced to $[Pt^{II}(bpym)]$ unit first and then Pd(II) ion was reacted with the precursor. Namely $[Pt(bpym)Cl_2]$ was reacted with Me_2pzH (2 equiv) in the presence of KOH to give a mononuclear complex, $[Pt(bpym)(Me_2pz)(Me_2pzH)]Cl$ (**3b**). The reaction of **3b** with $[Pd(bpym)(CH_3CN)_2](NO_3)_2$, which was prepared by the reaction of $[Pd(bpym)Cl_2]$ with $AgNO_3$, and an addition of NH_4PF_6 afforded a mixed-metal complex, $[PdPt(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**4b**) (Scheme 2). The ^{1}H NMR spectrum of **4b** is shown in Figure 1 with those of **1b** and **2b**. Numerical data are also summarized in Table 1. The ^{1}H NMR spectrum of **4b** is very similar to the superposition of NMR spectra of **1b** and **2b** in the range of 9.5–7.5 ppm. However, **4b** exhibits only one H4 resonance of Me_2pz ligand at 6.18 ppm, which has different

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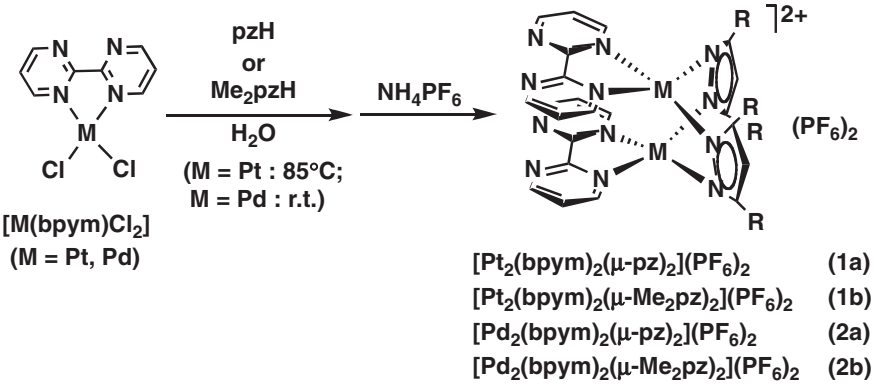
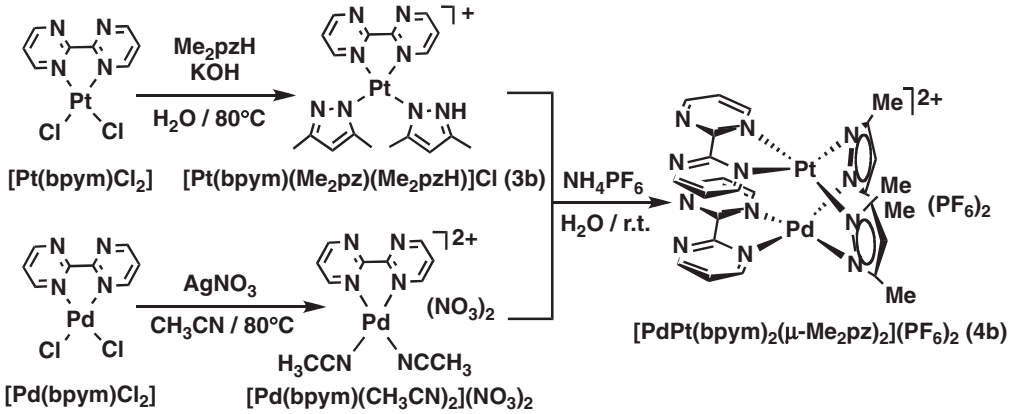


Scheme 1. Preparative methods for $[M_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (M = Pt and Pd) and $[M_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (M = Pt and Pd).



Scheme 2. Preparative methods for $[PdPt(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**4b**).

Table 1. ^{1}H NMR Data in CD_3CN (δ)

	1a	1b	2a	2b	3b[a)]	4b
$H6_{bpym}$	9.35	9.30	9.29	9.26	9.33	9.32 (Pt site) 9.25 (Pd site)
$H4_{bpym}$	8.68	8.57	8.41	8.30	9.23	8.57 (Pt site) 8.30 (Pd site)
$H5_{bpym}$	7.85	7.80	7.81	7.77	7.68	7.81 (Pt site) 7.77 (Pd site)
$H3_{pz}$ and $H5_{pz}$	7.85		7.78			
$H4_{pz}$	6.65		6.58			
$H4_{Me_2pz}$		6.24		6.10	5.75	6.18
CH_3		2.35		2.38	2.35, 1.65	2.41, 2.35

a) Measured in $CDCl_3$.

