Electronic Supplementary Information

Syntheses, Characterization, and Photochemical Properties of Amidate-Bridged Pt(bpy) Dimers Tethered to Ru(bpy)₃²⁺ Derivatives

Masanari Hirahara,^a Shigeyuki Masaoka,^{a,b} and Ken Sakai^{*a}

^aDepartment of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan. ^bPRESTO, Japan Science and Technology Agency (JST), Honcho 4-1-8, Kawaguchi, Saitama, ¹⁰ 332-0012, Japan.

E-mail: ksakai@chem.kyushu-univ.jp

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Materials used in experiments reported in Electronic Supplementary Information

²⁰ [Pt₂(bpy)₂(μ-pivalamidato)₂](PF₆)₂. [Pt₂(bpy)₂(μ-pivalamidato)₂](NO₃)₂·5H₂O (Pt₂) (0.05 g) was dissolved in 5 mL of water with heat followed by filtration for the removal of Pt₂. To the filtrate was added an aqueous saturated KPF₆ solution (0.5 g). The reddish-orange powder deposited in a quantitative yield was filtered, washed with a small amount of water, air-dried by suction, and dried in vacuo (this compound is insoluble in water). Anal. Calcd. for Pt₂P₂F₁₂O₂N₆C₃₀H₃₆: C, 30.21; H, 3.04; N, 7.05. Found: C, 30.07; H, 3.04; N, 6.98.



5 Figure S1.

(a) ¹H NMR spectrum (JEOL JNM-ESA, 600.13 MHz) of HT-[Pt₂(bpy)₂(μ -pivalamidato)₂]-(NO₃)₂·5H₂O (**Pt₂**) in CD₃CN in air at room temperature (data acquisition started at 5 min after the time of dissolution), showing the presence of the head-to-head (HH) and head-to-tail (HT) isomers in solution, which is evident from the non-integral intensity ratios of several sets of doublets in the lowest field region (marked with lines and integrated intensity ratios). These doublets correspond to the protons at the 6,6'-positoins of the bipyridyl ligands bound to the equatorial positions of the diplatinum(II) entity (see below). As depicted in the following illustration, the HH and HT isomers respectively have a mirror and a two-fold axis passing through the center of the molecule. Therefore,

Figure S1 (continued).

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each isomer has two independent pyridyl rings. In other words, there are two magnetically nonequivalent pyridyl rings in each isomer. Thus, four doublets are expected to be observed if the two isomers co-exist in solution. The spectral pattern remained unchanged over days, revealing that the ⁵ HH-HT isomerization equilibrium is established right after dissolution of the complex.

(b) ¹H NMR spectrum (JEOL JNM-ECS400, 399.78 MHz, in CD₃CN) of $[Pt_2(bpy)_2(\mu-pivalamidato)_2](PF_6)_2$, prepared as described above to gain improved solubility of the compound in acetonitrile to measure the ¹⁹⁵Pt NMR of the complex. The measurement was carried out for a nearly saturated solution of the complex in CD₃CN in air at room temperature. The fundamental features well resemble to those in Figure S1a but the N-H protons of pivalamidate bridges show a split into two geometries, suggesting that there are slight shifts in the chemical shifts between the two different salts presumably due to the presence of ion-pair adducts in solution. The solution was used in the following ¹⁹⁵Pt NMR measurement.



(c) ¹⁹⁵Pt NMR spectrum (JEOL JNM-ECS400, 85.94 MHz, single pulse, non-decoupled) of $[Pt_2(bpy)_2(\mu-pivalamidato)_2](PF_6)_2$ in CD₃CN. The central singlet (-2027 ppm) is assignable to the ²⁰ signal arising from the HT isomer, which possesses two magnetically equivalent Pt nucleuses (the N₃O-coordinated Pt atoms). The observed value is also consistent with the value reported for the HT isomer in D₂O (-2064 ppm; ref. 15f). The two singlets on both sides of the central singlet are assigned to the N₂O₂-coordinated Pt atom (-1647 ppm) and the N₄-coordinated Pt atom (-2401 ppm), where the

Figure S1 (continued).

