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Syntheses and photophysical properties of visible-light-absorbing Ru(II) polypyridyl complexes possessing (pyridylpyrazolyl)metal tethers

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ABSTRACT

Novel Ru(II) polypyridyl complexes possessing pyridylpyrazolyl tethers were synthesized. Reactions with various organometallic precursors readily afforded multinuclear complexes which possess a light-harvesting Ru(II) core and (pyridylpyrazolyl)metal fragments in high yields. Analysis of the photophysical properties of the obtained multinuclear complexes revealed that the complexes had similar absorption and emission characteristics; however, their emission quantum yields decreased in proportion to the number of metal fragments. The di- and trinuclear complexes were stable under donating solvent such as CH_3CN.

1. Introduction

A significant research effort has been focused on the synthesis and photophysical characterization of various Ru(II) polypyridyl complexes [1]. Because of their chemical stability, facile electron transfer, strong luminescence, and relatively long-lived excited state, research area of such compounds now spans widely from basic photochemistry and photophysics to photocatalysts, molecular recognition, and DNA probes. Recently, increased research attention has been placed on the polynuclear systems with incorporating the $[Ru(bpy)_3]^{2+}$ moiety mainly focused on the study of understanding the elementary processes of electron or energy transfer, or constructing photoactive supramolecular structures [2]. On the other hand, works aimed at photocatalytic molecular transformation still remain to be explored [3].

We have reported Pd catalysts possessing the Ru(II) polypyridyl moiety bridged by various 2,2′-bipyrimidine (bpm) ligands, $[(bpy)_2Ru(bpm)PdMe(Me_2CO)]^{3+}$, and the complex catalyzed selective dimerization of α-methylstyrene under visible-light irradiation [4]. The bpm ligand used in this system is rigid and capable of connecting the light-harvesting Ru(II) polypyridyl unit and the reaction center. However, some of the reaction center dissociates under coordinating solvent such as CH_3CN probably due to the decrease of the electron density by the adjacent $[(bpy)_2Ru]^{2+}$ dicationic unit. Thus we have focused our attention on connecting the independent $[(bpy)_3Ru]^{2+}$ moiety and the (pyridylpyrazolyl)metal fragment with the methylene linker to maintain the coordination ability of the pyridylpyrazolyl (pypz) ligand. In order to expand the research in this field and establish the suitable molecular design for the effective photocatalytic system, we report herein the synthesis and photophysical properties of visible-light-absorbing Ru(II) polypyridyl complexes possessing (pyridylpyrazolyl)metal tethers.

2. Synthesis

2.1. Synthesis of mononuclear ruthenium complexes

The established procedure for synthesizing $[(bpy)_2Ru(L\text{-}L)]^{2+}$ complexes [5], involves refluxing the L-L ligand with *cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$ in EtOH [6]. We followed this procedure. Treatment of the bpy′ ligand (Fig. 1) with *cis*-$(bpy)_2RuCl_2$; this reaction afforded a mixture of the desired product $[(bpy)_2Ru(bpy')]^{2+}$ (**3**) and the dinuclear Ru···Ru product $[(bpy)_2Ru(bpy')Ru(bpy)_2)]^{4+}$, because the bpy′ ligand possessed two N–N binding sites. Hence we attempted a sequential procedure for the synthesis of our desired product: synthesis of Ru(II) complex **1** possessing 4-(bromomethyl)-4′-methyl-2,2′-bipyridyl ligand [7], followed by treatment of **1** with sodium 3-(2-pyridyl)pyrazolate [8]. In this procedure, addition of 1 equiv. of pyridylpyrazolate to **1** afforded **3** in a satisfactory yield. The di-tethered complex **4** was similarly prepared by treatment of 2 equiv. of sodium pyridylpyrazolate with the Ru(II) complex **2** (Scheme 1).

2.2. Spectroscopic determination

Complex **3** was spectroscopically characterized on the basis of ^1H, ^{13}C NMR, and ESI-MS data. In the ^1H NMR spectrum, a singlet corresponding to the methyl substituent in the bpy′ ligand was

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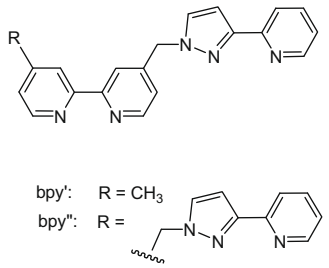


Fig. 1. bpy′ and bpy′′ ligands.

observed at 2.56 ppm. The characteristic signal due to the methylene protons was observed as a singlet at 5.73 ppm; this signal was shifted slightly downfield when compared to the corresponding signal (4.78 ppm) in **1**. This downfield shift of the methylene proton signal was found to be a good indicator of the insertion of metal fragments into the pyridylpyrazolyl (pypz) ligand (*vide infra*) (see Scheme 2).

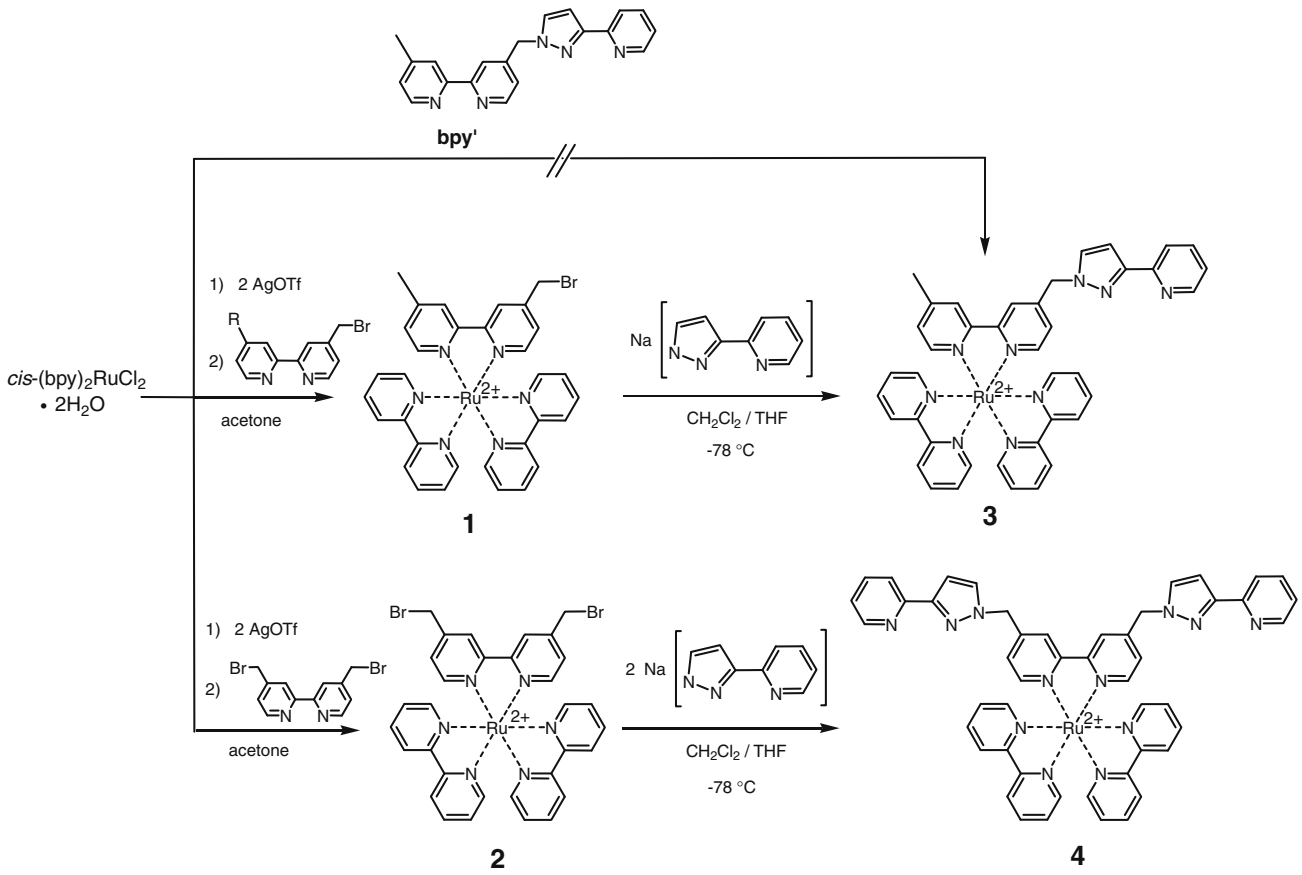
In the ^{13}C NMR spectrum, signals due to the methyl and methylene carbon atoms were observed at 21.3 and 54.8 ppm, respectively. Five carbon signals corresponding to the two bpy ligands were observed due to the equivalent environment of each pyridyl ring. On the contrary, nineteen inequivalent carbon signals corresponding to the bpy′ ligand were observed in the range of 100–160 ppm.

