This article is published as part of the Dalton Transactions themed issue entitled:

Contributions of Inorganic Chemistry to Energy Research

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Published in issue 15, 2011 of *Dalton Transactions*



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Cite this: Dalton Trans., 2011, 40, 3967

PAPER

Syntheses, characterization, and photochemical properties of amidate-bridged Pt(bpy) dimers tethered to $Ru(bpy)_3^{2+}$ derivatives[†]

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Received 7th November 2010, Accepted 25th February 2011 DOI: 10.1039/c0dt01548b

Amidate-bridged diplatinum(II) entities $[Pt_2(bpy)_2(\mu-amidato)_2]^{2+}$ (amidate = pivalamidate and/or benzamidate; bpy = 2,2'-bipyridine) were covalently linked to one or two $Ru(bpy)_{3}^{2+}$ -type derivatives. An amide group was introduced at the periphery of $Ru(bpy)_3^{2+}$ derivatives to give metalloamide precursors $[Ru(bpy)_2(BnH)]^{2+}$ (abbreviated as RuBnH, n = 1 and 2), where deprotonation of amide BnH affords the corresponding amidate **Bn**, B1H = 4-(4-carbamoylphenyl)-2,2'-bipyridine, and B2H = ethyl4'-[N-(4-carbamovlphenyl)carbamovl]-2.2'-bipyridine-4-carboxylate. From a 1:1:1 reaction of $[Pt_2(bpy)_2(\mu-OH)_2](NO_3)_2$, **RuBnH**, and pivalamide, trinuclear complexes $[Pt_2(bpy)_2(\mu-RuBn)(\mu-pivalamidato)]^{4+}$ (abbreviated as **RuBn-Pt₂**) were isolated and characterized. Tetranuclear complexes $[Pt_2(bpy)_2(\mu-RuBn)_2]^{6+}$ (abbreviated as (**RuBn**),-**Pt**₂) were separately prepared and characterized in detail. The quenching of the triplet excited state of the $Ru(bpy)_{3^{2+}}^{2+}$ derivative (*i.e.*, $Ru^{*}(bpy)_{3}^{2+})$ upon tethering the $Pt_{2}(bpy)_{2}(\mu$ -amidato)₂²⁺ moiety is strongly enhanced in **RuB1-Pt_2** and (RuB1)₂-Pt₂, while it is only slightly enhanced in RuB2-Pt₂ and (RuB2)₂-Pt₂. These are partly explained by the driving forces for the electron transfer from the Ru*(bpy)₃²⁺ moiety to the $Pt_2(bpy)_2(\mu-amidato)_2^{2+}$ moiety (ΔG°_{ET}); the ΔG°_{ET} values for RuB1-Pt₂, (RuB1)₂-Pt₂, RuB2-Pt₂, and (RuB2)₂-Pt₂ are estimated as -0.01, 0.00, +0.22, and +0.28 eV, respectively. The considerable difference in the photochemical properties of the B1- and B2-bridged systems were further examined based on the emission decay and transient absorption measurements, which gave results consistent with the above conclusions

Introduction

Visible light-induced water splitting into molecular oxygen and hydrogen has been considered as one of the most attractive solar energy conversion processes.^{1,2} In this context, tris(2,2'bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) has attracted considerable attention for many years due to its capability of driving both photoinduced water oxidation and reduction processes.³ Scheme 1 depicts one of the most widely studied half-cell systems for hydrogen evolution reaction (HER), where methylviologen (N,N'-dimethyl-4,4'-bipyridinium, abbreviated as MV²⁺) is used as an electron relay and EDTA (ethylenediaminetetraacetic acid disodium salt) is adopted as a sacrificial electron donor.⁴

As catalysts for HER, colloidal platinum,^{4,5a} Co- and Rh-based molecular systems,⁵ and hydrogenase⁶ were reported to be active. We later found that amidate-bridged *cis*-diammineplatinum(II)



Scheme 1 Three-component system consisting of $Ru(bpy)_{3}^{2+}$, MV^{2+} , and an H_2 -evolving catalyst.

dimers $[Pt(II)_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = acetamidate, 2fluoroacetamidate, α -pyrrolidinonate, α -pyridonate, *etc.*)^{7a-c} are also highly active as catalysts for HER. During our on-going studies on the catalytic activities of various mononuclear and dinuclear platinum(II) complexes,⁷ the major concern has been focused on the catalytic enhancement arising from the filled-filled interaction between the Pt(II) d_{z^2} orbitals within the dimeric units. Our recent study further demonstrated that the formation of a hydridodiplatinum(II,III) intermediate, stabilized with a metalmetal bond, plays a crucial role in the catalytic enhancement.8 On the other hand, attempts have also been made by us⁹ and others¹⁰ to develop hybrid molecules driving both photoinduced charge separation and catalytic reduction of water into molecular hydrogen. The first active model of such a 'photo-hydrogenevolving (abbreviated as PHE) molecular device', developed in our group, is depicted below (RuPt in Scheme 2).9

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[†] Electronic supplementary information (ESI) available: ¹H NMR spectra, transient absorption spectra, ESI-TOF mass spectra, and additional absorption spectral data. See DOI: 10.1039/c0dt01548b



Scheme 2 Photo-hydrogen-evolving molecular device.

Importantly, the HER driven by such hybrid systems has also been shown to proceed *via* the formation of a diplatinum intermediate.^{9a,e,h}

An important new approach would be to replace the catalyst core with the more highly active one to improve the PHE activity. Since the amidate-bridged diplatinum(II) cores have been proven to exhibit higher H₂-evolving activity in comparison with the PtCl₂(bpy) unit in **RuPt** (Scheme 2), the diplatinum(II) systems tethered to $Ru(bpy)_{3}^{2+}$ derivatives have been considered to exhibit higher PHE activity. In this context, a tetranuclear complex **Ru**₂Pt₂ (Scheme 3) was previously prepared by reacting the original **RuPt** system with pivalamidate ligand. Nevertheless, **Ru**₂Pt₂ was found to exhibit no PHE activity at all.^{74,9e} Moreover, the **Ru**₂Pt system depicted in Scheme 3 was also found to show no PHE activity.^{74,9e} Consequently, we postulated that deactivation of the ³MLCT excited state is greatly enhanced through the energy transfer (ENT) or electron transfer (ET) among the closely located $Ru(bpy)_{3}^{2+}$ moieties in these systems.





Scheme 3 Diruthenium models exhibiting no PHE activity.^{7d,9c}

In the above context, our prediction has been to realize improved PHE activity in a trinuclear $RuPt_2$ system in which the amidate-bridged type of diplatinum(II) core is tethered to a

single $Ru(bpy)_3^{2+}$ derivative. In this work, two bridging spacer ligands B1 and B2 have been prepared to develop such RuPt₂ systems, *i.e.*, RuB1-Pt₂ and RuB2-Pt₂ (illustrated below). Each trinuclear compound was prepared through a one-pot reaction of $[Pt_2(bpy)_2(\mu-OH)_2]^{2+}$, $[Ru(bpy)_2(BnH)]^{2+}$ (abbreviated as RuBnH) (n = 1 and 2), and pivalamide followed by separation of the trinuclear product RuBn-Pt₂ from three possible diplatinum products (*i.e.*, Pt₂, RuBn-Pt₂, and (RuBn)₂-Pt₂). The tetranuclear derivative of each ligand system (*i.e.*, (RuBn)₂-Pt₂) was separately prepared from a reaction of $[Pt_2(bpy)_2(\mu-OH)_2]^{2+}$ and **RuBnH**. Although all of these compounds have been found to exhibit no PHE activity, we have succeeded in establishing a facile synthetic strategy applicable to the development of such asymmetric and symmetric supramolecular architectures. More importantly, through examining the photochemical and electrochemical properties of these compounds, some important concepts have been established with regard to the design strategies to the more efficient PHE molecular devices.