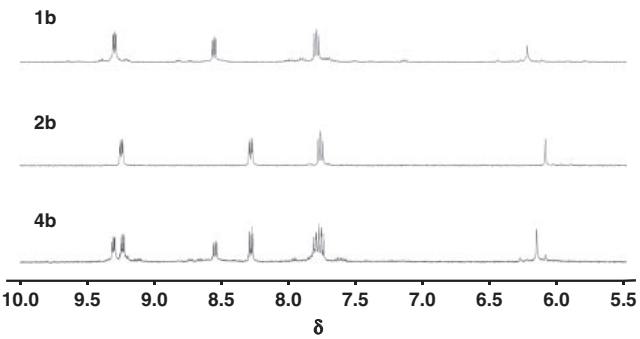


Figure 1. ^{1}H NMR spectra of $[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**1b**), $[Pd_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**2b**), and $[PdPt(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**4b**) in CD_3CN.

chemical shift from those of **1b** and **2b**. This fact clearly indicates that **4b** is the mixed-metal complex of Pt and Pd and is not a mixture of **1b** and **2b**. Actually the ^{1}H NMR spectrum of the mixture of **1b** and **2b** exhibits two H4 resonances of Me_2pz ligand at 6.24 and 6.10 ppm (Figure S1).

We have not succeeded in obtaining single crystals suitable for the X-ray structural analysis of **4b**. However, it is obvious from the ^{1}H NMR spectrum that the complex cation of **4b** has C_s symmetry, because only single H4 resonance of Me_2pz ligands, a set of single H4, H5, and H6 resonances for Pt(bpym) unit and also a set of single H4, H5, and H6 resonances for Pd(bpym) unit were observed. These observations indicate that the structure of **4b** in solution is similar to that of **1b** and **2b**. Unfortunately **4b** does not exhibit luminescent properties in the solid state at ambient temperature upon exposure to UV radiation.

Crystal Structures. X-ray structural analyses of **1a**, **1b**, **2a**, and **2b** were performed (Table 2). The structure of the complex cation of **1a** is shown in Figure 2. Two Pt(bpym) units are bridged by two pyrazolate anions with face-to-face association of the coordination planes. The Pt···Pt distance in **1a** is 3.3589(5) Å, and the tilt angle between adjacent platinum coordination planes defined by the four donor atoms, respectively, is 86(1)° (Table 3). The Pt···Pt distance and the tilt angle

Table 2. Crystallographic Data for $[Pt_2(bpym)_2(\mu\text{-pz})_2](PF_6)_2$ (**1a**), $[Pt_2(bpym)_2(\mu\text{-Me}_2pz)_2](PF_6)_2$ (**1b**), $[Pd_2(bpym)_2(\mu\text{-pz})_2](PF_6)_2$ (**2a**), and $[Pd_2(bpym)_2(\mu\text{-Me}_2pz)_2](PF_6)_2$ (**2b**)

	1a	**1b**	**2a**	**2b**
Empirical formula	$C_{22}H_{18}F_{12}N_{12}P_2Pt_2$	$C_{26}H_{26}F_{12}N_{12}P_2Pt_2$	$C_{22}H_{18}F_{12}N_{12}P_2Pd_2$	$C_{26}H_{26}F_{12}N_{12}P_2Pd_2$
Formula weight	1130.57	1186.68	953.19	1009.30
T/K	296	296	296	296
λ/Å	0.71070	0.71070	0.71070	0.71070
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group (No.)	$Pca2_1$ (29)	$Pbca$ (61)	$Pna2_1$ (33)	$Pbca$ (61)
a/Å	17.7518(5)	16.8152(9)	21.527(1)	16.4988(5)
b/Å	14.2988(4)	14.9288(7)	11.0681(8)	14.9573(5)
c/Å	12.7530(4)	29.996(2)	13.1289(5)	30.661(1)
V/Å^3	3237.1(3)	7529(1)	3128.1(5)	7566.3(7)
Z	4	8	4	8
ρ_{calcd}/g cm^{-3}	2.320	2.093	2.024	1.772
Crystal size/mm^3	0.50 × 0.30 × 0.15	0.20 × 0.20 × 0.20	0.70 × 0.10 × 0.04	0.60 × 0.40 × 0.40
$2\theta_{max}$/°	55.0	55.0	55.0	55.0
μ(Mo Kα)/mm^{-1}	8.805	7.576	1.364	1.133
Reflections collected	25259	58942	24545	57460
No. of unique reflections	3877 ($R_{int} = 0.022$)	8581 ($R_{int} = 0.062$)	3728 ($R_{int} = 0.028$)	8605 ($R_{int} = 0.021$)
Data/restraints/parameters	3877/0/422	8581/0/487	3728/0/452	5356/0/487
Final R indices	$R1$[a] = 0.028 [$I > 2\sigma(I)$]	$R1 = 0.047$ [$I > 2\sigma(I)$]	$R1 = 0.050$ [$I > 2\sigma(I)$]	$R1 = 0.058$ [$I > 3\sigma(I)$]
R indices	R[b] = 0.052, R_w[c] = 0.071	$R = 0.085$, $R_w = 0.147$	$R = 0.069$, $R_w = 0.121$	$R = 0.105$, $R_w = 0.174$
Goodness-of-fit on F^2	0.95	0.91	1.22	1.50
Largest diffraction peak/hole/eÅ^{-3}	0.99/−0.69	1.54/−1.38	1.48/−0.63	1.44/−0.80

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. c) $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