Complex **4** was also determined on the basis of NMR and ESI-MS data. A singlet corresponding to the methylene protons in the bpy′′ ligand was observed at 4.80 ppm, which was well consistent with the position of the signal due to the methylene protons in **3**.

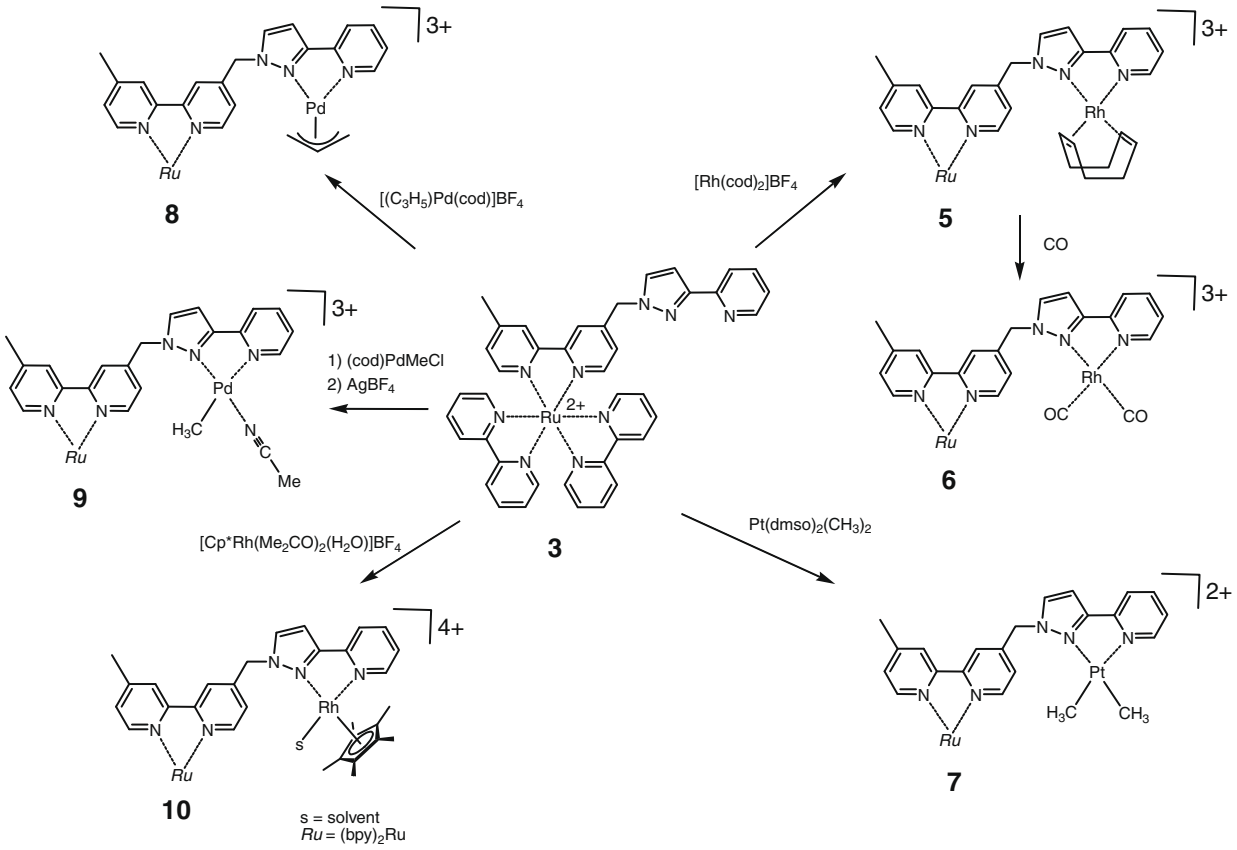
2.3. Introduction of organometallic fragments

Mono(pyridylpyrazolyl) complex **3** readily reacted with various organometallic precursors such as $[Rh(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene), $Pt(dmso)_2$, $[(C_3H_5)Pd(cod)]BF_4$, (cod)PdMeCl, and $[Cp^*Rh(Me_2CO)_2(H_2O)]BF_4$ to yield the corresponding dinuclear Ru···M complexes (Scheme 2). Addition of a Pd precursor, (cod)PdMeCl, to **3** afforded a dicationic complex in which a PdMeCl fragment was coordinated to the pypz moiety, and subsequent abstraction of the Cl^- ligand from the dicationic complex using $AgBF_4$ in CH_3CN afforded the solvated complex **9**. Reaction of 1 equiv. of $[(cod)_2Rh]BF_4$ with **3** afforded a Ru···Rh(cod) complex **5**, which on subsequent treatment with CO (1 atm) gave the Rh dicarbonyl complex **6** in a quantitative yield. Similarly, the reaction of 2 equiv. of each of the abovementioned precursors with the di(pyridylpyrazolyl) complex **4** led to the formation of the corresponding trinuclear M···Ru···M complexes (Scheme 3). Unfortunately, reactions with 2 equiv. of (cod)PdMeCl resulted in a mixtures of di- and trinuclear complexes, Ru···$\{PdMeCl\}_n$ (n = 1, 2); subsequent treatment of these complexes with $AgBF_4$ did not afford the desired product.

All the dinuclear (Ru···M) and trinuclear (M···Ru···M) complexes were spectroscopically determined on the basis of their NMR and ESI-MS data; the signal assignments are shown in the Section 5. Contrary to the singlet observed for the precursors **3** and **6**, the methylene signals in the ^1H NMR spectrum of the dinuclear Ru···Rh(cod) complex, were observed as AB quartet at δ 5.56 and 5.71 ppm (J_{HH} = 18.0 Hz). This difference could be attributed to the steric hindrance caused by the bulky Rh(cod) fragment, which hinders free rotation of the methylene linker parts around the



Scheme 1.



Scheme 2.

$C(sp^2)$-$C(sp^3)$ and $C(sp^3)$-N bonds and creates different magnetic environments of the two protons.

The signal due to the methylene protons of **6** was observed as a singlet at δ 6.20 and was shifted slightly downfield with respect to the corresponding signal in **3**. The carbonyl carbon signal was observed as a doublet because of coupling (J_{Rh-C} = 66 Hz) with the Rh nucleus. The IR spectrum of **6** in CH_3NO_2 showed two C–O stretching bands at 2100 and 2038 cm^{-1}, which were comparable to the positions of the C–O stretching bands in the model complex, $[(bpy)Rh(CO)_2]^+$ (ν_{co} = 2100, 2040); this indicated that electron density at the introduced metal centers were not affected by the attachment of the dicationic Ru(II) polypyridyl moiety.

The Rh–carbony complexes **6** and **12** were stable in CH_3CN in contrast to the bpm-bridged complex, $[(bpy)_2Ru(bpm)Rh(CO)_2]^{3+}$, which easily dissociated to $[(bpy)_2Ru(bpm)]^{2+}$ and $[Rh(CO)_2L_2]^+$ (L = solvent) in the donating solvents [9].

