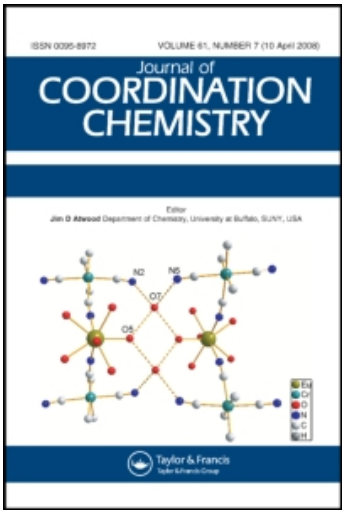

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and properties of ruthenium(II) complexes of 3,3'-polymethylene-2-(pyrid-2'-yl)benzo[*b*]-1,10-phenanthrolines

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First published on: 11 June 2010

To cite this Article Jahng, Yurngdong , Hong, Young Hwan and Rahman, A.F.M. Motiur(2010) 'Synthesis and properties of ruthenium(II) complexes of 3,3'-polymethylene-2-(pyrid-2'-yl)benzo[*b*]-1,10-phenanthrolines', Journal of Coordination Chemistry, 63: 10, 1774 — 1784, First published on: 11 June 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.487101
URL: http://dx.doi.org/10.1080/00958972.2010.487101

Journal of Coordination Chemistry
Vol. 63, No. 10, 20 May 2010, 1774–1784

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Synthesis and properties of ruthenium(II) complexes of 3,3′-polymethylene-2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthrolines

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(*Received 5 October 2009; in final form 11 March 2010*)

Coordination abilities of unsymmetrical tridentate ligands, 3,3′-polymethylene-2-(pyrid-2′-yl)-benzo[*b*]-1,10-phenanthrolines (**4**) were studied. Reactions of the 3,3′-di- and 3,3′-trimethylene-2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthrolines (**4b** and **4c**) with $RuCl_3 \cdot 3H_2O$ afforded $[Ru(\mathbf{4b})_2]^{2+}$ and $[Ru(\mathbf{4c})_2]^{2+}$ in 57% and 78% yield, respectively, while reactions of the parent non-bridged ligand (**4a**), tetramethylene-bridged ligand (**4d**), and fully aromatized ligand (**4e**) afforded a messy mixture. Reactions of **4** with $Ru(tpy)Cl_3$ (tpy = 2,2′;6′,2″-terpyridine) afforded $[Ru(tpy)(\mathbf{4})]^{2+}$ in 61–72% yields. UV absorption spectra of the ligands showed four ligand-centered (LC) π–π^* transitions and their Ru complexes showed four LC π–π^* transitions and one $Ru(d_\pi) \rightarrow$ ligand(π^*) MLCT. The ligands showed three major emission maxima ($\lambda_{emission}$) in the region of 393–418, 416–445, and 437–471 nm in which $\lambda_{emission}$ is highly dependent on the length of the methylene bridge connecting C3 of benzo[*b*]-1,10-phenanthroline and C3 of pyridine. Ru complexes with fully aromatic ligand, $[Ru(tpy)(\mathbf{4e})]^{2+}$, and the most distorted ligand, $[Ru(tpy)(\mathbf{4d})]^{2+}$, showed two emission maxima at 410 and 444–446 nm, while the others showed one emission at 410 nm. Each of the emission maxima is bathochromatically shifted from the complex with the most distorted ligand (**4d**) to the complex with fully aromatized planar ligand (**4e**) indicating lower energy emission.

Keywords: $RuCl_3$; $Ru(tpy)Cl_3$; 3,3′-Polymethylene-2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthroline; Unsymmetrical tridentate; Photoluminescence

1. Introduction

Ru(II) complexes of planar polycyclic aromatic ligands are used in the field of biotechnology owing to their DNA binding ability [1–3] and as precursors for photoredox-active catalysts used to convert solar energy into chemical energy [4–6] and water to oxygen [7–9]. Such potentials led to the design and synthesis of new polydentates to improve detection limits and selectivity toward nucleic acids [10–12] and also the efficiency for photoredox-active catalyst [13]. Complex formation chemistry and the structures of Ru complexes of various polydentates are still popular [14, 15].