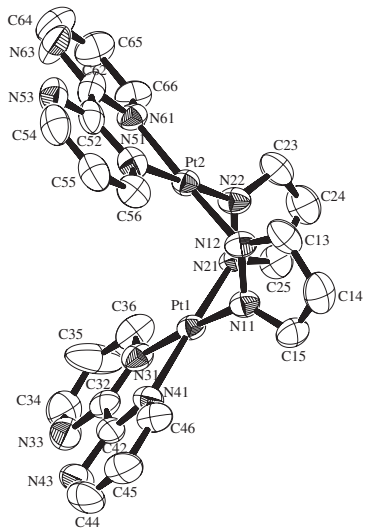


Figure 2. Perspective drawing of the complex cation of $[Pt_2(bpym)_2(\mu\text{-pz})_2](PF_6)_2$ (**1a**) with the atomic labeling scheme (50% probability ellipsoids).

in **1a** are slightly larger than the corresponding values in analogous complex, $[Pt_2(bpy)_2(\mu\text{-pz})_2](BF_4)_2 \cdot H_2O$ (3.231(1) Å, 77.9(3)°).[20] On the other hand, the Pt···Pt distance in Me_2pz-bridged complex, **1b**, is 3.1968(7) Å and the tilt angle is 75.6(3)° (Figure 3). The shorter Pt···Pt distance and the smaller tilt angle of **1b** than **1a** may be attributed to the steric effect of the methyl group. Similar steric effect is also seen in the pyrazolato-bridged cyclometalated platinum(II) complexes, $[Pt_2(C\text{^}N)_2(\mu\text{-pz}')_2]$ ($C\text{^}N$ = 2-(2,4-difluorophenyl)pyridyl; pz′ = pz and Me_2pz).[8] The Pt–N distances in **1a** and **1b** are in the range of 1.98–2.03 Å.

The structures of the complex cations of palladium analogs, **2a** and **2b**, are illustrated in Figures S1 and S2, respectively. The Pd···Pd distance (3.3337(9) Å) and tilt angle (84.5(9)°) in **2a** are very similar to the Pt···Pt distance and the tilt angle in **1a**. The Pd–N distances in **2a** are also very similar to the Pt–N distances in **1a**. Similarly to the observation for **1a** and **1b**, the shorter Pd···Pd distance and the smaller tilt angle of **2b** than **2a** were observed probably due to the steric effect of the methyl group. The Pd···Pd distance (3.1966(8) Å) and tilt angle (76.4(2)°) in **2b** are also very similar to the Pt···Pt distance and the tilt angle in **1b**. The dimer structures have recently been reported for neutral pyrazolato-bridged dinuclear palladium(II) complexes.[21] However, such intermolecular π–π interactions were not observed for the crystal structures of **1a**, **1b**, **2a**, and **2b** probably due to the presence of the counter ions, as discussed in the literature.

Photophysical Properties. The pyrazolato-bridged dinuclear platinum complexes, **1a** and **1b**, exhibit greenish blue and yellow-green luminescence, respectively, in the solid state upon exposure to UV radiation. These observations prompted us to study photophysical properties of these complexes. The absorption spectra of **1a** and **1b** in CH_3CN are depicted in Figure 4, in which **1a** exhibits absorption bands at 239 and 353 nm, while **1b** exhibits them at 239 and 377 nm. Although the higher energy bands in both complexes appear at the same position, the lower energy band in **1b** is red-shifted by 24 nm from that in **1a**. This is probably attributed to the increase of intramolecular Pt···Pt interactions in **1b** due to decrease of Pt···Pt distance. The shapes of absorption spectra of **1a** and **1b** resemble each other except for the position of the lowest energy bands. Furthermore, the absorption bands corresponding to the lowest energy bands in **1b** are not observed in the absorption

Table 3. Selected Bond Distances (Å) and Bond Angles (°) for **1a**, **1b**, **2a**, and **2b**