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former is more deshielded due to the ligation of the oxygen atoms which have higher electronegativity in comparison with the nitrogen atoms. The integrated intensity ratio of the peaks reveal that the relative abundances of the HT and HH isomers are 65.7% and 34.3%, respectively, supposing that the signal sensitivities of them are equal. These ratios are consistent with the ratio observed above in the ¹H NMR spectrum under the same condition (see Figure S1b), allowing us to give assignment of two doublets for each isomer, as depicted in Figures S1b.

Apart from the symmetrically bridged dimers, like Pt₂, all the four pyridyl ligands within each diplatinum(II) entity become magnetically non-equivalent in the **RuBn-Pt**₂ complexes, which are asymmetrically bridged by two different bridging amidate ligands. Therefore, eight independent pyridyl protons on the 6-position of pyridyl moieties are expected to be observed, as will be seen for **RuB1-Pt**₂ and **RuB2-Pt**₂ (Figures S2 and S4). On the other hand, the presence of two isomers can also be confirmed by the broad singlets at around 6-7 ppm, which correspond to the signals for the amidate N-H protons for the two isomers. These results are consistent with the discussion made in this paper.





Figure S2. ¹H NMR Spectrum (600.13 MHz) of **RuB1-Pt**₂ (CD₃CN; TMS as a standard). Integrated intensity ratios are depicted for several sets of doublets corresponding to the protons at the 6-position of pyridyl rings, showing the presence of the HH and HT isomers in solution, even though the s assignment of the peaks are not successful at the moment. However, the non-integral intensity ratios support the presence of two isomers.



Figure S3. ¹H NMR Spectrum (600.13 MHz) of (**RuB1**)₂-**Pt**₂ (CD₃CN; TMS as a standard). Integrated intensity ratios are depicted for several sets of doublets corresponding to the protons at the 6-position of pyridyl rings, showing the presence of the HH and HT isomers in solution, even though the ⁵ assignment of the peaks are not successful at the moment. However, the non-integral intensity ratios support the presence of two isomers.





Figure S4. ¹H NMR Spectrum (600.13 MHz) of **RuB2-Pt₂** (CD₃CN; TMS as a standard). Integrated intensity ratios are depicted for several sets of doublets corresponding to the protons at the 6-position ⁵ of pyridyl rings, showing the presence of the HH and HT isomers in solution, even though the assignment of the peaks are not successful at the moment. However, the non-integral intensity ratios support the presence of two isomers.

solvent : CD₃CN







Figure S6. Transient absorption traces probed for **RuB1**H at (a) 360 nm, (b) 450 nm, and (c) 540 nm. The red line corresponds to a calculated line based on a least-squares fit to a single exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S7. Transient absorption traces probed for $\mathbf{RuB1-Pt}_2$ at (a) 360 nm, (b) 450 nm, and (c) 540 nm. The red line corresponds to a calculated line based on a least-squares fit to a double exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S8. Transient absorption traces probed for $(\mathbf{RuB1})_2$ -Pt₂ at (a) 360 nm, (b) 450 nm, and (c) 540 nm. The red line corresponds to a calculated line based on a least-squares fit to a double exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S9. Transient absorption traces probed for **RuB2**H at (a) 380 nm, (b) 480 nm, and (c) 550 nm. The red line corresponds to a calculated line based on a least-squares fit to a single exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S10. Transient absorption traces probed for $\mathbf{RuB2-Pt}_2$ at (a) 380 nm, (b) 480 nm, and (c) 550 nm. The red line corresponds to a calculated line based on a least-squares fit to a double exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S11. Transient absorption traces probed for $(\mathbf{RuB2})_2$ -Pt₂ at (a) 380 nm, (b) 480 nm, and (c) 550 nm. The red line corresponds to a calculated line based on a least-squares fit to a double exponential function. The measurement was carried out under Ar atmosphere at room temperature. The fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source.