Results and discussion

Syntheses

Hybrid systems **RuBn-Pt**₂ and (**RuBn**)₂-**Pt**₂ (n = 1 and 2) were prepared according to the synthetic scheme illustrated in Scheme 4. In the synthesis of RuBn-Pt₂, an aqueous solution containing [Pt₂(bpy)₂(µ-OH)₂](NO₃)₂, RuBnH, and pivalamide in a 1:1:1 ratio was reacted at 70 °C to yield three types of diplatinum(II) complexes (Scheme 4, route I). If RuBnH and pivalamide are similar in the rate of ligand substitution, the distribution of product (i.e., Pt₂, RuBn-Pt₂, and (RuBn)₂-Pt₂) should be in a 1:2:1 ratio. Indeed, ESI-TOF MS revealed that all these three diplatinum species were involved in the crude product (data not shown). For each ligand system, only the monoruthenium complex $RuBn-Pt_2$ was isolated from the crude product by gel permeation chromatography. On the other hand, each diruthenium complex (RuBn)₂-Pt₂ was separately prepared from a 1:2 reaction of [Pt₂(bpy)₂(µ-OH)₂](NO₃)₂ and **RuBnH** in aqueous media to improve the synthetic yield and the purity (Scheme 4, route II). It must be also noted that the diplatinum(II) complexes of this series have been extensively investigated in our group with the aim of developing new one-dimensional platinum chain complexes,¹¹ which involves the study on a reference compound Pt₂.^{11h}

Absorption spectra

The absorption spectra of **RuBn**, **RuBn-Pt**₂, (**RuBn**)₂-**Pt**₂, and **Pt**₂ in acetonitrile are shown in Fig. 1. The insets show the magnifications of the MLCT bands for the Ru(bpy)₃²⁺ chromophores and the MMLCT (metal-metal-to-ligand charge transfer) band for the Pt₂(bpy)₂(μ -amidato)₂ choromophore.^{11h,12} The maximum absorption wavelengths and the molar absorptivities are summarized in Table 1. For each system, the ligand-based absorption bands corresponding to the $\pi \rightarrow \pi^*$ transitions in the UV region, and the MLCT bands for the Ru(bpy)₃²⁺ chromophore are fundamentally unaffected by linking the Ru(bpy)₃²⁺ and Pt₂(bpy)₂(μ -amidato)₂ moieties. The MLCT band of the **B2**-bridged system is *ca*. 20 nm red-shifted in comparison with that of the **B1**-bridged system (see Table 1), indicating that the lowest π^* orbital of the Ru(bpy)₃²⁺



Scheme 4 Synthetic strategies to the hybrid compounds prepared in this work, exemplified with use of RuB1H.

moiety in the **B2**-bridged system is lower in energy than that in the **B1**-bridged system. This is clearly due to the electron-withdrawing effects of both ethoxycarbonyl and carbamoyl groups attached to the bpy ligand of **B2**. The spectra of **RuBn-Pt**₂ and (**RuBn**)₂-**Pt**₂ are both fundamentally similar to that of the corresponding precursor **RuBnH**. The absorptivity in the visible region of (**RuBn**)₂-**Pt**₂ is roughly twice as large as that of **RuBn-Pt**₂. It must be also noted that both (**RuBn**)₂-**Pt**₂ and **RuBn-Pt**₂ involve a weak component based on the MMLCT transition at the Pt_2 (bpy)₂(µ-amidato)₂ chromophore, as shown by the spectrum of **Pt**₂ in Fig. 1c.

Emission spectra

As recently reported,^{9b-h} platination-induced quenching of the ³MLCT emission is considerably enhanced when the photoin-

duced electron transfer (PET) leading to HER is effectively promoted. In other words, no PHE activity has been exhibited by the RuPt-based system whose ³MLCT emission intensity is rather comparable to that of the non-platinated ruthenium precursor.^{7e} The emission bands of the **B1**- and **B2**-bridged systems are centered at 620 and 675 nm, respectively (Fig. 2a,b; see also Table 1). Note that [**Pt**₂](PF₆)₂ exhibits phosphorescence (*i.e.*, ³MMLCT emission) in the solid state at 720 nm (see Fig. S17†), even though emission from the acetonitrile solution of the complex is extremely weak (see Table 1 and Fig. S18†). Therefore, the Pt₂(bpy)₂(µamidato)₂ core in (**RuBn**)₂-**Pt**₂ and **RuBn**-**Pt**₂ must be considered as potentially emissive. However, due to the extremely low emission quantum yield of **Pt**₂ in acetonitrile (see Table 1), the ³MMLCT emission component must have a negligible contribution to the emission bands for the hybrid systems. The ³MLCT emission

Table 1 Absorption and emission spectral data^a

Complex	Absorption	Emission at	Emission at 77 K					
	$\lambda_{\rm max}/{\rm nm}~(\epsilon/10^4~{\rm M}^{-1}~{\rm cm}^{-1})$	$\overline{\lambda_{\max}/nm}$	Φ	$\Phi_{ m rel}{}^c$	τ/µs		$\overline{\lambda_{\max}/nm}$	τ/µs
RuB1H	455 (1.77)	620	0.178	1	1.63		594	5.50
RuB1-Pt ₂	456 (2.15)	623	0.052	0.29	0.35 (73%)	1.41 (27%)	594	5.12
$(RuB1)_2 - Pt_2$	456 (3.59)	619	0.128	0.62	0.42 (44%)	1.38 (56%)	593	4.93
RuB2H	477 (1.46)	667	0.117	1	1.01	× /	621	5.14
RuB2-Pt ₂	477 (1.82)	669	0.092	0.79	0.90		617	5.24
$(RuB2)_2 - Pt_2$	476 (3.01)	666	0.110^{b}	0.94	1.02		621	4.64
Pt ₂	472 (0.185)	6201	0.004⁄		1.07		626	1.44,
$Ru(bpy)_3^{2+d}$	450	611	0.095		0.89			5.85°
Ru(bpy) ₂ (debpy) ^{2+e}			0.074		1.03			

^{*a*} Measured for the PF_6^- salts in CH₃CN at 25 °C. Absorption spectra were measured in air and emission data were observed under degassed condition. ^{*b*} The luminescence quantum yields of **RuB1**H and **RuB2**H were determined by using the absolute luminescence quantum yield measurement system (see Experimental section). The quantum yields for the platinated systems were determined by the relative method based on the values determined for **RuB1**H and **RuB2**H. ^{*c*} Relative quantum yields, estimated by comparing its quantum yield with that for the parent complex **RuBn**H. ^{*d*} Values taken from ref. 13. ^{*c*} Values taken from ref. 14. ^{*f*} Measured for the nitrate salt of the complex. The quantum yield was estimated by the relative method using Ru(bpy)₃²⁺. ^{*s*} Two decay components were observed at 77 K (see Fig. S23).

bands of the **B2**-bridged systems are red-shifted relative to those of the **B1**-bridged systems, clearly due to the lower lying π^* level of **B2**, as discussed above.