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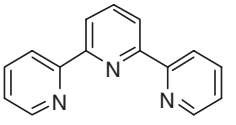
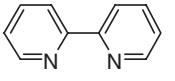
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.487101

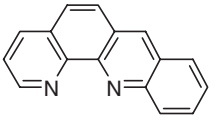
The 2,2′;6′,2″-terpyridine (**1**, tpy), a next higher homologue of 2,2′-bipyridine (**2**), is a symmetrical *N*,*N*,*N*-tridentate first prepared in 1932 [16], tpy is the most studied symmetrical tridentate with metal complexes employed for photophysical [17] and biological utilities [18, 19].



1 (tpy)



2 (bpy)



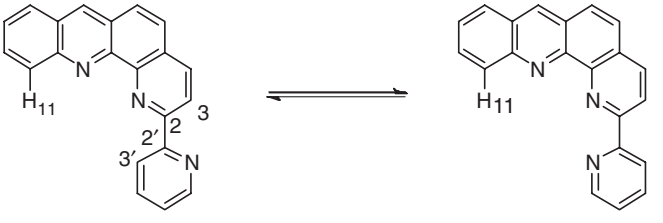
3

However, studies on the polypyridine-derived unsymmetrical *N*,*N*,*N*-tridentates (L) are limited [20–22], especially tridentates with acridine moiety, even though unsymmetrical tridentates have advantages. The major merit of unsymmetrical tridentate ligands is their potentials to form chiral ML_2 complexes and chiral M(L)(L′)X-type mixed complexes with d_6 metals, where L′ is a symmetric bidentate and X a leaving group [23].

Recently, we reported the synthesis of 4-aminoacridine-3-carbaldehyde as a Friedländer synthon for the preparation of polydentates with benzo[*b*]-1,10-phenanthroline (**3**) [24] and related compounds such as **4** [25, 26]. However, the metal complex chemistry of these compounds has not been pursued as yet.

Although clear evidence for the conformation of **4a** has not been established, studies on bpy [27–29] and tpy [30–32] may lead to a tentative conclusion that the transoid conformation (*trans*-**4a**) is favored, especially in the solution. However, the *cisoid* conformation (*cis*-**4a**) is responsible for coordination chemistry and the steric role of *peri*-H (H-11) becomes important. The steric hindrance of *peri*-H in complexation is severe enough to lower the yield of bis-complex significantly, even the rigid *cis*-conformation in symmetric tridentate [33].

Introduction of a polymethylene bridge onto 3- and 3′-positions of **4a** forces a *cis*-conformation. Such polymethylene bridge additionally controls the dihedral angle between the benzo[*b*]-1,10-phenanthroline and pyridine rings, and thus releases steric congestion in the complex caused by hydrogen (H11) at the *peri*-position by twisting two aromatic planes through the 2,2′-bond.



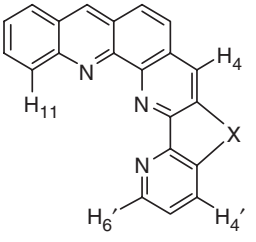
trans-**4a** (more stable)

cis-**4a** (responsible for coordination)

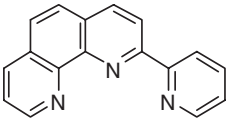
As a part of our interest in the design and synthesis of new polydentate ligands, especially unsymmetrical *N*,*N*,*N*-tridentate ligands, and their metal complex chemistry, we herein describe the synthesis and properties of Ru complexes of **4a** and its 3,3′-polymethylene-annulated derivatives **4b**–**e**.

2. Results and discussion

The ligands, 2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthrolines (**4a**) and 3,3′-polymethylene-2-(pyrid-2′-yl)-benzo[*b*]-1,10-phenanthrolines (**4b–e**), were prepared *via* Friedländer condensation of 4-aminoacridine-3-carbaldehyde [24] with 2-acetylpyridine and pyrido[*b*]cycloalkanones [34, 35], by the previously reported method [26].