Figure S12. Top: ESI-TOF mass spectrum of [**RuB1-Pt**₂](PF₆)₄·H₂O in acetonitrile. Bottom: Comparison of isotopic distribution pattern between the observed and calculated peaks at 372.49 (372.57, $[M - 4PF_6 - H_2O]^{4+}$), 544.98 (545.08, $[M - 3PF_6 - H_2O]^{3+}$), and 889.99 (890.11, $[M - 2PF_6 - H_2O]^{2+}$) m/z.



Figure S13. Top: ESI-TOF mass spectrum of $[(RuB1)_2-Pt_2](PF_6)_6\cdot 8H_2O$ in acetonitrile. Bottom: ⁵ Comparison of isotopic distribution pattern between the observed and calculated peaks at 346.29 $(346.39, [RuB1-Pt(bpy)]^{3+})$ and 536.92 $(537.09, [(RuB1-Pt(bpy)) + OH^- + H_2O]^{3+})$ m/z.

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Figure S14. Top: ESI-TOF MS spectrum of [**RuB2-Pt**₂](PF₆)₄·2H₂O in acetonitrile. Bottom: Comparison of isotopic distribution pattern between the observed and calculated peaks at 384.64 $(384.73, [RuB2-Pt(bpy)]^{3+}), 401.25 (401.33, [M - 4PF_6 - 2H_2O]^{4+}), 583.29 (583.43, [M - 3PF_6 - 2H_2O]^{3+}), and 947.41 (947.61, [M - 2PF_6 - 2H_2O]^{2+}) m/z.$

Figure S14 (continued).





Figure S15. Top: ESI-TOF mass spectrum of $[(\mathbf{RuB2})_2 - \mathbf{Pt}_2](\mathbf{PF}_6)_6 \cdot \mathbf{6H}_2\mathbf{O}$ in acetonitrile. Bottom: ⁵ Comparison of isotopic distribution pattern between the observed and calculated peaks at 384.58 (384.73, $[M - 6PF_6 - 6H_2O]^{6+}$, overlapped with $[\mathbf{RuB2}-\mathbf{Pt}(\mathbf{bpy})]^{3+}$), 490.48 ($[M - 5PF_6 - 6H_2O]^{5+}$), 649.37 (649.58, $[M - 4PF_6 - 6H_2O]^{4+}$, overlapped with $[(\mathbf{RuB2}-\mathbf{Pt}(\mathbf{bpy})) + \mathbf{PF}_6]^{2+}$), and 914.11 (914.43, $[M - 3PF_6 - 6H_2O]^{3+}$) m/z.

Figure S15 (continued).





650 m/z

655

. 645





Figure S16. Absorption spectra in acetonitrile, in air, at 25°C of (a) $[Ru(bpy)_3](PF_6)_2 \cdot 2H_2O(-)$, $[RuB1H](PF_6)_2 (--)$, and $[RuB2H](PF_6)_2 (--)$.



Figure S17. Corrected emission spectra at room temperature of (a) a powder sample of $[Pt_2(bpy)_2(\mu-10) pivalamidato)_2](PF_6)_2$ spread over BaSO₄ (excitation at 440 nm) and (b) a solution of $[Pt_2(bpy)_2(\mu-pivalamidato)_2](PF_6)_2$ in acetone (0.18 mM) in air (excitation at 400 nm). No emission was observed for either the solid sample or an aqueous solution of $[Pt_2(bpy)_2(\mu-pivalamidato)_2](NO_3)_2 \cdot 5H_2O$ (**Pt**₂) at room temperature.



Figure S18. Emission spectra (uncorrected) of $[Pt_2(bpy)_2(\mu-pivalamidato)_2](NO_3)_2 \cdot 5H_2O$ in ³ acetonitrile at 25°C under degassed condition (excitation at 455 nm).