The emission quantum yields are comparable to the related polypyridyl ruthenium complexes; *e.g.*, $\Phi = 0.095^{13b}$ for [Ru(bpy)₃](PF₆)₂, and $\Phi = 0.074^{14}$ for [Ru(bpy)₂(debpy)](PF₆)₂ (debpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine). The emission intensities of **RuB2-Pt₂** and (**RuB2**)₂-**Pt₂** are decreased by only 6– 21% upon platination of the corresponding Ru-only precursor (see th Φ_{rel} values in Table 1), indicating that PET is little enhanced in the **B2**-bridged systems. This also confirms that the intramolecular quenching of the triplet due to ET or ENT among the two Ru(bpy)₃²⁺ moieties is not enhanced in (**RuB2**)₂-**Pt**₂. On the other hand, the emission quenching is relatively large in **RuB1-Pt**₂; the emission intensity is decreased by 71% upon platination of **RuB1H** into **RuB1-Pt**₂ (see Fig. 2a). Similarly, relatively large quenching (38%) is induced upon platination of **RuB1H** into (**RuB1**)₂-**Pt**₂ (see Fig. 2a).

Emission decay

The RuB2-Pt₂ and $(RuB2)_2$ -Pt₂ systems were confirmed to possess an emission lifetime consistent with that of the precursor RuB2H (see Table 1; Fig. S24[†]). On the other hand, the RuB1-Pt₂ and (RuB1)₂-Pt₂ systems, which show considerable quenching in the steady-state emission, both exhibit a double exponential decay profile. The PET in such hybrid systems were reported to be considerably retarded in a frozen medium due to the high reorganization energy required for the ET events, while such an effect is much smaller for the ENT processes.¹⁵ In other words, the activation free energy for an ET process considerably increases in a frozen medium. As summarized in Table 1 (see also Fig. S19[†]), the double exponential features observed for RuB1-Pt₂ and $(RuB1)_2$ -Pt₂ at room temperature are completely lost in the decay profiles for the frozen samples at 77 K. These results strongly support that the considerable quenching of emission for RuB1- Pt_2 and $(RuB1)_2$ - Pt_2 at room temperature clearly arises from the PET events. In addition, it was also confirmed that the lifetimes for both components are essentially insensitive to the complex

concentration, indicating that the PET occurs in a unimolecular (*i.e.*, intramolecular) fashion (Fig. S20†).

For **RuB1-Pt**₂ at room temperature, the long-lived species ($\tau_2 = 1.4 \,\mu$ s; 27%) has a minor contribution to the overall decay process and may not be correlated with any PET events, since the lifetime is quite consistent with that of the non-platinated precursor **RuB1**H ($\tau = 1.63 \,\mu$ s). On the other hand, the short-lived species ($\tau_1 = 0.35 \,\mu$ s; 73%) must be relevant to the PET giving rise to the platination-induced quenching (71% of quenching in Fig. 2a). Similarly, **(RuB1)**₂-**Pt**₂ shows a biexponential feature; $\tau_1 = 0.42 \,\mu$ s (44%) and $\tau_2 = 1.38 \,\mu$ s (56%).

Considerations for the two decay components

For the first active model of a molecular device, *i.e.*, **Ru–Pt** in Scheme 3, the emission decay profile exhibited a triple exponential feature,^{9g} which was in part attributed to the presence of several conformers based on the rotation around the C(carbamoyl)– C(bpy) bond connecting the Ru(bpy)₂(phen-carbamoyl)²⁺ unit and the PtCl₂(bpy) unit.^{9e} However, such a consideration is not applicable to **RuB1-Pt₂** and (**RuB1**)₂-**Pt₂**, since the rotation around either the C(pyridine)-C(benzene) or C(benzene)–C(amidate) bond in **B1** is not likely to give a considerable change in the net distance between the Ru center and the Pt₂(bpy)₂(µ-amidate)₂ core. Nevertheless, the double-exponential features observed for **RuB1-Pt₂** and (**RuB1**)₂-**Pt**₂ indicate that each compound affords two major species exhibiting different excited-state properties in solution.

A possible interpretation may be that the so-called head-tohead (HH) and head-to-tail (HT) isomers exist in solution, and the ET rates in these isomers are different to each other due to the considerable difference in the bridged Pt–Pt distance¹⁶ leading to an effective difference in the electronic coupling between the Ru(bpy)₃²⁺ and bpy(Pt) moieties. As previously reported,¹⁶ some of such diplatinum compounds doubly bridged by amidates are extremely slow in the HH-HT isomerization,^{16b} while others are quite rapid and reaches its equilibrium immediately after dissolution.^{16c} Complex [Pt₂](NO₃)₂·5H₂O was shown to possess the HT isomerism in the crystal (unpublished results) and to show





Fig. 1 Absorptivity spectra in acetonitrile, in air, at 25 °C. (a) $[RuB1H](PF_6)_2$ (—), $[RuB1-Pt_2](PF_6)_4$ (---), and $[(RuB1)_2-Pt_2](PF_6)_6$ (···). (b) $[RuB2H](PF_6)_2$ (—), $[RuB2-Pt_2](PF_6)_4$ (---), and $[(RuB2)_2-Pt_2](PF_6)_6$ (···). (c) $[Pt_2](NO_3)_2$ (—).

a singlet in the ¹⁹⁵Pt NMR at -2064 ppm right after dissolution of the complex in water (D₂O).^{11h} Moreover, the compound undergoes gradual HT \rightarrow HH isomerization in either water (D₂O) or acetone (($(CD_3)_2CO$) over a day, which was confirmed by ¹⁹⁵Pt NMR (unpublished results). However, the compound is now shown to give a mixture of the HH and HT isomers right after dissolution to acetonitrile (CD₃CN), as observed by both ¹H and ¹⁹⁵Pt NMR (see Fig. S1[†]). Based on the ¹H NMR features observed for [Pt₂](NO₃)₂·5H₂O in CD₃CN (Fig. S1[†]), the hybrid compounds prepared in this work are also suggested to give a mixture of the HH and HT isomers in CD₃CN, even though their ¹⁹⁵Pt NMR spectra could not be acquired due to the limitation of samples available for the measurements. In the ¹H NMR spectrum of RuB1- Pt_2 (Fig. S2[†]), two sets of bpy ligands attached to the Pt(II) ions, attributable to the presence of the HH and HT isomers, are clearly observable with the integrated intensity ratio being ca. 37:63 in three domains; 8.70-8.61, 8.51-8.43 and 8.39-8.28 ppm. Similar features are also observed for RuB2-Pt₂ and (RuB1)₂-Pt₂ (Figs.



Fig. 2 (a) Emission spectra of [**RuB1H**](PF₆)₂ (—), [**RuB1-Pt**₂](PF₆)₄ (---), and [(**RuB1**)₂-**Pt**₂](PF₆)₆ (···) in acetonitrile at 25 °C under degassed condition. The excitation wavelength was 455 ± 2.5 nm and the solutions had an equal absorbance (0.1) at 455 nm. (b) Emission spectra of [**RuB2H**](PF₆)₂ (—), [**RuB2-Pt**₂](PF₆)₄ (---), and [(**RuB2**)₂-**Pt**₂](PF₆)₆ (···) in acetonitrile at 25 °C under degassed condition. The excitation wavelength was 475 ± 2.5 nm and the solutions had an equal absorbance (0.1) at 475 nm.

S3 and S4[†]), even though it is rather ambiguous in the ¹H NMR spectrum of (**RuB2**)₂-**Pt**₂ (Fig. S5[†]). Thus, it is obvious that all these diplatinum systems are considered as a mixture of the HH and HT isomers. However, lack of more concrete evidence prevents us from firmly concluding that the two decay components arise from the presence of these two isomers.