1a			
Pt1···Pt2	3.3589(5)		
Pt1–N11	2.013(10)	Pt2–N12	2.00(1)
Pt1–N21	1.987(8)	Pt2–N22	1.982(8)
Pt1–N31	2.026(10)	Pt2–N51	2.019(8)
Pt1–N41	2.021(9)	Pt2–N61	1.998(10)
N11–Pt1–N21	85.4(4)	N12–Pt2–N22	85.3(4)
N11–Pt1–N31	176.3(4)	N12–Pt2–N51	97.3(4)
N11–Pt1–N41	96.4(4)	N12–Pt2–N61	176.3(4)
N21–Pt1–N31	97.9(4)	N22–Pt2–N51	177.2(5)
N21–Pt1–N41	177.4(4)	N22–Pt2–N61	97.1(4)
N31–Pt1–N41	80.2(4)	N51–Pt2–N61	80.5(4)
1b			
Pt1···Pt2	3.1968(7)		
Pt1–N11	1.98(1)	Pt2–N12	1.99(1)
Pt1–N21	2.003(9)	Pt2–N22	1.997(10)
Pt1–N31	2.009(9)	Pt2–N51	2.000(9)
Pt1–N41	2.016(9)	Pt2–N61	1.985(10)
N11–Pt1–N21	86.6(4)	N12–Pt2–N22	85.0(4)
N11–Pt1–N31	177.3(4)	N12–Pt2–N51	96.6(4)
N11–Pt1–N41	97.0(4)	N12–Pt2–N61	177.1(4)
N21–Pt1–N31	96.1(4)	N22–Pt2–N51	178.0(4)
N21–Pt1–N41	176.4(4)	N22–Pt2–N61	97.5(4)
N31–Pt1–N41	80.3(4)	N51–Pt2–N61	80.9(4)
2a			
Pd1···Pd2	3.3337(9)		
Pd1–N11	2.015(9)	Pd2–N12	2.00(1)
Pd1–N21	2.000(8)	Pd2–N22	2.010(7)
Pd1–N31	2.026(9)	Pd2–N51	2.032(8)
Pd1–N41	2.044(7)	Pd2–N61	2.020(10)
N11–Pd1–N21	86.6(3)	N12–Pd2–N22	86.6(3)
N11–Pd1–N31	177.5(4)	N12–Pd2–N51	95.5(4)
N11–Pd1–N41	96.9(3)	N12–Pd2–N61	176.8(3)
N21–Pd1–N31	95.6(4)	N22–Pd2–N51	177.5(3)
N21–Pd1–N41	176.1(4)	N22–Pd2–N61	96.4(3)
N31–Pd1–N41	80.9(4)	N51–Pd2–N61	81.6(4)
2b			
Pd1···Pd2	3.1966(8)		
Pd1–N11	2.007(7)	Pd2–N12	1.971(8)
Pd1–N21	2.002(6)	Pd2–N22	1.987(6)
Pd1–N31	2.018(6)	Pd2–N51	1.998(6)
Pd1–N41	2.013(6)	Pd2–N61	1.998(7)
N11–Pd1–N21	87.1(3)	N12–Pd2–N22	85.7(3)
N11–Pd1–N31	177.2(2)	N12–Pd2–N51	95.3(3)
N11–Pd1–N41	97.3(3)	N12–Pd2–N61	176.0(3)
N21–Pd1–N31	95.3(2)	N22–Pd2–N51	178.0(2)
N21–Pd1–N41	175.6(3)	N22–Pd2–N61	98.1(3)
N31–Pd1–N41	80.3(2)	N51–Pd2–N61	80.8(3)

spectrum of $[Pt(bpym)(Me_2pzH)_2](PF_6)_2$ (Figure S4). The failure of the synthesis of $[Pt(bpym)(pzH)_2](PF_6)_2$, however, prevents us from unambiguous assignment of the absorption bands at 353 nm in **1a**. Thus we tentatively assigned the lowest

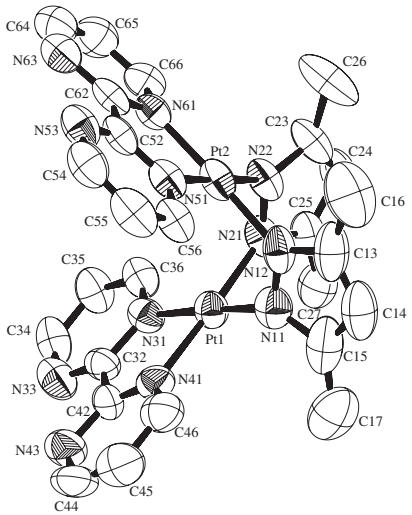


Figure 3. Perspective drawing of the complex cation of $[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**1b**) with the atomic labeling scheme (50% probability ellipsoids).

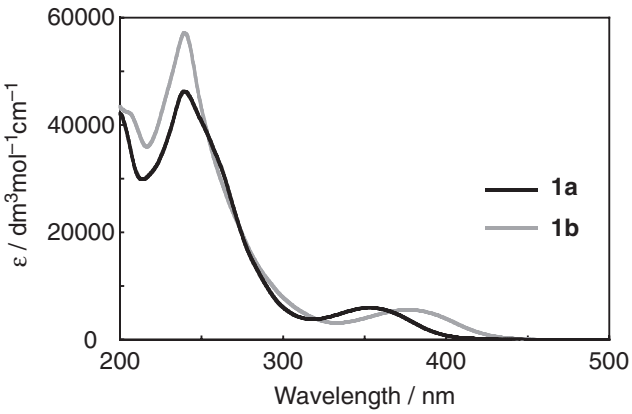


Figure 4. Electronic absorption spectra of **1a** (——) and **1b** (——) in CH_3CN at 298 K.