3. Physical properties

3.1. Electrochemical properties

In this section, the electrochemical properties of the dinuclear Ru···M (M = Rh, Pd, Pt) and the trinuclear M···Ru···M (M = Rh, Pd, Pt) complexes are compared with those of the parent compounds **3**, **4** and relevant dinuclear complexes containing the same metal fragments bridged by 2,2′-bipyrimidine ligands, $(bpy)_2$-Ru(bpm)MLn [4] .

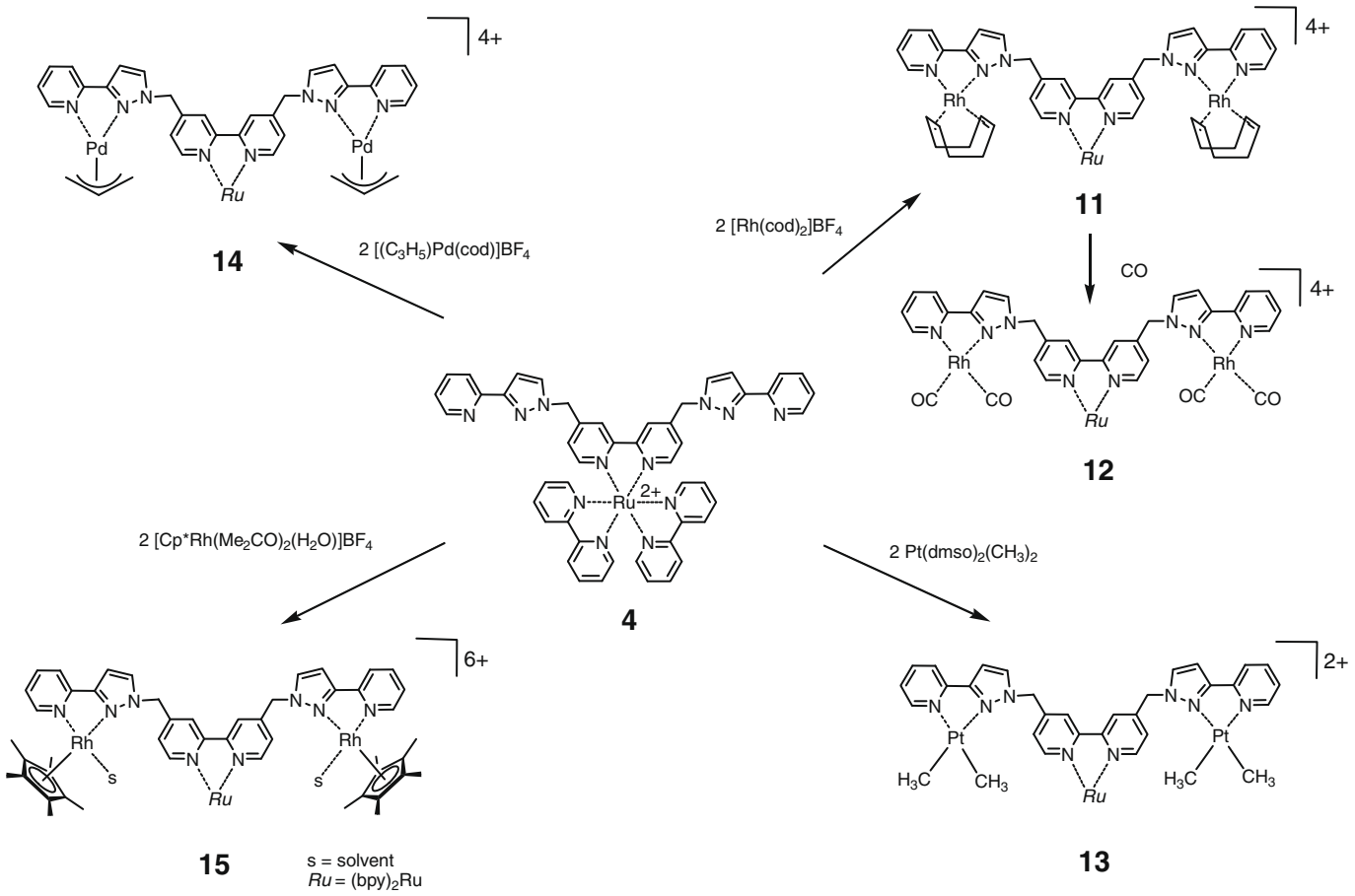
Cyclic voltammograms (CVs) were measured at room temperature in CH_3CN solutions using a Ag/Ag^+ reference electrode, a Pt counter electrode, and a Pt working electrode. DMF was chosen for the measurements of di- and trinuclear complexes containing the Cp^*Rh fragment because this fragment could dissociate to $Cp^*Rh(CH_3CN)_3$ and **3** (or **4**) in CH_3CN. The redox potentials (vs. Fc/Fc^+) of each compound are summarized in Table 1, and the CVs of **3**, **4**, **8**, and **14** are shown in Fig. 2. The CVs of all the compounds showed one reversible wave attributable to the Ru(II)/(III) redox process at around +900 mV and three reversible waves attributable to the one-electron redox process of the diimine ligands between −1600 and −2100 mV. In CVs of the complexes containing the Cp^*Rh and $Rh(CO)_2$ fragments (entries 8, 13, and 17), additional irreversible waves, which were possibly due to Rh(I)/(III) and Rh(III)/(I) redox processes [10], were observed.

3.1.1. Comparison of the mononuclear complexes

The $E_{1/2}(Ru^{II/III})$ values obtained for the mononuclear complexes $[Ru(bpy)]^{2+}$, $[Ru(bpy^{4,4'\text{-}Me2})]^{2+}$, $[Ru(bpy')]^{2+}$, $[Ru(bpy'')]^{2+}$, and $[Ru(bpm)]^{2+}$ [11] (entries 1, 2, 3, 9, and 14), decrease in the following order: $[Ru(bpy^{4,4'\text{-}Me2})]^{2+} < [Ru(bpy')]^{2+} < [Ru(bpy)]^{2+} < [Ru(bpy'')]^{2+} < [Ru(bpm)]^{2+}$. This order can be reworded to the following order of electron density on the diimine ligands: $bpy^{4,4'\text{-}Me2} > bpy' > bpy > bpy'' > bpm$. This indicates that the (pyridyl)pyrazolylmethyl group is a slightly electron-withdrawing substituent.

3.1.2. Comparison of di- and trinuclear complexes with their parent mononuclear complexes

Upon introduction of the cationic (entries 4, 5, 7, and 8) and neutral metal fragments (entry 6), the redox potential of the resulting complexes shifted slightly (ca. 30 mV) toward the positive side as compared to that of the parent complex **3**. The shift observed for the trinuclear complexes **9**, **13**, **14**, and **15** (entries 10–13) upon introduction of the two metal fragments into **4** was even smaller.



Scheme 3.

Table 1
Electrochemical properties of $[Ru(bpy')]^{2+}$ and $[Ru(bpy'')]^{2+}$ complexes.[a]