As an alternative possibility, an ion-paired species and a nonion-paired species may be different in the ET rate if there is a prominent difference in the conformational feature of the two species, as described elsewhere.¹⁷

Transient absorption spectra

Fig. 3 shows the transient absorption spectra of all the compounds, taken at 25 ns after laser pulse excitation at 266 nm, showing the decay of the triplet (*i.e.*, Ru*(bpy)₃²⁺). The spectral features are fundamentally similar to each other except that the absorption intensities at around 550 nm for the **B1**-bridged systems are considerably higher than those for the **B2**-bridged systems. The **B1**-bridged systems show positive absorptions at 370 and 550 nm and bleaching at 455 and 620 nm. On the other hand, the **B2**-bridged systems show positive absorptions at 385 nm and bleaching at 475 and 620 nm, which is characteristic of Ru(bpy)₃²⁺.¹⁸ The absorption intensities at 550 nm for the **B1**-bridged systems, corresponding to the absorption of bpy⁻⁺, are relatively strong compared with that observed for Ru(bpy)₃²⁺, ^{18b} suggesting that the ³MLCT excited state of **RuB1H** may be described as [Ru(III)(bpy)₂(**B1H**⁻⁺)]²⁺. Very similar descriptions can



Fig. 3 Transient absorption spectra of (a) RuB1H (black), $RuB1-Pt_2$ (blue), and $(RuB1)_2-Pt_2$ (red), and (b) RuB2H (black), $RuB2-Pt_2$ (blue), and $(RuB2)_2-Pt_2$ (red) in acetonitrile at room temperature under Ar atmosphere, where the fourth-harmonic (266 nm) of a Nd:YAG pulsed laser was used as a pump source. All the solutions had an equal absorbance at 266 nm (1.0). Each spectrum was recorded after 25 ns laser pulse excitation.

be applied to the platinated derivatives; **RuB1-Pt**₂ and (**RuB1**)₂-**Pt**₂. The time course of absorbance changes at each band for **RuB1-Pt**₂ and (**RuB1**)₂-**Pt**₂ follows a double-exponential function (see Figs. S7 and S8†), consistent with the observed emission decay profiles (*vide supra*). On the other hand, a monoexponential feature is seen in the time course of absorbance changes for **RuB2-Pt**₂ and (**RuB2**)₂-**Pt**₂ (see Figs. S9 and S10†). As shown in Fig. 3, the degree of quenching of the triplet at the early stage of the decay process is much larger in **RuB1-Pt**₂ compared to that in **RuB1**H. Moreover, the triplet of **RuB1-Pt**₂ decays much faster than that of **RuB1**H (Fig. S24a; see also Figs. S6 and S7†). These are consistent with the results obtained by the steady-state emission spectroscopy together with the emission decay measurements.

Electrochemistry

The electrochemical parameters determined are summarized in Table 2. Complex Pt_2 displays irreversible oxidation at 0.66 V vs. Fc/Fc⁺, assignable to the Pt(II)₂/Pt(III)₂ couple, as previously reported.²⁰ The diplatinum(III) species are, in general, axially ligated at both ends of the unit^{11h,20d} and therefore the irreversible character must be relevant to the relatively slow axial ligation upon oxidation. On the other hand, two reversible reduction peaks appear at -1.34 and -1.52 V, assignable to the reductions at the byy ligands bound to the Pt(II) ions (abbreviated as bpy(Pt)).

The reversible oxidation and reduction at 0.86 and -1.66 V for **RuB1H** are consistent with those reported for **Ru**(bpy)₃²⁺ (see Table 2). Since **RuB1H** and **Ru**(bpy)₃²⁺ show quite similar spectral features at the MLCT band (Fig. S16†), the assignment of the first reduction site of **RuB1H** is not straightforward. However, **B1H** is likely to have a slightly lower π^* level in comparison with the non-substituted bpy because of its more extended aromatic character as well as the electron-withdrawing effect of the peripheral carbamoyl group. On the other hand, the corresponding redox potentials of **RuB2H** (oxidation at 0.96 V and reduction at -1.43 V) are both shifted to the positive potential, reflecting the electron-withdrawing effects of the ethoxycarbonyl and carbamoyl groups at the 4,4'-positions of bpy in **B2**H.

The redox properties of the Ru(bpy)₃²⁺ and Pt₂(bpy)₂(μ -amidato)₂ moieties in the hybrid systems are roughly consistent with those of their individual precursor or reference complexes (see Fig. S25† and Table 2). For **RuB1-Pt₂** and **RuB2-Pt₂**, the first and the second oxidations are attributed to those of the Pt₂(bpy)₂(μ -amidato)₂ and Ru(bpy)₃²⁺ moieties, respectively. As for (**RuB1**)₂-**Pt**₂ and (**RuB2**)₂-**Pt**₂, the oxidations at the Ru and Pt centers are overlapped, showing that the oxidation potentials at the Pt₂(bpy)₂(μ -amidato)₂ moieties are shifted to the positive potential due to the electron-withdrawing effect of the positively charged

 Table 2
 Redox potentials for the B1- and B2-bridged systems, together with the related compounds^a

	$E_{1/2}/\mathrm{V}\left(\Delta E_{\mathrm{p}}^{b}\right)$					
Complex	Oxidation		Reduction	$\Delta G^{0}_{\rm ET}/{\rm eV}$		
RuB1H RuB1-Pt ₂ (RuB1) ₂ -Pt ₂	0.86 (78) 0.69 (irr) ^e 0.83 (77)	0.86 (70)	-1.66 (66) -1.33 (71) -1.38 (79)	-1.87 (70) -1.53 (66) -1.55 (68)	-1.70 (138) -1.72(irr) ^c	-0.01 0.00
RuB2H RuB2-Pt ₂ (RuB2) ₂ -Pt ₂ Pt ₂ Ru(bpy) ₃ ^{2+d}	0.96 (71) 0.84 (irr) ^e 0.95 (78) 0.66 (irr) ^e 0.905 (79)	0.95 (79)	-1.43 (78) -1.34 (irr) ^c -1.38 (irr) ^c -1.34 (67) -1.725 (69)	-1.41 (irr) ^c -1.54 (irr) ^c -1.52 (75) -1.915 (72)	-1.55(irr) ^c	0.22 0.28

^{*a*} Measured for the acetonitrile solutions of the complexes containing 0.1 M TBAP at 25 °C under Ar atmosphere. Potentials are given in volts *vs.* Fc/Fc⁺. ^{*b*} ΔE_p denotes the peak-to-peak separation between the anodic and cathodic waves. ^{*c*} The values are those for the irreversible processes. For such cases, ΔE_p is written as irr. The redox potentials reported for such cases are taken from the peak potentials in each differential pulse voltammogram (see Fig. S25†). ^{*d*} Values taken from ref. 19.

 $Ru(bpy)_{3}^{2+}$ moiety covalently linked to the bridging amidate. Such trends are also seen in the trinuclear systems (see Fig. S25[†]); the Ptbased oxidations are shifted to the positive potential in comparison with that of Pt₂ (see Table 2). Importantly, RuB1-Pt₂ and (RuB1)₂- Pt_2 show the first and the second reductions at the bpy(Pt) units and the third one at those attached to the Ru(II) ion (abbreviated as bpy(Ru)). These indicate that the $\pi^*(bpy(Pt))$ orbital could be used to mediate ET from the $Ru^{*}(bpy)_{3^{2+}}$ moiety prior to the H₂evolving event, as well discussed for the RuPt derivatives.^{7e,9} On the other hand, reductions at **B2** and bpy(Pt) in **RuB2-Pt**₂ and (RuB2)₂-Pt₂ are overlapped. However, since the first reduction of Pt_2 is observed at a much more positive potential compared to that of RuB2H (see Table 2), the first and the second reductions for $RuB2-Pt_2$ and $(RuB2)_2-Pt_2$ are reasonably assigned to those for bpy(Pt) and B2, respectively. In these systems, the third one is assignable to the reduction at bpy(Pt). These suggest that the $\pi^*(bpy(Pt))$ orbital rather than the $\pi^*(B2)$ orbitals becomes the LUMO. Using the observed electrochemical and spectroscopic parameters, the driving force for the intramolecular ET from the $\operatorname{Ru}^{*}(\operatorname{bpy})_{3}^{2+}$ moiety to the bpy(Pt) moiety (ΔG°_{ET}) is estimated based on the Rehm-Weller equation,²¹