energy bands in **1b** at 377 nm as metal–metal-to-ligand charge transfer (MMLCT) transition. The systematic shift of the lowest energy absorption bands to lower energy was also observed for series of cyclometalated platinum(II) complexes, $[Pt_2(C\text{^}N)_2(\mu\text{-}pz')_2]$ (pz′ = pz, Me_2pz, Me^tBupz, and $^tBu_2pz$; Me^tBupz: 3-methyl-5-*tert*-butylpyrazolate, $^tBu_2pz$: 3,5-bis(*tert*-butyl)pyrazolate),[8] and $[Pt_2(ppy)_2(\mu\text{-}pz')_2]$ (pz′ = pz, Ph_2pz, and $^tBu_2pz$; Ph_2pz: 3,5-diphenylpyrazolate),[22] with increase of the bulkiness of substituent groups on the pyrazolate ligands. The lowest energy absorption bands absent in the absorption spectrum of related mononuclear complex are assigned to MMLCT transition for $[Pt_2(C\text{^}N)_2(\mu\text{-}pz')_2]$.[8] It is noteworthy that the MMLCT transitions are not observed explicitly for the cyclometalated platinum(II) complexes with pyrazolate and dimethylpyrazolate bridging ligands, $[Pt_2(C\text{^}N)_2(\mu\text{-}pz')_2]$ (pz′ = pz and Me_2pz),[8] $[Pt_2(ppy)_2(\mu\text{-}pz)_2]$,[22] and $[Pt_2(fppz)_2(\mu\text{-}pz')_2]$ (fppz: 3-trifluoromethyl-5-(2-pyridyl)pyrazolate; pz′ = pz and Me_2pz).[23]

The pz-bridged complex, **1a**, exhibits an emission spectrum with distinct vibronic features in the solid state (λ_{max} =

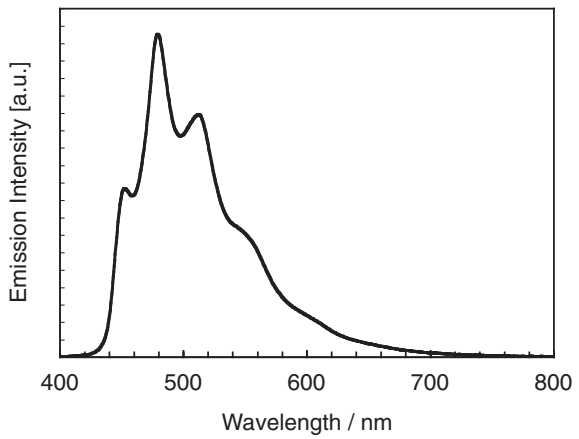


Figure 5. Emission spectra of $[Pt_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (**1a**) in the solid state at 295 K ($\lambda_{ex} = 355$ nm).

Table 4. Emission Properties of $[Pt_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (**1a**)[a)] and $[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**1b**)

	Crystal			In CH_3CN		
	λ_{max}/nm	τ/μs	Φ	λ_{max}/nm	τ/μs	Φ
1a	479	τ_1, 0.47; A_1, 0.38 τ_2, 1.5; A_2, 0.62	0.03	—	—	—
1b	536	0.0872	0.01	451	0.0047	0.0005

a) Emission decay curve was analyzed by the equation ($I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$) using the nonlinear least-squares method.

479 nm, Figure 5). The vibronic peaks spaced by ca. 1300 cm^{-1} indicate that this transition is coupled to aromatic ring-breathing modes. The close similarity of the emission of **1a** in the solid state to those of $[Pt_2(C\text{^}N)_2(\mu\text{-}pz')_2]$ and $[Pt_2(fppz)_2(\mu\text{-}pz')_2]$ ($pz' =$ pz and Me_2pz) in the solid state as well as in frozen solution at 77 K indicates that the emissions of **1a** can also be assigned to the transition from the mixture of ligand-centered π–π^* excited state and the metal-to-ligand charge transfer excited state (^{3}LC/MLCT).[8,23–25] The observed luminescent lifetime for **1a** is in the microsecond regime, indicating that the emission is phosphorescence (Table 4). Although $[Pt_2(ppy)_2(\mu\text{-}pz)_2]$ exhibits distinct emission from ^{3}LC/MLCT state in 2-methyltetrahydrofuran (2-MeTHF) solution even at 295 K, **1a** does not exhibit emission in CH_3CN solution at room temperature. Details of the photophysical properties including suppression of the emission in CH_3CN solution have been theoretically investigated and they are discussed elsewhere.[25]

The Me_2pz-bridged complex, **1b**, displays broad featureless emission spectra both in the solid state ($\lambda_{max} = 536$ nm) and in CH_3CN solution ($\lambda_{max} = 451$ nm) (Figure 6). The observed lifetime ($\tau = 0.0872$ μs) of the emission in the solid state for **1b** is shorter than that for **1a**. The change of the emissive states from ^{3}LC/MLCT excited state to ^{3}MMLCT excited state is observed for the cyclometalated Pt(II) complexes, $[Pt_2(C\text{^}N)_2(\mu\text{-}pz')_2]$ ($pz' =$ pz, Me_2pz, Me^{t}Bupz, and ^{t}Bu$_2$pz)[8,24] and $[Pt_2(ppy)_2(\mu\text{-}pz')_2]$ ($pz' =$ pz, Ph_2pz, and ^{t}Bu$_2$pz)[22] with decrease of Pt···Pt distances. The driving force for the change of emissive states is attributed to the steric influence of bulkier