Entry	Complexes	$E_{1/2}$ (mV)				
		$E_{1/2}$ ($Ru^{II/III}$)	E ($Rh^{I/III}$), E ($Rh^{I/III}$)	$E_{1/2}$ ($L^{0/-1}$)		
1	$[Ru(bpy)]^{2+}$	884		−1714	−1913	−2162
2	$[Ru(bpy^{4,4'\text{-}Me2})]^{2+}$	834		−1733	−1931	−2186
3	$[Ru(bpy')]^{2+}$ (**3**)	846		−1746	−1918	−2169
4	$[Ru(bpy')Rh(cod)]^{3+}$ (**5**)	879		−1721	−1900	−2166
5	$[Ru(bpy')Rh(CO)_2]^{3+}$ (**6**)	870		−1718	−1899	−2155
6	$[Ru(bpy')Pt(CH_3)_2]^{2+}$ (**7**)	885		−1707	−1893	−2142
7	$[Ru(bpy')Pd(allyl)]^{3+}$ (**8**)	819		−1715	−1887	−2144
8[*b]	$[Ru(bpy')Rh(Cp^*)(solvent)]^{4+}$ (**10**)	873	−1240, −1175	−1743	−1911	−2182
9	$[Ru(bpy'')]^{2+}$ (**4**)	903		−1662	−1880	−2151
10	$[Ru(bpy'')Rh_2(cod)_2]^{4+}$ (**9**)	821		−1687	−1878	−2217
11	$[Ru(bpy'')Pt_2(CH_3)_4]^{2+}$ (**13**)	932		−1658	−1857	−2142
12	$[Ru(bpy'')Pd_2(allyl)_2]^{4+}$ (**14**)	893		−1671	−1871	−2121
13[*b]	$[Ru(bpy'')Rh(Cp^*)(solvent)]^{4+}$ (**15**)	880	−1234, −1157	−1661	−1848	−2149
14[*c]	$[Ru(bpm)]^{2+}$	1009		−1401	−1850	
15[*c]	$[Ru(bpm)Pd(allyl)]^{3+}$	1334		−1409	−1790	−2122
16[*c]	$[Ru(bpm)Pt(CH_3)_2]^{2+}$	1291		−1692	–	
17[*b,c]	$[Ru(bpm)Rh(CO)_2]^{3+}$	1187	−816	−1420	−1856	−2094

[a] *Ru*: $(bpy)_2Ru$. Measurements were carried out in 0.1 M CH_3CN solution with 0.1 M TBAP. All potentials are reported in mV vs. Fc^+/Fc. For the irreversible processes, peak potentials E_a and E_c are listed.
[b] Solvent: DMF.
[c] Synthesized and measured by our group.

This small shift was thought to be due to the effect of the broken π-conjugation at the sp^3-methylene carbon. These results were in contrast to those obtained for the dinuclear bpm complexes (entries 15–17), where substantially larger peak shifts was observed.

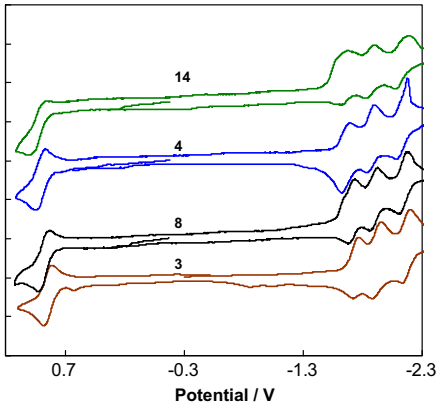


Fig. 2. Cyclic voltammogram of **3**, **8**, **4**, and **14**.

3.2. Photophysical properties

3.2.1. Electronic absorption

The absorption spectra of the obtained complexes are displayed in Figs. 3 and 4, and the corresponding data are listed in Table 2 together with the luminescence data to be discussed; for comparison, the data corresponding to $[Ru(bpy)]^{2+}$ and $[Ru(bpy^{4,4'\text{-}Me2})]^{2+}$

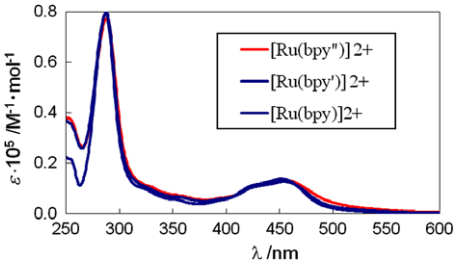


Fig. 3. UV–Vis absorption spectra of $[(bpy)_3Ru]^{2+}$, $[(bpy)_2Ru(bpy')]^{2+}$, and $[(bpy)_2Ru(bpy'')]^{2+}$.

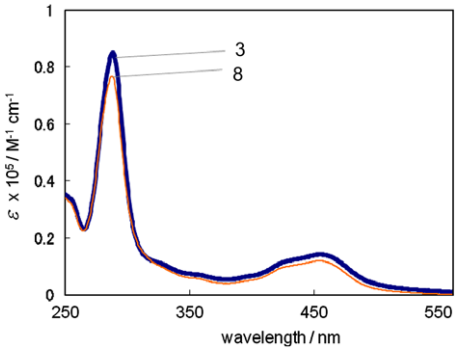


Fig. 4. UV–Vis absorption spectra of $[(bpy)_2Ru(bpy')]^{2+}$ (blue) and $[(bpy)_2Ru(bpy')Pd(C3H5)]^{3+}$ (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are also included. The spectral profiles in Figs. 3 and 4 reveal the occurrence of intense, narrow $^1\pi$–π^* bpy-centered transitions that are localized in the UV region (290 nm) and broad ^{1}MLCT ($[d\pi(Ru) \rightarrow \pi^*(bpy)]$ and $[d\pi(Ru) \rightarrow \pi^*(BL)$, where BL = bpy′ or bpy″]) transitions in the visible region, that maximizes at around 455 nm. The band maxima and absorption intensities of all the mononuclear complexes $[(bpy)_3Ru]^{2+}$, $[(bpy)_2Ru(bpy')]^{2+}$, and $[(bpy)_2Ru(bpy'')]^{2+}$ are very similar (Fig. 3). In other words, introduction of metal fragments such as $[Pd(C_3H_5)]^+$ into these complexes did not bring about any change in their photophysical properties (Fig. 4). These characteristics were also commonly observed in complexes bearing bpy″ ligands. These results indicated that photophysical properties of the Ru(II) polypyridyl core were maintained even after the introduction of various metal fragments into the pendant moieties.

3.2.2. Emission properties

The emission spectra of the mono-, di-, and trinuclear complexes were recorded in deaerated CH_3CN or DMF at room temperature. As mentioned in the previous section, the spectra of complexes containing the Cp^*Rh fragment were recorded in DMF solution. The concentrations of the solutions were adjusted in such a manner that their absorption intensities at the excitation wavelength (450 nm) were equal (0.1). The complexes showed emission behavior typical of the ^{3}MLCT state; these emission properties are listed in Table 2. The φ_{rel} values are the emission quantum yields relative to those of the parent mononuclear complexes **3** or **4**. For all the complexes, the energy maxima was around 600 nm, and no changes were observed upon changing the ligand from bpy to bpy′/bpy″ or upon the introduction of metal fragments. However, the emission intensities (φ) of the dinuclear and trinuclear complexes were smaller than those of **3** or **4**. These data indicated that quenching occurred via energy transfer from the Ru(II) polypyridyl moiety to the introduced metal centers. Since this quenching was more pronounced in the trinuclear complexes than in the corresponding dinuclear complexes, the magnitude of energy transfer was thought to be proportional to the number of metal fragments incorporated into the Ru(II) core.

4. Summary

In summary, we have synthesized novel Ru(II) polypyridyl complexes bearing pendant pypz ligands. Complexation of these ligands with various late-transition organometallic precursors led to the quantitative formation of novel dinuclear (Ru···M)- and trinuclear (M···Ru···M) complexes. The complexes were fully characterized on the basis of NMR and ESI-MS spectral data. The luminescence spectra of the di- and trinuclear complexes showed that the quantum yields of the products were substantially lower than those of the parent mononuclear complexes as a result of the introduction of the organometallic fragments; this observation suggested that energy transfer occurred from the Ru(II) center to the pendant moiety ((pypz)M). Reactivity studies of these com-

Table 2
Electronic absorption and luminescence data.[a]