$$\Delta G^{0}_{\rm ET} = E_{\rm ox} - E_{\rm red} - E_{\rm T} - e^2 / \varepsilon d \tag{1}$$

where E_{ox} is the first oxidation potential of the Ru center, E_{red} is the reduction potential of the bpy(Pt) moiety, E_T is the energy of the ³MLCT excited state, ε is the dielectric constant of acetonitrile, and d is the distance between the donor and the acceptor. Since the ε values are high for polar solvents like acetonitrile, the last term is negligible. In addition, E_T is estimated from a tangent to the highenergy side of the corresponding emission spectrum (see Table 1.).²² As a result, the ΔG°_{ET} values for **RuB1-Pt₂**, **(RuB1)₂-Pt₂**, **RuB2-Pt₂**, and **(RuB2)₂-Pt₂** are estimated as -0.01, 0.00, +0.22, and +0.28 eV, respectively. These clearly indicate that the PET processes in **RuB2-Pt₂** and **(RuB2)₂-Pt₂** are much less favorable in comparison with those in **RuB1-Pt₂** and **(RuB1)₂-Pt₂**, consistent with the results obtained by the emission and transient absorption spectroscopy (*vide supra*).

Based on the results described so far, the observed photochemical events for the hybrid systems can be illustrated by the energy diagrams in Scheme 5. The ET from the $Ru^*(bpy)_3^{2+}$ moiety (*i.e.*, donor) to the $Pt_2(bpy)_2(\mu$ -amidato)_2²⁺ moiety (*i.e.*, acceptor) is an uphill process in the **B2**-bridged systems, while it is neither an uphill nor a downhill process in the **B1**-bridged systems. This can be correlated with the higher emission energies observed for the **B1**-bridged systems (*vide supra*) as well as the more negative first reduction potentials at the bpy moieties bound to the Ru(II) ion in the **B1**-bridged systems (*vide supra*). Thus, it seems probable that the prominent difference in the ET rate between the two *geometrically different* species (*e.g.*, the HH and HT isomers) only appears in the case of **RuB1-Pt**_2 and (**RuB1**)₂-**Pt**_2 due to the shorter distance between the donor and the acceptor and also due to the larger driving forces for the ET.

Photochemical hydrogen production

As mentioned above, none of these new hybrids evolves H_2 in the presence of EDTA at pH = 5 under visible light illumination. It must be also noted that the H_2 -evolving activity of $[Pt_2(bpy)_2(\mu-(CH_3)_3CCONH)_2]^{2+}$ (Pt_2) is fundamentally lower than that of $[Pt_2(NH_3)_4(\mu-CH_3CONH)_2]^{2+}$ (compare the $\Phi(H_2)$ values in Table 3; see also Fig. S21b†).

As recently demonstrated by $us_{7^{e,9^{f}}}$ if the $Ru(bpy)_{3^{2^{+}}}$ moiety incorporated in the hybrid preserves activity as a photosensitizer, oxidative quenching of the Ru*(bpy)₃²⁺ moiety will be promoted by addition of MV²⁺ to give MV⁺⁺. A simple dark reaction of an active Pt(II)-based catalyst and MV+* must then result in catalytic H₂ evolution from water at this pH, as recently communicated.7g If the Ru*(bpy)32+ moiety in a hybrid is efficiently quenched even in the absence of MV2+, addition of both [Ru(bpy)₃]²⁺ and MV²⁺ is required to generate MV⁺⁺. These methods were adopted to evaluate the functionality of each component incorporated in these hybrids. As a result, only a trace amount of H₂ was detected for all the hybrids even in the presence of MV2+, in spite of the development of a dark blue chromophore of MV⁺ during the photolysis. These clearly indicate that the $Pt_2(bpy)_2(\mu-amidato)_2^{2+}$ cores incorporated in these hybrids are not active as catalysts for HER. Moreover, no H₂ evolves from the EDTA/Ru(bpy)₃²⁺/MV²⁺/RuB1-Pt₂ system (see Table 3), reconfirming the ineffectiveness of $RuB1-Pt_2$ as



Scheme 5 Energy level diagrams of the photochemical events for RuB1-Pt2, (RuB1)2-Pt2, RuB2-Pt2, and (RuB2)2-Pt2.

 Table 3 PHE activities of hybrid systems and standard catalysts under various conditions^a

Photosystem (concentration of $(RuBn)_m$ -Pt ₂ in mM) ($m = 1$ or 2)	$\begin{array}{l} Ru(bpy)_{3}{}^{2+}\\ (mM) \end{array}$	MV ²⁺ (mM)	Pt ₂ Catalyst ^b (mM)	Photolysis Time (h)	H_2 evolved (μ L)	TON	Initial Rate of $H_2 (\mu L h^{-1})$	$\Phi(\mathrm{H}_2)^d$
$EDTA/Ru(bpy)_{3^{2+}}/MV^{2+}/Pt_{2}$	0.04	2.0	0.05 ^b	6	215	9.3	140	0.037
$EDTA/Ru(bpy)_{3}^{2+}/MV^{2+}/Pt_{2}-STD$	0.04	2.0	0.05 ^c	3.5	1982	85.8	1180	0.31 ^e
$EDTA/RuB1-Pt_2(0.1)$				4				_
$EDTA/RuB1-Pt_2/MV^{2+}$ (0.1)		2.0		4	<1.0	< 0.1		_
$EDTA/RuB1-Pt_2/Ru(bpy)_3^{2+}/MV^{2+}(0.1)$	0.04	2.0		3.5	<1.0	< 0.1		_
$EDTA/RuB1-Pt_2/MV^{2+}/Pt_2$ (0.1)	_	2.0	0.05^{b}	3.5	184	7.96	61	0.016
$EDTA/(RuB1)_2 - Pt_2(0.1)$	_		_	3	_		_	_
$EDTA/(RuB1)_2 - Pt_2/MV^{2+}$ (0.1)	_	2.0	_	3.5	_		_	_
$EDTA/RuB2-Pt_2(0.1)$	_		_	3	_		_	_
$EDTA/RuB2-Pt_2/MV^{2+}(0.1)$	_	2.0	_	3.5	_		_	_
$EDTA/(RuB2)_2-Pt_2(0.1)$				3				_
$EDTA/(RuB2)_2-Pt_2/MV^{2+}(0.1)$	_	2.0	_	3.5		_	_	_

^{*a*} All the measurements were carried out using an aqueous acetate buffer solution containing 30 mM EDTA (disodium salt) at pH = 5.0 (0.03 M CH₃COOH and 0.07 M CH₃COONa) under Ar atmosphere at 20 °C, in the presence of additional components listed in this table, where [Ru(bpy)₃](NO₃)₂·3H₂O and MV(NO₃)₂ were used as Ru(bpy)₃²⁺ and MV²⁺, respectively. ^{*b*} [Pt₂](NO₃)₂·5H₂O. ^{*c*} Pt₂-STD denotes [Pt₂(NH₃)₄(μ -CH₃CONH)₂]²⁺ (see Experimental section for details). ^{*d*} The quantum efficiency for the H₂ formation is estimated based on the relative method by comparing the initial slope of H₂ formation for the each solution with that for the [Pt₂(NH₃)₄(μ -CH₃CONH)₂]²⁺ (1180 µL h⁻¹ per 10 mL solution). ^{*e*} Taken from the literature.^{7e}

an H₂-evolving catalyst. In addition, H₂ does evolve from the EDTA/RuB1-Pt₂/MV²⁺/Pt₂ system (Table 3; Fig. S22d†). Thus, RuB1-Pt₂ preserves activity as a photosensitizer but does not possess catalytic activity for HER.