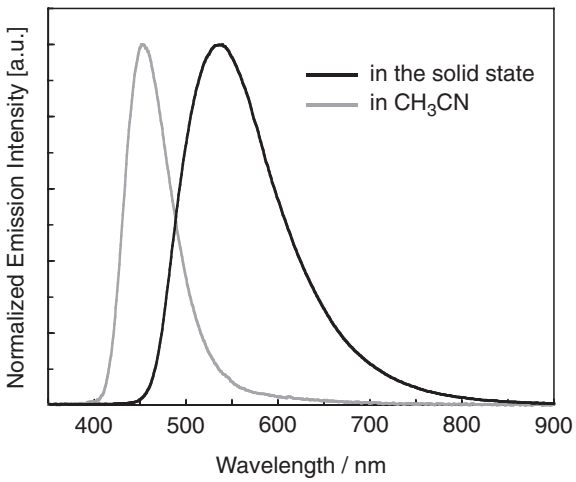


Figure 6. Normalized emission spectra of $[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (**1b**) in the solid state (——) and in CH_3CN (——) at 295 K ($\lambda_{ex} = 355$ nm).

substituent groups on pyrazolate rings. Thus we tentatively assigned the emission of **1b** in the solid state as well as in CH_3CN solution as the emission from the ^{3}MMLCT excited state. It is interesting that the emissive state of **1b** (^{3}MMLCT) is different from that of $[Pt_2(C\text{^}N)_2(\mu\text{-}Me_2pz)_2]$ (^{3}LC/MLCT) in the solid state in spite of their similar Pt···Pt distances (**1b**, 3.1968(7) Å; $[Pt_2(C\text{^}N)_2(\mu\text{-}Me_2pz)_2]$, 3.1914(9) Å),[8] though the emission of $[Pt_2(C\text{^}N)_2(\mu\text{-}Me_2pz)_2]$ in fluid solution at room temperature was assigned as the emission from the ^{3}MMLCT excited state.[24]

Conclusion

The pyrazolato- and dimethylpyrazolato-bridged Pt_2, Pd_2, and PdPt complexes of bipyrimidine have been synthesized and characterized. The photophysical measurement of these complexes revealed that only Pt_2 complexes, **1a** and **1b**, exhibit luminescent properties at room temperature. The pz-bridged complex, **1a**, exhibits an emission spectrum with distinct vibronic features in the solid state. The emission was tentatively assigned as the emission from the mixture of ligand-centered π–π^* excited state and the metal-to-ligand charge-transfer excited state (^{3}LC/MLCT). On the other hand, the Me_2pz-bridged complex, **1b**, displays broad featureless emission spectra both in the solid state and in CH_3CN solution. The emission of **1b** may be assigned as the emission from the ^{3}MMLCT excited state. The dependence of the emissive state on the Pt···Pt distance was observed for **1a** and **1b**. The Pt···Pt interaction in **1b** is strong enough to produce MMLCT photoluminescence in the solid state.

Experimental

Materials and Instrumentation. $[Pt(bpym)Cl_2]$[26,27] and $[Pd(bpym)Cl_2]$[28,29] were prepared by the reaction of $[Pt(C_2H_5CN)_2Cl_2]$[30] and $[Pd(CH_3CN)_2Cl_2]$[31] with 2,2′-bipyrimidine, respectively, in acetonitrile. All other commercially available reagents were used as purchased. UV–vis spectra were recorded on a Hitachi U-3300 spectrophotometer at 20 °C. The ^{1}H NMR spectra were obtained at 300 MHz with a Varian Gemini 300 spectrometer.

Preparation of Complexes. **$[Pt_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (1a):** $[Pt(bpym)Cl_2]$ (86 mg, 0.20 mmol) and pzH (16 mg, 0.23 mmol) were suspended in water (10 mL), and the mixture was stirred for 24 h at 85 °C under air. The red suspension was filtered, and NH_4PF_6 (65 mg, 0.40 mmol) was added to the filtrate to give red-orange precipitate. The solid was filtered, washed with water and diethyl ether, and dried in vacuo. Yield 90 mg (80%). It was recrystallized from CH_3CN/acetone/CH_2Cl_2 to give crystals suitable for X-ray structural analysis. Anal. Found: C, 23.41; H, 1.45; N, 14.71%. Calcd for $C_{22}H_{18}F_{12}N_{12}P_2Pt_2$: C, 23.37; H, 1.60; N, 14.87%. ^{1}H NMR (CD_3CN): δ 9.35 (dd, 4H, $H6_{bpym}$, $J = 1.9$, 4.9 Hz), 8.68 (dd, 4H, $H4_{bpym}$, $J = 1.9$, 5.8 Hz), 7.85 (m, 8H, ($H3_{pz}$, $H5_{pz}$, $H5_{bpym}$)), 6.65 (t, 2H, $H4_{pz}$, $J = 2.5$ Hz).