Entry	Complexes[b]	Absorption λ_{max}, nm (ε, 10^4 M^{-1} cm^{-1})	Luminescence[c] λ_{max}, nm	φ_{rel1}[d]	φ_{rel2}[e]
1	$[Ru(bpy)][PF_6]_2$	452 (1.4)	615	1.00	
2	$[Ru(4,4'\text{-}Me_2bpy)][PF_6]_2$	455 (1.4)	627	1.04	
3	$[Ru(bpy')][PF_6]_2$ (**3**)	454 (1.3)	627	0.88	1.00
4	$[Ru(bpy')Rh(cod)][PF_6]_2[BF_4]$ (**5**)	453 (1.5)	633	0.82	0.93
5	$[Ru(bpy')Rh(CO)_2][PF_6]_2[BF_4]$ (**6**)	454 (1.2)	627	0.63	0.72
6	$[Ru(bpy')Pt(CH_3)_2][PF_6]_2$ (**7**)	454 (1.5)	629	0.69	0.78
7	$[Ru(bpy')Pd(allyl)][PF_6]_2[BF_4]$ (**8**)	454 (1.2)	632	0.82	0.93
8[f]	$[Ru(bpy')Rh(Cp^*)(solvent)][PF_6]_2[BF_4]_2$ (**10**)	458(1.3)	627	0.76	0.86
9	$[Ru(bpy'')][PF_6]_2$ (**4**)	453 (1.3)	633	0.73	1.00
10	$[Ru(bpy'')Rh_2(cod)_2][PF_6]_2[BF_4]_2$ (**11**)	454 (1.5)	633	0.16	0.22
11	$[Ru(bpy'')Pd_2(allyl)_2][PF_6]_2[BF_4]_2$ (**13**)	456 (1.4)	632	0.46	0.63
12	$[Ru(bpy'')Pt_2(CH_3)_4][PF_6]_2$ (**14**)	455 (1.3)	633	0.38	0.52
13[f]	$[Ru(bpy'')Rh(Cp^*)(solvent)][PF_6]_2[BF_4]_6$ (**15**)	455 (1.3)	638	0.53	0.73

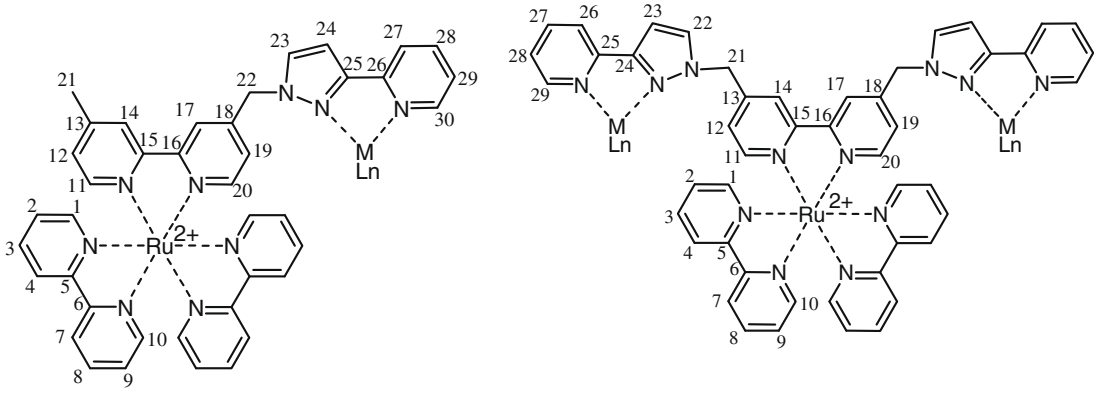
[a] Measurements were carried out in deaerated CH_3CN at RT, unless otherwise indicated.
[b] *Ru*: $(bpy)_2Ru$.
[c] Excitation at 450 nm.
[d] Luminescence intensity relative to that of $[Ru(bpy)][PF_6]_2$.
[e] Intensity relative to that of **3** or **4**.
[f] Measured in DMF.

plexes under light-irradiated condition will be the subject in the future.

5. Experimental

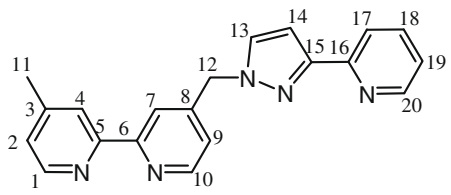
5.1. General

Standard Schlenk and vacuum line techniques under N_2 atmosphere were employed for the reactions. Acetone (molecular sieves), acetonitrile (P_2O_5), and nitromethane ($CaCl_2$) were treated with appropriate drying agents, distilled, and stored under N_2. The metal reagents $[Pd(C_3H_5)(cod)]BF_4$ [12], [Pd(cod)MeCl] [13], $[Rh(cod)_2]BF_4$ [14], $[(C_5Me_5)Rh(Me_2CO)_2(H_2O)]BF_4$ [15], and $Pt(DMSO)_2(CH_3)_2$ [16] were prepared according to the published procedures. Other chemicals were purchased and used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200, JEOL GX-270, JEOL EX-400, and JEOL LA-500 spectrometers. Solvents for NMR measurements were dried over molecular sieves, degassed, and stored under N_2. IR, UV–Vis, and steady-state emission spectra were obtained on a JASCO FT/IR 5300, JASCO V-570, and SHIMADZU RF-5300PC spectrometer, respectively. ESI-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer. Electrochemical measurements were made with a BAS CV-50W analyzer. In the following section, $^3J_{HH}$ and $^1J_{CH}$ are abbreviated as J and J_{CH}, respectively.



5.2. Synthesis of the ligand and complexes

5.2.1. Synthesis of 4-methyl-4′-3-(2-pyridyl)pyrazolyl-2,2′-bipyridyl (= bpy′) (**2**)



bpy′ ligand was synthesized following the similar procedure in synthesizing 6-(N-pyrazolylmethyl)-2,2′-bipyridine [17]. Reaction of 4-bromomethyl-4′-methyl-2,2′-bipyridyl [7] (934 mg, 3.55 mmol) with 3-(2-pyridinyl)pyrazole [18] (775.1 mg, 5.34 mmol) in toluene (100 mL) at 100 °C for 15 h gave bpy′ as a white solid (648 mg, 1.98 mmol, 55%). ^1H NMR (400 MHz, acetone-d_6, RT): δ 2.41 (s, 3H, CH_3), 5.61 (s, 2H, –CH_2–), 6.98 (d, 1H, J = 2.4 Hz, H14), 7.20–7.26 (3H, H2, H9, H19), 7.76 (ddd, 1H, J = 8.4, 7.6, 1.7 Hz, H18), 7.92 (d, 1H, J = 2.4 Hz, H13), 8.00 (d, 1H, J = 8.4 Hz, H17), 8.29 (s, 1H, H4), 8.38 (s, 1H, H7), 8.47–8.61 (3H, H1, H10, H20). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 21.4 (q, J_{CH} = 126 Hz, CH_3), 55.7 (t, J_{CH} = 140 Hz, C12), 105.8 (dd, J_{CH} = 177 9.1 Hz, C14), 120.1–125.8 (d, J_{CH} = 164 Hz, C2, C4, C7, C9, C17, C19), 133.0 (d, J_{CH} = 187 Hz, C13), 137.3 (d, J_{CH} = 160 Hz, C18), 148.5, 148.9 (s × 2, C3, C8), 150.0–150.5 (d × 3, J_{CH} = 177 Hz, C1, C10, C20), 153.4, 153.5, 156.4, 157.5 (s × 4, C5, C6, C15, C16).