As reported so far,⁹ such hybrid systems can be classified into four categories as follows. For those possessing a catalytically active Pt(II) center, (i) H_2 may evolve if the PET is efficiently promoted, (ii) the amount of H_2 evolved may be greatly diminished if the PET becomes much less favorable, and (iii) no H_2 evolves if no PET takes place. As for those whose Pt(II) centers are inactive towards HER, (iv) no H_2 evolves regardless of the PET efficiency. In this context, all the four hybrids prepared in this work belong to group (iv), even though there is a marked difference in the PET efficiency between the **B1**- and **B2**-bridged systems.

Conclusions

In the present study, we have succeeded in the syntheses and characterization of four new RuPt₂ and Ru₂Pt₂ complexes whose H₂-evolving sites are made up of a $Pt_2(bpy)_2(\mu-amidato)_2$ core. All the compounds have been shown to preserve photosensitizing ability at the Ru(bpy)₃²⁺ moieties but exhibit no PHE activity due to the loss of H₂-evolving activity at the diplatinum cores. At the moment, we assume that the ineffectiveness at these diplatinum cores may be caused by the electron-withdrawing effect of the positively charged Ru(bpy)₃²⁺ tethers, giving rise to the electron poor character at the Pt(II) centers and to the elongation of the bridged Pt(II) ··· Pt(II) distance, as previously observed for the analogous dimers tethered to viologen or pyridinium moieties.²³ These must be viewed as related to our previous indications that the catalytic activity is enhanced by (i) the destabilization of the HOMO corresponding to the filled d_{z^2} orbital and also by (ii) the shortening in the bridged Pt(II) ··· Pt(II) distance.^{7d} Moreover, these are also relevant to the fact that the H₂-evolving activity of $[Pt_2(bpy)_2(\mu-(CH_3)_3CCONH)_2]^{2+}$ is an order of magnitude lower than that of $[Pt_2(NH_3)_4(\mu-CH_3CONH)_2]^{2+}$ (see Table 3), since the oxidation potential, corresponding to the $Pt(II)_2/Pt(III)_2$ couple, for the former (0.66 V vs. Fc/Fc⁺, regarded as 1.13 V vs. SCE)

is much higher than that of the latter (0.42 V vs. SCE^{7c,11b}). On the other hand, the PET is more or less enhanced in **RuB1-Pt**₂ and (**RuB1**)₂-**Pt**₂ due to the higher driving force for the PET as well as the closer location of the donor and the acceptor. These provide somewhat reasonable directions for developing and testing new model systems applicable to the PHE cycle. An important new approach would be to develop and examine the compounds having a [Pt₂(NH₃)₄(μ -amidato)₂]²⁺ moiety as an H₂-evolving site, even though some electron reservoirs accepting the electron transferred from the Ru*(bpy)₃²⁺ moiety must be introduced as additional tethers. Further studies are still in progress in our laboratory.

Experimental section

Materials

2,2'-bipyridyl-4-boronic acid. This compound was prepared by the '*in situ* quench' protocol, as previously described.²⁸ To a Schlenk-type flask (200 mL) equipped with a rubber septum was added 4-bromo-2,2'-bipyridine (2.14 g, 9.1 mmol). The flask was purged with Ar followed by charging with THF (40 mL) and triisopropyl borate (3.2 mL, 13.9 mmol). The mixture was cooled to -78 °C using a liquid N₂/acetone bath. *n*-Buthyllithium (1.6 M in hexane, 6.5 mL; 10.4 mmol) was added using a syringe over 25 min followed by stirring it for an additional 30 min. The liquid N₂/acetone bath was removed and then the reaction mixture was allowed to warm to -20 °C followed by addition of 1 N HCl solution (27 mL). After raising the temperature to room temperature, the mixture was washed with ethyl acetate by extraction (50 mL × 3). The aqueous layer was collected and its pH was adjusted to 7 using an aqueous 1 N NaOH solution. The colorless solid deposited was collected by filtration, washed with acetonitrile (*ca.* 10 mL × 2), and dried *in vacuo* to yield the product as a colorless solid (Yield: 65%, 1.18 g). Anal. calcd. for, $C_{10}H_9N_2O_2B$: C, 60.05; H, 4.54; N, 14.01. Found: C, 59.94; H, 4.55; N, 14.01. ¹H NMR (300.50 MHz, CD₃OD) δ ppm 8.81 (m, J = 4.8 Hz, 1H, H-6), 8.64 (s, 1H, H-3), 8.54 (d, 1H, H-6', J = 5.5 Hz), 8.33 (dt, 1H, H-3', J = 7.9, 1.0 Hz), 8.06 (td, 1H, H-4', J = 7.8, 1.7 Hz), 7.96 (m, 1H, H-5), 7.57 (dd, 1H, H-5', J = 7.4, 5.2 Hz).

4-(4-carbamovlphenyl)-2,2'-bipyridine (B1H). 2,2'-bipyridyl-4-boronic acid (0.74 g, 3.7 mmol), 4-bromobenzamide (1.1 g, 5.5 mmol), Pd(OAc)₂ (66 mg 8 mol%), dppf (326.2 mg, 16 mol%), and DMF (14 mL) were added to a Schlenk-type flask (100 mL) equipped with a rubber septum. The solution was first degassed by the conventional freeze-pump-thaw technique, followed by purging with Ar. An aqueous 1 M Cs₂CO₃ solution (8.0 mL, 8.0 mmol), similarly degassed and purged with Ar, was added to the mixture using the syringe technique. The mixture was then stirred at 100 °C for 60 h. After cooling it to room temperature, the solvent was removed by evaporation. The crude product was added to a mixture of an aqueous 0.5 N NaOH solution (30 mL) and ethyl acetate (30 mL). The aqueous layer was washed with ethyl acetate (30 mL \times 3) to remove the unreacted boronic acid. The combined organic layers were washed with an aqueous 0.5 N NaOH solution (40 mL \times 3). Then, the organic layer was extracted with an aqueous 3 N HCl solution (40 mL \times 3). The washings were combined and the pH of the solution was adjusted to 5 using an aqueous 0.5 N NaOH solution. The resulting colorless precipitate was collected by filtration and dried in vacuo (Yield: 29%, 0.23 g). Anal. calcd. for **B1** $H^{1/2}$ $HCl^{1/2}$ H_2O , $C_{17}H_{14.5}N_3O_{1.5}Cl_{0.5}$: C, 67.49; H, 4.83; N, 13.89. Found: C, 67.11; H, 4.85; N, 13.63. ¹H NMR $(300.50 \text{ MHz}, \text{CD}_3\text{Cl}) \delta$ ppm 8.77 (d, 1H, H-6, J = 5.2 Hz), 8.72 (m, 2H, H-6' and H-3), 8.49 (d, 1H, H-3', J = 8.1 Hz), 7.97-7.85 (m, 5H, H-4' and p-C₆ H_4), 7.58 (d, 1H, H-5, J = 5.2 Hz), 7.37 (dd, 1H, H-5', J = 7.5, 4.8 Hz) 6.15, 5.70 (s broad, 1H, -CON H_2).