$[Pt_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (1b): $[Pt(bpym)Cl_2]$ (86 mg, 0.20 mmol) and Me_2pzH (19 mg, 0.20 mmol) were suspended in water (10 mL), and the mixture was stirred for 48 h at 85 °C under air. The red suspension was filtered, and NH_4PF_6 (65 mg, 0.40 mmol) was added to the filtrate to give red-orange precipitate. The solid was filtered, washed with water and diethyl ether, and dried in vacuo. Yield 71 mg (59%). It was recrystallized from CH_3CN/acetone/CH_2Cl_2 to give crystals suitable for X-ray structural analysis. Anal. Found: C, 25.91; H, 2.34; N, 13.78%. Calcd for $C_{26}H_{26}F_{12}N_{12}P_2Pt_2$: C, 26.32; H, 2.21; N, 14.16%. ^{1}H NMR (CD_3CN): δ 9.30 (dd, 4H, $H6_{bpym}$, $J = 2.0$, 4.9 Hz), 8.57 (dd, 4H, $H4_{bpym}$, $J = 2.0$, 5.8 Hz), 7.80 (dd, 4H, $H5_{bpym}$, $J = 4.9$, 5.8 Hz), 6.24 (s, 2H, $H4_{Me_2pz}$), 2.35 (s, 12H, CH_3).

$[Pd_2(bpym)_2(\mu\text{-}pz)_2](PF_6)_2$ (2a): $[Pd(bpym)Cl_2]$ (28 mg, 0.08 mmol) and pzH (14 mg, 0.21 mmol) were suspended in water (8 mL), and the mixture was stirred for 4 h at ambient temperature under air. The yellow suspension turned to a yellow solution. The addition of NH_4PF_6 (92 mg, 0.57 mmol) to the solution resulted in white precipitate. The solid was filtered, washed with water, and dried in vacuo. Yield 23 mg (59%). It was recrystallized from CH_3CN/EtOH to give crystals suitable for X-ray structural analysis. Anal. Found: C, 27.67; H, 1.58; N, 17.61%. Calcd for $C_{22}H_{18}F_{12}N_{12}P_2Pd_2$: C, 27.72; H, 1.90; N, 17.63%. ^{1}H NMR (CD_3CN): δ 9.29 (dd, 4H, $H6_{bpym}$, $J = 2.0$, 4.9 Hz), 8.41 (dd, 4H, $H4_{bpym}$, $J = 2.0$, 5.8 Hz), 7.81 (dd, 4H, $H5_{bpym}$, $J = 4.9$, 5.8 Hz), 7.78 (d, 4H, $H3_{pz}$ and $H5_{pz}$, $J = 2.4$ Hz), 6.58 (t, 2H, $H4_{pz}$, $J = 2.4$ Hz).

$[Pd_2(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (2b): $[Pd(bpym)Cl_2]$ (22 mg, 0.06 mmol) and Me_2pzH (14 mg, 0.14 mmol) were suspended in water (8 mL), and the mixture was stirred for 3 h at ambient temperature under air. The yellow suspension turned to yellow solution. The addition of NH_4PF_6 (30 mg, 0.18 mmol) to the solution resulted in white precipitate. The solid was filtered, washed with water, and dried in vacuo. Yield 13 mg (43%). It was recrystallized from CH_3CN/EtOH to give crystals suitable for X-ray structural analysis. Anal. Found: C, 31.04; H, 2.81; N, 16.51%. Calcd for $C_{26}H_{26}F_{12}N_{12}P_2Pd_2$: C, 30.94; H, 2.60; N, 16.65%. ^{1}H NMR (CD_3CN): δ 9.26 (dd, 4H, $H6_{bpym}$, $J = 2.1$, 4.9 Hz), 8.30 (dd, 4H, $H4_{bpym}$, $J = 2.0$, 5.7 Hz), 7.77 (dd, 4H, $H5_{bpym}$, $J = 4.9$, 5.7 Hz), 6.10 (s, 2H, $H4_{Me_2pz}$), 2.38 (s, 12H, CH_3). FABMS: m/z 864.4 $[M]^+$.

[Pt(bpym)(Me$_2$pz)(Me$_2$pzH)]Cl (3b): $[Pt(bpym)Cl_2]$ (102 mg, 0.24 mmol) and Me_2pzH (52 mg, 0.54 mmol) were added to an aqueous solution (8 mL) of KOH (34 mg, 0.61 mmol), and the mixture was stirred for 2 h at 80 °C under air. The red-orange precipitate was filtered, washed with ether, and dried in vacuo. Furthermore, the product dissolving in the reaction solution was also extracted three times with CH_2Cl_2 (10 mL). The orange solution was filtered and concentrated. The addition of *n*-hexane into the solution resulted in orange precipitate. The precipitate was washed with *n*-hexane and dried in vacuo. Total yield 71 mg (49%). Anal. Found: C, 36.20; H, 3.91; N, 18.43%. Calcd for $C_{18}H_{23}ClN_8OPt$ (**3b**$\cdot H_2O$): C, 36.16; H, 3.88; N, 18.74%. ^{1}H NMR ($CDCl_3$): δ 9.33 (dd, 2H, $H6_{bpym}$, $J = 2.2$, 4.2 Hz), 9.23 (dd, 2H, $H4_{bpym}$, $J = 2.1$, 4.8 Hz), 7.68 (dd, 2H, $H5_{bpym}$, $J = 4.8$, 5.7 Hz), 5.75 (s, 2H, $H4_{Me_2pz}$), 2.35 (s, 6H, CH_3), 1.65 (s, 6H, CH_3). FABMS: m/z 543.2 $[M - HCl]^+$.