5.2.2. Synthesis of $[(bpy)_2Ru(bpy')](PF_6)_2$ (**3**)

The CH_2Cl_2 solution of $[(bpy)_2Ru(bpy^{CH_2Br})](PF_6)_2$ [9] (bpy^{CH_2Br} = 4-bromomethyl-4′-methyl-2,2′-bipyridyl) (382 mg, 0.395 mmol) was added to the THF solution of Na[3-(2-pyridyl)pyrazolate] (98 mg, 0.586 mmol) and stirred for 2 h at −78 °C and another 2 h at ambient temperature. The solution was filtered through Celite and the volatile of the filtrate was removed under reduced pressure. The obtained solid was dissolved into acetone and precipitated by the addition of Et_2O. The precipitate was dissolved into CH_2Cl_2, washed with H_2O, and dried with $MgSO_4$. The volatile was evaporated after filtration and the solid was reprecipitated with acetone/Et_2O to yield $[(bpy)_2Ru(bpy')](PF_6)_2$ as an red solid (259 mg, 0.251 mmol, 63%). ^1H NMR (200 MHz, acetone-d_6, RT): δ 2.56 (s, 3H, –CH_3), 5.73 (s, 2H, –CH_2–), 6.94–8.86 (28H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 21.3 (q, J_{CH} = 127 Hz, CH_3), 54.8 (t, J_{CH} = 140 Hz, –CH_2–), 105.9 (dd, J_{CH} = 179, 9 Hz, C24), 120.4–129.7 (d, J_{CH} = 165 Hz, C12, C14, C17, C19, C27, C29), 125.2 (d, J_{CH} = 167 Hz, C4, C7), 128.7 (d, J_{CH} = 169 Hz, C2, C9), 133.4 (d, J_{CH} = 181 Hz, C23), 137.3 (d, J_{CH} = 164 Hz, C28), 138.8 (d, J_{CH} = 169 Hz, C3, C8), 150.0, 151.4 (s, C13, C18), 150.1, 151.7, 152.7 (d × 3, J_{CH} = 176 Hz, C11, C20, C30), 152.5 (d, J_{CH} = 184 Hz, C1, C10), 153.0, 153.8, 157.2 (s, C15, C16, C25, C26), 158.1 (s, C5, C6). ESI-MS: m/z = 886: $\{[(bpy)_2Ru(bpy')](PF_6)\}^+$. Anal. Calc. for $C_{40}H_{33}N_9Ru\cdot(PF_6)_2$: C, 46.61; H, 3.23; N, 12.23. Found: C, 46.89; H, 3.33; N, 12.26%.

5.2.3. Synthesis of $[(bpy)_2Ru(bpy'')](PF_6)_2$ (**4**)

The CH_2Cl_2 solution of $[(bpy)_2Ru(bpy^{(CH_2Br)_2})](PF_6)_2$ [9] ($bpy^{(CH_2Br)_2}$ = 4,4′-bis(bromomethyl)-2,2′-bipyridyl) (586 mg, 0.561 mmol) was added to the THF solution of Na[3-(2-pyridyl)pyrazolate] (403 mg, 0.2.41 mmol) and stirred for 2 h at −78 °C and another 2 h at ambient temperature. The solution was filtered through Celite and the volatile of the filtrate was removed under reduced pressure. The obtained solid was dissolved into acetone and precipitated by the addition of Et_2O. The precipitate was dissolved into CH_2Cl_2, washed with H_2O, and dried with $MgSO_4$. The

volatile was evaporated after filtration and the solid was reprecipitated with acetone/Et_2O to yield $[(bpy)_2Ru(bpy'')](PF_6)_2$ as an red solid (342 mg, 0.291 mmol, 52%). ^1H NMR (200 MHz, acetone-d_6, RT): δ 5.71 (s, 4H, $-CH_2-$), 6.94–8.80 (34H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 54.9 (t, J_{CH} = 145 Hz, $-CH_2-$), 106.0 (dd, J_{CH} = 178, 9 Hz, C23), 120.5, 123.5, 123.8, 127.0 (d × 4, J_{CH} = 164 Hz, C12, C14, C26, C28), 125.4 (d, J_{CH} = 163 Hz, C4, C7), 128.8 (d, J_{CH} = 169 Hz, C2, C9), 133.5 (d, J_{CH} = 187 Hz, C22), 137.4 (d, J_{CH} = 158 Hz, C27), 138.9–139.0 (d, J_{CH} = 161 Hz, C3, C8), 150.2 (s, C13, C18), 150.3, 152.9 (d, J_{CH} = 181 Hz, C11 or C29), 152.6–152.7 (d, J_{CH} = 181 Hz, C1, C10), 153.1, 154.0, 158.0 (s, C15, C16, or C24, C25), 158.1 (s, C5, C6). ESI-MS: m/z = 1029: $\{[(bpy)_2Ru(bpy'')](PF_6)\}^+$, 442: $\{[(bpy)_2Ru(bpy'')]\}^{2+}$. Anal. Calc. for $C_{48}H_{38}N_{12}Ru\cdot(PF_6)_2$: C, 49.11; H, 3.26; N, 14.32. Found: C, 49.42; H, 3.40; N, 14.05%.

5.2.4. Synthesis of $[(bpy)_2Ru(bpy')Rh(cod)](PF_6)_2(BF_4)$ (**5**)

$[(bpy)_2Ru(bpy')](PF_6)_2$ (183 mg, 0.178 mmol) and $[Rh(cod)_2]BF_4$ (86 mg, 0.212 mmol) was dissolved in acetone (10 mL) and stirred at ambient temperature for 1 h. The solvent was removed under reduced pressure and the obtained solid was precipitated from acetone/Et_2O. The solid was washed with hexane and ether, and dried under vacuum to yield $[(bpy)_2Ru(bpy')Rh(cod)](PF_6)_2(BF_4)$ as an orange solid (212 mg, 0.160 mmol, 89%). ^1H NMR (200 MHz, acetone-d_6, RT): δ 1.96–2.57 (8H, cod), 2.53 (s, 3H, CH_3), 4.73 (d, J = 21.3 Hz, 4H, cod), 5.56 (d, J = 18.0 Hz, 1H, –CH*H*–), 5.71 (d, J = 18.0 Hz, 1H, –CH*H*–), 7.04–8.83 (28H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 21.1 (q, J_{CH} = 128 Hz, *C*H_3), 30.8, 31.0 (cod), 54.3 (t, J_{CH} = 145 Hz, $-CH_2-$), 83.7, 84.1 (d × 2, J_{RhC} = 13 Hz, cod), 107.0 (dd, J_{CH} = 184, 7.8 Hz, C24), 123.0, 123.4, 125.4, 126.4, 127.1, 129.8 (d × 6, J_{CH} = 162 Hz, C12, C14, C17, C19, C27, C29), 125.2, (d, J_{CH} = 167 Hz, C4, C7), 128.7 (d, J_{CH} = 165 Hz, C2, C9), 138.8 (d, J_{CH} = 169 Hz, C3, C8), 139.5 (d, J_{CH} = 195 Hz, C23), 142.3 (d, J_{CH} = 169 Hz, C28), 147.8, 151.4 (s × 2, C25, C26), 148.8 (d, J_{CH} = 197 Hz, C30), 151.6, 153.1 (d × 2, J_{CH} = 181 Hz, C11, C20), 152.5 (d, J_{CH} = 179 Hz, C1, C10), 156.2, 156.9, 158.4 (s × 3, C13, C18, C15, C16), 158.0 (s, C5, C6). ESI-MS (acetone): m/z = 1242: $\{[(bpy)_2Ru(bpy')Rh(cod)](PF_6)_2\}^+$, 1184: $\{[(bpy)_2Ru(bpy')Rh(cod)](PF_6)(BF_4)\}^+$, 1126: $\{[(bpy)_2Ru(bpy')Rh(cod)](BF_4)_2\}^+$.