[RuB1H](PF₆)₂·H₂O. A solution of RuCl₂(bpy)₂·2H₂O (195 mg, 0.375 mmol) and B1H $\cdot^{1}/_{2}$ HCl $\cdot^{1}/_{2}$ H₂O (103 mg, 0.342 mmol) in ethanol (80 mL) was refluxed for 14 h. After the solution was cooled down to room temperature, ethanol was removed by evaporation followed by addition of water (2 mL). The solution was then filtered for the removal of insoluble materials. Addition of an aqueous saturated NH_4PF_6 solution (1 mL) to the filtrate resulted in prompt deposition of a red solid, which was collected by filtration, washed with water (10 mL \times 2), and dried in vacuo. The compound (316 mg) was recrystallized from a 4:1 water-ethanol mixture to give the product as orange crystals (Yield: 55%, 205 mg). Anal. calcd. for $[RuB1H](PF_6)_2 \cdot H_2O$, C₃₇H₂₉N₇ORuP₂F₁₂·H₂O: C, 44.58; H, 3.14; N, 9.84. Found: C, 44.40; H, 3.10; N, 9.81. ¹H NMR (300.50 MHz, CD₃CN) δ ppm 8.79 (s, 1H, substituted bpy H-3), 8.71 (d, 1H, substituted bpy H-3', J = 8.0 Hz), 8.54, (d, 4H, bpy H-3 and H-3', J = 8.6 Hz), 8.15–7.96 (m, 9H, bpy H-4, H-4' and -C₆H₄-), 7.84–7.76 (m, 6H, bpy H-6 and H-6'), 7.70 (d, 1H, substituted bpy H-5, J = 6.0 Hz), 7.47-7.41 (m, 5H, bpy H-5 and H-5'), 6.89, 6.16 (s broad, 2H, -CON H_2). ESI-TOF MS m/z (calcd): 344.43 (344.57, [M – 2PF₆ $-H_2O]^{2+}$, 883.83 (834.11, $[M - PF_6 - H_2O]^+$).



 $[RuB1-Pt_2](PF_6)_4 \cdot H_2O.$ $[RuB1H](PF_6)_2 \cdot H_2O$ (100)mg, 0.10 mmol) was dissolved in a minimum amount of a mixed solvent consisting of acetonitrile, methanol and water (1:1:2 v/v/v (ca. 3 mL) and the solution was treated with an Amberlite 400 ion exchange resin (nitrate form, obtained by treating the chloride form with 1 N HNO₃). The organic solvents were removed by evaporation and the resulting aqueous layer was freeze-dried to give [RuB1H](NO₃)₂. To this was added pivalamide (13 mg, 0.13 mmol), [Pt₂(bpy)₂(µ-OH)₂](NO₃)₂ (115 mg, 0.13 mmol), and water (6 mL). Then, the mixture was stirred at 70 °C for 5 days followed by filtration for the removal of insoluble materials. To the filtrate was added an aqueous saturated NH₄PF₆ solution (1 mL). The black solid deposited was filtered and dried by suction. The crude product over the glass filter was redissolved in a minimum amount of acetonitrile and was purified on a Sephadex LH-20 column (60 cm × 1.4 cm i.d.) using a mixed solvent consisting of acetonitrile, methanol, and water (10:10:1 v/v/v) as eluent. The first and the second red bands corresponded to (RuB1)₂-Pt₂ and RuB1-Pt₂, respectively, and the third band corresponded to RuB1H and Pt₂. The second band was collected and dried in vacuo (Yield: 11%, 23 mg). Anal. calcd. for $[RuB1-Pt_2](PF_6)_4 \cdot H_2O$, $C_{62}H_{54}N_{12}O_2RuPt_2P_4F_{24} \cdot H_2O$: C, 35.66; H, 2.70; N, 8.05. Found: C, 35.47; H, 2.58; N, 8.01. ¹H NMR (600.13 MHz, CD₃CN) δ ppm 8.83 (s, 1H), 8.75 (t, J = 7.7 Hz, 1H), 8.70-8.61 (m, 1H), 8.60-8.51 (m, 5H), 8.51-8.43 (m, 1H), 8.39-8.28 (m, 1H), 8.24-8.16 (m, 2H), 8.16-8.02 (m, 11H), 8.01–7.88 (m, 4H), 7.88–7.72 (m, 7H), 7.59–7.37 (m, 10H), 6.86-6.52 (m, 1H), 1.46-1.24 (m, 9H). ESI-TOF MS m/z (calcd): 372.49 (372.57, $[M - 4PF_6 - H_2O]]^{4+}$); 544.98 (545.08, $[M - 3PF_6]^{4+}$ $(-H_2O]^{3+}$; 889.99 (890.11, $[M - 2PF_6 - H_2O]^{2+}$).

 $[(RuB1)_2-Pt_2](PF_6)_6\cdot 8H_2O$. The freeze-dried sample of $[RuB1H](NO_3)_2$ was prepared from $[RuB1H](PF_6)_2\cdot H_2O$ (64.9 mg, 59.4 µmol) in the same manner as described above for

[**RuB1-Pt**₂](PF₆)₄·H₂O. To this was added [Pt₂(bpy)₂(μ -OH)₂](NO₃)₂ (26.2 mg, 29.4 µmol), and water (3 mL). Then, the mixture was stirred at 70 °C for 60 h followed by filtration for the removal of insoluble materials. The crude product was crushed out in the same manner as described above and was similarly purified using Sephadex LH-20. The first reddish-brown band was collected, evaporated to dryness, and dried in vacuo (Yield: 40%, 36 mg). Anal. calcd. for [(RuB1)₂-Pt₂](PF₆)₆·8H₂O, C₉₄H₇₂N₁₈O₂Ru₂Pt₂P₆F₃₆·8H₂O: C, 36.51; H, 2.87; N, 8.15. Found: C, 36.21; H, 2.53; N, 8.26. ¹H NMR (600.13 MHz, CD₃CN) δ ppm 8.82 (s, 2H), 8.76 (d, J = 7.93 Hz, 2H), 8.70–8.63 (m, 2H), 8.61-8.44 (m, 10H), 8.29-8.19 (m, 4H), 8.17-8.03 (m, 18H), 8.00 (d, J = 8.02 Hz, 2H), 7.97–7.90 (m, 2H), 7.89–7.76 (m, 12H), 7.76–7.65 (m, 4H), 7.53–7.36 (m, 14H). ESI-TOF MS m/z (calcd): 346.29 (346.39, [RuB1-Pt]³⁺); 536.92 (537.09, [(RuB1-Pt) $+ OH^{-} + H_2O]^{2+}$).

 $[RuB2-Pt_2](PF_6)_4 \cdot 2H_2O$. The freeze-dried sample of $[RuB2H](NO_3)_2$ was prepared from $[RuB2H](PF_6)_2$ (117 mg, 107 µmol) in the same manner as described above for [RuB1- Pt_2](PF₆)₄·H₂O. To this was added pivalamide (11.2 mg, 112 μ mol), [Pt₂(bpy)₂(μ -OH)₂](NO₃)₂ (89.6 mg, 104 μ mol), and water (2 mL). Then, the mixture was stirred at 70 °C for 21 h followed by filtration for the removal of insoluble materials. The crude product was crushed out in the same manner as described above and was similarly purified using Sephadex LH-20. The first and the second red bands corresponded to (RuB2)₂-Pt₂ and RuB2-Pt₂, respectively. The second band was collected, evaporated to dryness, and dried in vacuo (Yield: 8.7%, 11.8 mg). Anal. calcd. for $[RuB2-Pt_2](PF_6)_4 \cdot 2H_2O$, $C_{66}H_{59}N_{13}O_5RuPt_2P_4F_{24} \cdot 2H_2O$: C, 35.69; H, 2.86; N, 8.20. Found: C, 35.56; H, 2.81; N, 8.27. ¹H NMR (600.13 MHz, CD₃CN) δ ppm 9.42 (s, 1H), 9.15–9.05 (m, 2H), 8.75-8.25 (m, 8H), 8.20-7.85 (m, 18H), 7.80-7.65 (m, 4H), 7.60-7.20 (m, 8H), 6.80-6.50 (m, 2H), 4.55-4.45 (m, 2H), 1.50-1.44 (m, 3H), 1.40-1.25 (m, 9H). ESI-TOF MS m/z (calcd): 384.64 (384.73, [RuB2-Pt]³⁺); 401.25 (401.33, [M - 4PF₆ - $2H_2O^{4+}$; 583.29 (583.43, $[M - 3PF_6 - 2H_2O^{3+}]$; 947.41 (947.61, $[M - 2PF_6 - 2H_2O]^{2+}).$