$[PdPt(bpym)_2(\mu\text{-}Me_2pz)_2](PF_6)_2$ (4b): $[Pd(bpym)Cl_2]$ (35 mg, 0.11 mmol) and $AgNO_3$ (38 mg, 0.22 mmol) were suspended in CH_3CN (10 mL), and the mixture was stirred for 4 h at 80 °C under air. The yellow suspension was filtered to remove white precipitate of AgCl, and the yellow filtrate was concentrated to dryness. The yellow solid was dissolved in water (5 mL), and to this aqueous solution was added an aqueous solution (10 mL) of **3b** (60 mg, 0.10 mmol). The mixture was stirred for 1 h at an ambient temperature, and filtered. An addition of an aqueous solution (3 mL) of NH_4PF_6 (61 mg, 0.38 mmol) into the filtrate resulted in yellow precipitate. It was filtered, washed with water, and dried in vacuo. Yield 60 mg (50%). Anal. Found: C, 28.73; H, 2.51; N, 15.49%. Calcd for $C_{26}H_{26}F_{12}N_{12}P_2PdPt$: C, 28.44; H, 2.39; N, 15.31%. ^{1}H NMR (CD_3CN): δ 9.32 (dd, 2H, $H6_{bpym}$(Pt site), $J = 2.0$, 4.8 Hz), 9.25 (dd, 2H, $H6_{bpym}$(Pd site), $J = 2.0$, 4.8 Hz), 8.57 (dd, 2H, $H4_{bpym}$(Pt site), $J = 2.0$, 5.8 Hz), 8.30 (dd, 2H, $H4_{bpym}$(Pd site), $J = 2.0$, 5.8 Hz), 7.81 (dd, 2H, $H5_{bpym}$(Pt site), $J = 4.9$, 5.8 Hz), 7.77 (dd, 2H, $H5_{bpym}$(Pd site), $J = 4.9$, 5.8 Hz), 6.18 (s, 2H, $H4_{Me_2pz}$), 2.41 (s, 6H, CH_3), 2.35 (s, 6H, CH_3). FABMS: m/z 951.1 $[M]^+$.

X-ray Crystallography. Crystals suitable for X-ray structural analyses were obtained by recrystallization as mentioned above. The crystals, **1a**, **1b**, **2a**, and **2b** were mounted on glass fibers. Intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71070$ Å) radiation at 296 K. Final cell parameters were obtained from a least-squares analysis of reflections with $I > 10\sigma(I)$. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.[32]

The crystal structure of **1a** was solved by heavy-atom method by using DIRDIF94.[33] The positional and thermal parameters of non-H atoms were refined anisotropically except for the F atoms in one of the PF_6 ions (F21, F22, F23, F24, F25, and F26) by the full-matrix least-squares method, and those six F atoms were refined isotropically. The crystal structures of **1b**, **2a**, and **2b** were solved by direct method (SIR92).[34] The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. The minimized function was $\Sigma w(F_o^2 - F_c^2)$,[2] where $w^{-1} = \sigma^2(F_o^2) + (p(Max(F_o^2, 0) + 2F_c^2)/3)^2$ ($p = 0.03$ for **1a**, 0.05 for **1b** and **2a**, 0.09 for **2b**). Hydrogen atoms were included at calculated positions with fixed displacement parameters (1.2 times the displacement parameters of the host atom). In the final cycle of the refinement, parameter shifts were less than 0.1σ. No correction was made for secondary extinction.

All calculations were performed using teXsan.[35] Further crystallographic data are given in Table 2. Listings of the selected bond distances and angles are summarized in Table 3. Non-hydrogen atom coordinates, anisotropic thermal parameters, and full listings of bond distances and angles are provided as Supporting Information. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-776348–776351 for **1a**, **1b**, **2a**, and **2b**, respectively. Copies of the data can be obtained free of charge via http://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; e-mail: deposit@ccdc.cam.ac.uk).

Photophysical Measurement. Corrected emission spectra were obtained by using a red-sensitive photodetector (Hamamatsu PMA-11, model C5966-23) and the third-harmonic generation of an Nd:YAG Laser (Continuum Surelite) at 355 nm excitation. The instrumental responses of the system were corrected by using a software package for the detector. Lifetime measurements were conducted by using a streak camera (Hamamatsu C4334) as a detector. Emission quantum yields were estimated by using an acetonitrile solution of $[Ru(bpy)_3](PF_6)_2$ ($\Phi_{em} = 0.061$) as a standard.[36] Sample solutions were deaerated thoroughly by purging with an Ar gas stream for 15 min prior to the experiments and then sealed in their cells. Emission quantum yields in the solid state were determined by using a Hamamatsu Photonic Absolute PL Quantum Yield Measurement System C9920-02.

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Supporting Information

Additional characterization data (^{1}H NMR spectrum of a mixture of **1b** and **2b**, perspective drawing of the complex cation of **2a** and **2b**, absorption spectrum of $[Pt(bpym)(Me_2pzH)_2](PF_6)_2$, and emission decay curves of **1a** and **1b**). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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