5.2.5. Synthesis of $[(bpy)_2Ru(bpy')Rh(CO)_2](PF_6)_2(BF_4)$ (**6**)

$[(bpy)_2Ru(bpy')Rh(cod)](PF_6)_2(BF_4)$ (133 mg, 0.100 mmol) was dissolved in acetone (5 mL) and 1 atm of CO was charged after freeze–pump–thaw procedure. The solution was stirred at −78 °C for 1.5 h, and the temperature was gradually raised to room temperature and stirred for another 1.5 h. Hexane was added and the precipitate was washed with hexane, dried under vacuum to yield $[(bpy)_2Ru(bpy')Rh(CO)_2](PF_6)_2(BF_4)$ as an orange solid (104 mg, 0.0815 mmol, 81%). ^1H NMR (200 MHz, acetone-d_6, RT): δ 2.52 (s, 3H, $-CH_3$), 6.20 (s, 2H, $-CH_2-$), 7.23–8.91 (28H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 21.2 (q, J_{CH} = 130 Hz, $-CH_3$), 55.7 (t, J_{CH} = 144 Hz, $-CH_2-$), 107.6 (dd, J_{CH} = 186, 8.3 Hz, C24), 123.1, 124.1, 125.8, 126.4, 128.2, 129.8 (d × 6, J_{CH} = 167 Hz, C12, C14, C17, C19, C27, C29), 125.2 (d, J_{CH} = 167 Hz, C4), 128.6 (d, J_{CH} = 170 Hz, C2), 138.8 (d, J_{CH} = 169 Hz, C3), 140.0 (d, J_{CH} = 197 Hz, C23), 143.9 (d, J_{CH} = 170 Hz, C28), 146.8, 151.7 (s × 2, C25, C26), 151.4, 153.2 (d × 2, J_{CH} = 182 Hz, C11, C20), 152.5 (d, J_{CH} = 187 Hz, C1), 155.3 (d, J_{CH} = 191 Hz, C30), 156.5, 156.9, 158.6 (s × 3, C13, C18, C15, C16), 158.0 (s, C5, C6), 183.1 (d, J_{RhC} = 66 Hz, –CO). ESI-MS (acetone): m/z = 1190: $\{[(bpy)_2Ru(bpy')Rh(CO)_2](PF_6)_2\}^+$, 1132: $\{[(bpy)_2Ru(bpy')Rh(cod)](PF_6)(BF_4)\}^+$. IR ($CH_3NO_2$, cm^{-1}): ν_{CO} = 2100, 2038.

5.2.6. Synthesis of $[(bpy)_2Ru(bpy')Pt(CH_3)_2](PF_6)_2$ (**7**)

$[(bpy)_2Ru(bpy')](PF_6)_2$ (152 mg, 0.147 mmol) and $Pt(dmso)_2(CH_3)_2$ (67 mg, 0.176 mmol) were dissolved into 10 mL of acetone and stirred at ambient temperature for 1.5 h. The solvent was removed under reduced pressure. The obtained solid was precipitated from acetone/Et_2O and the precipitate was washed with Et_2O several times, dried under vacuum to yield $[(bpy)_2Ru(bpy')PdMe_2](PF_6)_2$ as a red solid (153 mg, 0.122 mmol, 83%). ^1H NMR (200 MHz, acetone-d_6, RT): δ 0.80 (s + d, $J_{Pt\text{-}H}$ = 88 Hz, 3H, Pt-*C*H_3), 0.94 (s + d, $J_{Pt\text{-}H}$ = 90 Hz, 3H, Pt-*C*H_3), 2.55 (s, 3H, bpy-CH_3), 6.02 (s, 2H, $-CH_2-$), 7.22–7.99 (28H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ −21.9, −15.0 (s, Pt-*C*H_3), 21.5 (q, J_{CH} = 127 Hz, bpy-*C*H_3), 54.3 (t, J_{CH} = 145 Hz, $-CH_2-$), 106.8 (dd, J_{CH} = 181, 8.3 Hz, C24), 123.0, 123.9, 126.3, 126.4, 126.5, 130.0 (d × 6, J_{CH} = 170 Hz, C12, C14, C17, C19, C27, C29), 125.4 (dd, J_{CH} = 167, 7 Hz, C4, C7), 128.8 (dd, J_{CH} = 169, 6 Hz, C2, C9), 135.5 (d, J_{CH} = 191 Hz, C23), 138.3 (d, J_{CH} = 167 Hz, C28), 138.9 (d, J_{CH} = 168 Hz, C3, C8), 147.0 (d, J_{CH} = 182 Hz, C30), 149.0, 151.6, 152.4, 153.3 (s × 4, C13, C18, C25, C26), 151.6, 153.0 (d × 2, J_{CH} = 182 Hz, C11, C20), 152.7, 152.8 (d × 2, J_{CH} = 184 Hz, C1, C10), 154.9, 157.4 (s × 2, C15, C16), 158.3 (s, C5, C6). ESI-MS (acetone): m/z = 1111: $\{[(bpy)_2Ru(bpy')^{195}Pt(CH_3)_2](PF_6)\}^+$. Anal. Calc. for $C_{42}H_{39}N_9PtRu\cdot(PF_6)_2$: C, 40.17; H, 3.13; N, 10.04. Found: C, 39.84; H, 3.39; N, 9.73%.

5.2.7. Synthesis of $[(bpy)_2Ru(bpy')Pd(C_3H_5)](PF_6)_2(BF_4)$ (**8**)

$[(bpy)_2Ru(bpy')](PF_6)_2$ (96.5 mg, 0.0936 mmol) and $[(C_3H_5)Pd(cod)]BF_4$ (36.6 mg, 0.107 mmol) was dissolved into 5 mL of acetone and stirred at ambient temperature for 1.5 h. Et_2O was added to the solution and the resulting precipitate was collected, washed with Et_2O, and dried under vacuum to yield $[(bpy)_2Ru(bpy')Pd(C_3H_5)](PF_6)_2(BF_4)$ as an orange solid (93 mg, 0.074 mmol, 78%). ^1H NMR (200 MHz, CD_3CN, RT): δ 2.51 (s, 3H, $-CH_3$), 3.03 (d, J = 13 Hz, 1H, C_3H_5 (*anti*)), 3.10 (d, J = 12 Hz, 1H, C_3H_5 (*anti*)), 4.21 (d, J = 7.3 Hz, 2H, C_3H_5 (*syn*)), 5.64–5.70 (m, 3H, C_3H_5, $-CH_2-$), 6.97–8.96 (29H, aromatic protons). ^{13}C NMR (100 MHz, CD_3CN, RT): δ 21.3 (q, J_{CH} = 128 Hz, C21), 55.8 (t, J_{CH} = 143 Hz, $-CH_2-$), 63.2, 63.4 (d × 2, J_{CH} = 178 Hz, C_3H_5), 107.0 (dd, J_{CH} = 183, 7.8 Hz, C24), 119.0 (d, J_{CH} = 147 Hz, C_3H_5), 122.7, 123.4, 125.7, 126.4, 127.3 (d × 5, J_{CH} = 165 Hz, C12, C14, C17, C19, C27, C29), 152.6 (d, J_{CH} = 179 Hz, C1, C10), 154.3, 156.9, 158.5 (s × 3, C13, C18, C15, C16), 158.0 (s, C5, C6). ESI-MS (acetone): m/z = 1178: $\{[(bpy)_2Ru(bpy')Pd(C_3H_5)](PF_6)_2\}^+$, 1120: $\{[(bpy)_2Ru(bpy')Pd(C_3H_5)](PF_6)(BF_4)\}^+$, 1062: $\{[(bpy)_2Ru(bpy')Pd(C_3H_5)](BF_4)_2\}^+$. Anal. Calc. for $C_{43}H_{38}N_9PdRu\cdot(PF_6)_2(BF_4)$: C, 40.83; H, 3.03; N, 9.96. Found: C, 41.22; H, 3.09; N, 9.92%.

5.2.8. Synthesis of $[(bpy)_2Ru(bpy')Pd(CH_3)(CH_3CN)](PF_6)_2(BF_4)$ (**9**)

$[(bpy)_2Ru(bpy')](PF_6)_2$ (100.3 mg, 0.0973 mmol) and [(cod)PdMeCl] (25.9 mg, 0.0977 mmol) was dissolved in acetone and stirred for 2 h. The solution was concentrated by evaporation and precipitation by Et_2O gave $[(bpy)_2Ru(bpy')PdMeCl](PF_6)_2$ (103.6 mg, 0.0872 mmol, 90%) as a reddish brown solid. ^1H NMR (200 MHz, acetone-d_6, RT): δ 1.07 (s, 3H, Pd-CH_3), 2.57 (s, 3H, bpy'-*C*H_3), 6.24 (s, 2H, $-CH_2-$), 7.22–9.10 (28H, aromatic protons).