 $[(RuB2)_2 - Pt_2](PF_6)_6 \cdot 6H_2O$. The freeze-dried sample of $[RuB2H](NO_3)_2$ was prepared from $[RuB2H](PF_6)_2$ (64.9 mg, 59.4 µmol) in the same manner as described above for [RuB1- Pt_2](PF₆)₄·H₂O. To this was added [Pt₂(bpy)₂(μ -OH)₂](NO₃)₂ (26.2) mg, 29.4 µmol) and water (3 mL). Then, the mixture was stirred at 70 °C for 60 h followed by filtration for the removal of insoluble materials. The crude product was crushed out in the same manner described above and was similarly purified using Sephadex LH-20. The first red-brown band was collected, evaporated to dryness, and dried in vacuo (Yield: 40%, 38 mg). Anal. Calcd. for $[(RuB2)_2-Pt_2](PF_6)_6 \cdot 6H_2O, C_{102}H_{82}N_{20}O_8Ru_2Pt_2P_6F_{36} \cdot 6H_2O:$ C, 37.28; H, 2.88; N, 8.52. Found: C, 37.13; H, 2.77; N, 8.91. ¹H NMR (600.13 MHz, CD₃CN) δ ppm 9.81–9.22 (m, 4H), 9.19-9.01 (m, 4H), 8.93-8.21 (m, 16H), 7.62-7.19 (m, 14H), 7.81-7.61 (m, 10H), 8.04-7.81 (m, 18H), 8.21-8.04 (m, 14H), 6.96-5.68 (m, 2H), 4.49 (d, J = 6.8 Hz, 4H), 1.43 (t, J = 6.8 Hz, 6H). ESI-TOF MS m/z (calcd): 384.58 (384.73, [M - 6PF₆ - $6H_2O$ ⁶⁺, overlapped with [**RuB2-Pt**]³⁺); 490.48 (490.47, [M - 5PF₆) $- 6H_2O$]⁵⁺); 649.37 (649.58, [M $- 4PF_6 - 6H_2O$]⁴⁺ overlapped with $[(\mathbf{RuB2-Pt}) + \mathbf{PF}_6]^{2+}); 914.11 (914.43, [\mathbf{M} - 3\mathbf{PF}_6 - 6\mathbf{H}_2\mathbf{O}]^{3+}).$

Measurements

¹H NMR spectra were acquired on a JEOL JNM-AL300 (300.50 MHz), a JEOL JNM-ESA600 (600.13 MHz), and, a JEOL JNM-ECS400 (399.78 MHz) spectrometer, in which tetramethylsilane was used as an internal standard. UV-Visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer at 25 °C, in air. Emission spectra were recorded on a Shimadzu RF5300PC spectrofluorophotometer at 25 °C. Emission decays were observed at 25 °C on an Iwatsu DS-4262 digitizing oscilloscope equipped with a Hamamatsu R928 photomultiplier tube. The excitation source was an N₂ laser (337 nm) (Usho KEN-1520). The grating monochromator used was a Jobin Vyvon H-20 instrument. Data acquisitions were carried out up to 512 scans. Electrospray ionization time-of-flight mass spectra (ESI-TOF MS) were obtained for the acetonitrile solutions of the complexes using a JEOL JMS-T100CS. The emission quantum yields of RuB1H and RuB2H were determined using a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system with a 150 W Xe lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as a sample chamber, and a Hamamatsu C10027-01 multichannel detector for the signal detection. Luminescence quantum yields for the multinuclear complexes **RuBn-Pt**₂ and (**RuBn**)₂-**Pt**₂ (n = 1, 2) were estimated on the basis of the quantum yields determined for RuB1H and RuB2H.

The cyclic voltammetric and differential pulse voltammetric measurements were performed on a BAS CV-50 W electrochemical analyzer for the argon-purged acetonitrile solutions of the complexes (1 mM) in the presence of 0.1 M tetra(*n*-butyl)ammonium perchlorate (TBAP) as a supporting electrolyte at room temperature. The platinum working electrode was polished with BAS polishing alumina suspension and rinsed with acetonitrile before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/Ag⁺ reference electrode (*ca.* 490 mV *vs.* NHE), but was corrected using the ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal standard.

For the nanosecond flash photolysis experiments, sample solutions were excited by a Nd:YAG laser (Minilite II-10, Continuum), and transient absorbance changes were monitored by a 150 W Xe lamp and an amplified photomultiplier tube (R2949, Hamamatsu). Transient absorption spectra were recorded using multichannel detector with a gated image-intensifier, C9546-03 (Hamamatsu). Each sample solution was purged with Ar for at least 20 min before the measurement.

Photochemical H₂ evolution from water was analyzed by using an automatic H₂ monitoring system developed in our group. In this system, a continuous flow of Ar (10.0 mL min⁻¹, controlled by an STEC SEC-E40/PAC-D2 digital mass flow controller) was bubbled through a photolysis solution (10 mL) contained in a Pyrex vial (*ca.* 20 mL). The vent gas from the vial was introduced into a 6-way valve which allowed the automatic injection of the sample gas onto a gas chromatograph (Shimadzu GC-14A equipped with a molecular sieve 5A column of 2 m × 3 mm i.d., thermostatted at 30 °C). The injection of the sample gas and the output signal from the thermal conductivity detector of the gas chromatograph were both controlled by control software operating on a Windows system. Photolysis solutions were deaerated with Ar for at least 30 min prior to the photolysis. The photoirradiation was carried

out by an Ushio Xe short arc lamp UXL500D-O (operated at 350 W). The photolysis vial was immersed in a water bath thermostatted at 20 °C to remove IR radiation and to eliminate the temperature effect. The photolysis solution of each hybrid compound was prepared using the nitrate salt of the complex, in situ prepared by the conventional ion-exchange technique, as previously described;^{9d} a weighed amount of the PF₆⁻ salt was first dissolved in a 1:1 water-methanol mixture and was treated with an anion-exchange resin (Amberlite IRA-400 in the NO₃⁻ form) followed by complete removal of solvents (finally freeze-dried). The photolysis solution containing $[Pt_2(NH_3)_4(\mu-CH_3CONH)_2]^{2+}$ (Pt_2 -STD), which was used to determine the quantum efficiency of H₂ formation catalyzed by Pt₂, was prepared by dissolving $[Pt(2.25+)_2(NH_3)_4(\mu-CH_3CONH)_2]_4(NO_3)_{10}\cdot 4H_2O$ into the photolysis solution. As previously described, 7c,e this mixed-valence octanuclear platinum complex was proven to give a pure solution of $[Pt_2(NH_3)_4(\mu-CH_3CONH)_2]^{2+}$ via the cleavage of the complex into the dimeric species and complete reduction into the $Pt(II)_2$ species in the presence of an excess of EDTA.

Acknowledgements

This work was in part supported by Grants-in-Aid for Scientific Research (A) (No. 17205008) and (B) (No. 21350036), a Grant-in-Aid for Specially Promoted Research (No. 18002016), and a Grant-in-Aid for the Global COE Program ('Science for Future Molecular Systems') from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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