Figure S19. Emission decays in acetonitrile at 77 K (glass state). (A) **RuB1**H (black), **RuB1-Pt**₂ (blue), and (**RuB1**)₂-**Pt**₂ (red). (B) **RuB2**H (black), **RuB2-Pt**₂ (blue), and (**RuB2**)₂-**Pt**₂ (red). The excitation source was always an N₂ laser (337.1 nm). All the profiles were well fitted to a single exponential function.



Figure S20. Dependence of the observed emission lifetimes (τ_1 and τ_2) on the **RuB1-Pt**₂ concentration ⁵ in acetonitrile at 20 °C under degassed condition. For closed triangles (τ_1) and circles (τ_2), the sample solutions were excited at 337.1 nm and the emission at 610 nm was followed using a digitizing oscilloscope equipped with a photomultiplier tube (see Experimental Section). For an open triangle (τ_1) and an open circle (τ_2), the emission decay was monitored using a Unisoku TSP-1000M-03R nanosecond laser flash photolysis system (see Experimental Section), where the excitation source was ¹⁰ the fourth harmonic of Nd:YAG at 266 nm.



Figure S21. Photochemical H₂ production from an acetate buffer solution (0.03 M CH₃COOH and $_{5}$ 0.07 M CH₃COONa; pH = 5.0) containing 0.04 mM [Ru(bpy)₃](NO₃)₂·3H₂O, 2 mM MV(NO₃)₂, and 30 mM EDTA (disodium salt) in the presence of (a) 0.05 mM [Pt₂(NH₃)₄(μ -CH₃CONH)₂]²⁺ (see experimental section for detail) and (b) 0.05 mM [Pt₂](NO₃)₂·3H₂O Each photolysis solution was deaerated with Ar for more than 30 min and was irradiated by 350 W Xe lamp at 20°C, during which Ar was continuously passed through the solution (10 mL/min) and the vent gas was analyzed by gas ¹⁰ chromatography in an automated system.



Figure S22. Photochemical H₂ production from an acetate buffer solution (0.03 M CH₃COOH and 0.07 M CH₃COONa; pH = 5.0) containing 30 mM EDTA in the presence of (a) 0.1 mM **RuB1-Pt**₂, (b) $_{5}$ 0.1 mM **RuB1-Pt**₂ and 2 mM MV(NO₃)₂, (c) 0.1 mM **RuB1-Pt**₂, 2mM MV(NO₃)₂ and 0.04 mM [Ru(bpy)₃](NO₃)₂·3H₂O, and (d) 0.1 mM **RuB1-Pt**₂, 2mM MV(NO₃)₂ and 0.1 mM **Pt**₂. Each photolysis solution was deaerated with Ar for more than 30 min and was irradiated by 350 W Xe lamp at 20°C, during which Ar was continuously passed through the solution (10 mL/min) and the vent gas was analyzed by gas chromatography in an automated system.



Figure S23. Emission decay of Pt_2 in acetonitrile at 77 K (glass state), where the solution was excited s at 337.1 nm. The observed data could be fitted to a double exponential function.



⁵ Figure S24. Emission decay in acetonitrile, degassed, at 25 °C. (A) RuB1 H (black), RuB1-Pt₂ (blue), and (RuB1)₂-Pt₂ (red). (B) RuB2H (black), RuB2-Pt₂ (blue), and (RuB2)₂-Pt₂ (red), where the solution was excited at 337.1 nm.



Figure S25. Cyclic voltammograms (solid lines) and differential pulse voltammograms (dotted lines) of (a) **RuB1**H, (b) **RuB1-Pt**₂, (c) (**RuB1**)₂-**Pt**₂, (d) **Pt**₂, (e) **RuB2**H, (f) **RuB2-Pt**₂ and (g) (**RuB2**)₂-**Pt**₂ (1 mM each) in an acetonitrile solution containing 0.1 M TBAP at room temperature under Ar atmosphere. The cyclic voltammograms were recorded at a scan rate of 50 mV/s. Differential pulse voltammograms were acquired under the following conditions: pulse width = 40.0 ms, sampling time = 35.0 ms, cycle period = 200 ms, pulse height = 50 mV.