To a $[(bpy)_2Ru(bpy')PdMeCl](PF_6)_2$ (76.0 mg, 0.0640 mmol)/Me_2CO (5 mL) solution, $AgBF_4$ (12.6 mg, 0.0647 mmol)/Me_2CO (10 mL) solution was added and stirred at RT for 3 h. The obtained solution was filtered through Celite and the filtrate was concentrated, and precipitation by Et_2O gave $[(bpy)_2Ru(bpy')PdMe(Me_2CO)](PF_6)_2(BF_4)$ (70.9 mg, 0.0547 mmol, 85%). The obtained solid (27.7 mg, 0.0022 mmol) was dissolved in CH_3CN, and precipitation by Et_2O resulted in the quantitative formation of the CH_3CN solvated complex, $[(bpy)_2Ru(bpy')PdMe(MeCN)](PF_6)_2(BF_4)$ (27.4 mg, 0.0022 mmol). ^1H NMR (200 MHz, acetone-d_6, RT): δ 1.15 (s, 3H, Pd-CH_3), 2.53 (s, 3H, bpy'-CH_3), 5.91 (s, 2H, $-CH_2-$), 7.24–9.16 (28H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6, RT): δ 3.9 (*C*H_3CN), 5.1 (Pd-*C*H_3), 21.4 (C21), 55.1 ($-CH_2-$), 106.9 (C24), 123.0, 124.3, 126.1, 126.5, 130.0

(C12, C14, C17, C19, C27, C29), 125.4 (C4), 128.8 (C2), 137.0 (C23), 139.0 (C3), 142.2 (C28), 148.1, 152.9 (C25, C26), 149.8, 152.1, 152.2 (C11, C20, C30), 152.7 (CH_3CN), 152.8 (C1), 153.4, 157.3, 158.6, 159.2 (C13, C15, C16, C18), 158.5 (C5).

*5.2.9. Synthesis of $[(bpy)_2Ru(bpy')(C_5Me_5)Rh(Me_2CO)](PF_6)_2(BF_4)_2$ (**10**)*

$[(bpy)_2Ru(bpy')](PF_6)_2$ (142 mg, 0.138 mmol) and $[(C_5Me_5)Rh(Me_2CO)(H_2O)](BF_4)_2$ (78 mg, 0.149 mmol) were dissolved into 5 mL of acetone and stirred at ambient temperature for 1.5 h. Et_2O was added to the solution and the resulting precipitate was washed with Et_2O for several times, and dried under vacuum to yield $[(bpy)_2Ru(bpy')Ru(C_5Me_5)(Me_2CO)](PF_6)_2(BF_4)_2$ as an orange solid (191 mg, 94.9%). ^{1}H NMR (200 MHz, acetone-d_6, RT): δ 1.81 (s, 15H, C_5Me_5), 2.53 (s, 3H, $-CH_3$), 6.27 (s, 2H, $-CH_2-$), 7.05–9.33 (28H, aromatic protons).

*5.2.10. Synthesis of $[(bpy)_2Ru(bpy'')\{Rh(cod)\}_2](PF_6)_2(BF_4)_2$ (**11**)*

The preparation of the complex was carried out in a similar manner as the synthesis of **5** by the addition of 2 equiv. of $[Rh(cod)_2]BF_4$ to $[(bpy)_2Ru(bpy'')](PF_6)$, which yielded $(bpy)_2Ru(bpy'')Rh(cod)_2](PF_6)_2(BF_4)_2$ (58 mg, 0.033 mmol, 91%). ^{1}H NMR (200 MHz, acetone-d_6, RT): δ 1.97–2.57 (16H, cod), 4.74 (8H, cod), 5.52, 5.65 (d, J_{CH} = 18 Hz, 4H, $-CH_2-$), 7.10–8.85 (34H, aromatic protons). ESI-MS (acetone): m/z = 1683: $\{[(bpy)_2Ru(bpy'')\{Rh(cod)\}_2](PF_6)_2BF_4\}^+$, 1625: $\{[(bpy)_2Ru(bpy'')\{Rh(cod)\}_2](PF_6)(BF_4)_2\}^+$, 1567: $\{[(bpy)_2Ru(bpy'')\{Rh(cod)\}_2](BF_4)_3^+$, Anal. Calc. for $C_{64}H_{62}N_{12}Rh_2Ru\cdot(PF_6)_2(BF_4)_2$: C, 43.44; H, 3.53; N, 9.50. Found: C, 43.64; H, 3.67; N, 9.39%.

*5.2.11. Synthesis of $[(bpy)_2Ru(bpy'')\{Rh(CO)_2\}_2](PF_6)_2(BF_4)_2$ (**12**)*

The preparation of the complex was carried out in a similar manner as the synthesis of **6**. ^{1}H NMR (200 MHz, acetone-d_6, RT): δ 6.13 (s, 4H, $-CH_2-$), 7.29–8.90 (34H, aromatic protons). Anal. Calc. for $C_{52}H_{38}N_{12}O_4Rh_2Ru\cdot(PF_6)_2(BF_4)_2$: C, 37.50; H, 2.30; N, 10.09. Found: C, 37.26; H, 2.57; N, 9.77.

*5.2.12. Synthesis of $[(bpy)_2Ru(bpy'')(PtMe_2)_2](PF_6)_2$ (**13**)*

The preparation of the complex was carried out in a similar fashion as the synthesis of **7** by treating 2 molar of $Pt(DMSO)_2(CH_3)_2$ to $[(bpy)_2Ru(bpy'')](PF_6)$, which yielded $[(bpy)_2Ru(bpy'')(PtMe_2)_2](PF_6)_2(BF_4)_2$. ^{1}H NMR (200 MHz, acetone-d_6, RT): δ 0.73 (s + d, J_{Pt-H} = 87 Hz, 3H, Pt-CH_3), 0.92 (s + d, J_{Pt-H} = 90 Hz, 3H, Pt-CH_3), 6.00 (s, 4H, $-CH_2-$), 7.21–9.02 (34H, aromatic protons). ESI-MS (acetone): m/z = 1479: $\{[(bpy)_2Ru(bpy'')(PtMe_2)_2]PF_6\}^+$.

*5.2.13. Synthesis of $[(bpy)_2Ru(bpy'')\{Pd(C_3H_5)\}_2](PF_6)_2(BF_4)_2$ (**14**)*

The preparation of the complex was carried out in a similar fashion as the synthesis of **8** by treating 2 equiv. of $[(C_3H_5)Pd(cod)]BF_4$ to $[(bpy)_2Ru(bpy'')](PF_6)$, which yielded $[(bpy)_2Ru(bpy'')\{Pd(C_3H_5)\}_2](PF_6)_2(BF_4)_2$. ^{1}H NMR (200 MHz, CD_3CN, RT): δ 3.04 (dd, J = 14, 13 Hz, 4H, C_3H_5), 4.19 (d, J = 6.8 Hz, 4H, C_3H_5), 5.63–5.70 (m, 6H, C_3H_5 + $-CH_2-$), 6.96–8.70 (34H, aromatic protons). ESI-MS (acetone): m/z = 1497: $\{[(bpy)_2Ru(bpy'')\{Pd(C_3H_5)\}_2](PF_6)(BF_4)_2\}^+$. Anal. Calc. for $C_{54}H_{48}N_{12}Pd_2Ru\cdot(PF_6)_2(BF_4)_2$: C, 39.49; H, 2.95; N, 10.23. Found: C, 39.86; H, 3.14; N, 10.04%.

*5.2.14. Synthesis of $[(bpy)_2Ru(bpy'')\{(C_5Me_5)Rh(Me_2CO)\}_2](PF_6)_2(BF_4)_2$ (**15**)*

The preparation of the complex was carried out in a similar manner as the synthesis of **10** by treating 2 equiv. of $[(C_5Me_5)Rh(acetone)_2(H_2O)](BF_4)_2$ to $[(bpy)_2Ru(bpy'')](PF_6)$, which yielded $[(bpy)_2Ru(bpy'')\{(C_5Me_5)Rh(Me_2CO)\}_2](PF_6)_2(BF_4)_2$. ^{1}H NMR (200 MHz, acetone-d_6, RT): δ 1.79 (s, 30H, C_5Me_5), 6.29 (s, 4H, $-CH_2-$), 6.88–9.40 (34H, aromatic protons).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.024.

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