4b X = –$(CH_2)_2$–
c X = –$(CH_2)_3$–
d X = –$(CH_2)_4$–
e X = –CH=CH–



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Initial attempts to prepare the metal complexes of **4a** with various d_6 metals did not afford bis-complex, but instead afforded a complex mixture of products that were either not isolable or not characterizable [36]. Such result can be compared with the behavior of 2-(pyrid-2′-yl)-1,10-phenanthroline (**5**), in which *peri*-H is absent and $[Ru(\mathbf{5})_2]^{2+}$ is formed in over 90% yield [37]. Steric congestion of the *peri*-H (H11) in the bis-complex and free-rotation of 2,2′-bond could explain such difference based on the previous reports. Low yields [33] of a tridentate system with *peri*-H and complex mixtures of the products due to the free rotation of the 2,2′-bond of tridentate ligands [38, 39] have also been previously reported.

Reactions of 3,3′-di- and 3,3′-trimethylene-2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthrolines (**4b** and **4c**) with $RuCl_3 \cdot 3H_2O$, however, afforded $[Ru(\mathbf{4b})_2](PF_6)_2$ and $[Ru(\mathbf{4c})_2](PF_6)_2$ in 57% and 78% yields, respectively, after anion exchange with NH_4PF_6. Reaction of **4d** gave a highly water insoluble dark brown solid (65%) which is expected to be a monocoordinated $Ru(\mathbf{4d})Cl_3$. Although a subsequent reaction with **4d** did not proceed to bis complex $[Ru(\mathbf{4d})_2]Cl_2$, a reaction with tpy afforded $[Ru(tpy)(\mathbf{4d})]^{2+}$ to confirm the structure. Reaction of **4e** with $RuCl_3 \cdot 3H_2O$ did not afford the desired $[Ru(\mathbf{4e})_2]^{2+}$, but instead highly insoluble dark brown solid, which did not convert into either $[Ru(\mathbf{4e})_2]^{2+}$ or $[Ru(tpy)(\mathbf{4e})]^{2+}$ by the addition of **4e** and tpy, respectively.

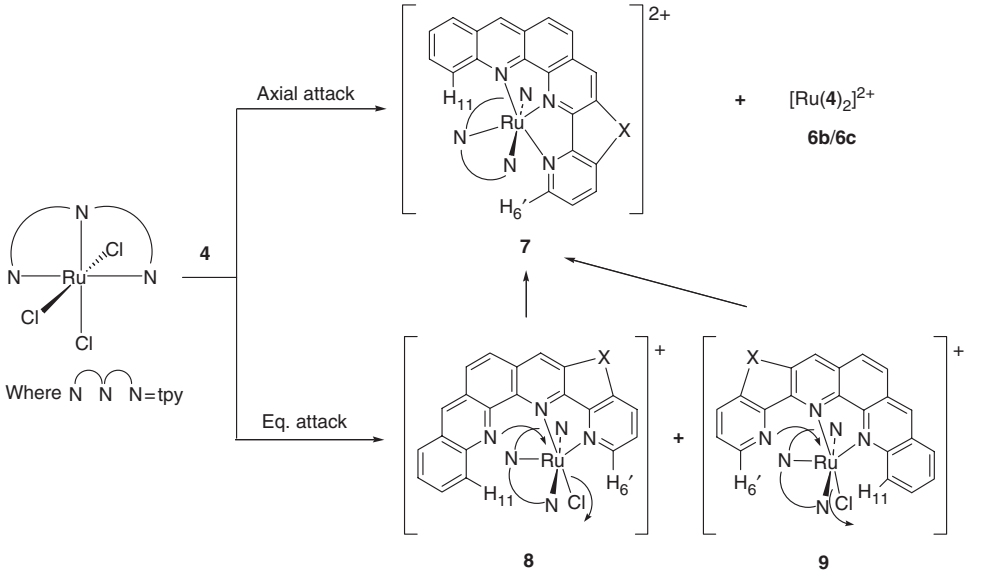
$$\underset{\mathbf{6}}{Ru(\mathbf{4})_2(PF_6)_2} \xleftarrow[\text{(ii) } NH_4PF_6]{\text{(i) } RuCl_3\text{-}3H_2O} \mathbf{4} \xrightarrow[\text{(ii) } NH_4PF_6]{\text{(i) } Ru(tpy)Cl_3} \underset{\mathbf{7}}{Ru(tpy)(\mathbf{4})(PF_6)_2}$$

Coordination of two unsymmetrical tridentates on d_6 metals would create a chirality axis. The $[Ru(\mathbf{4})_2]^{2+}$ complexes are chiral with two enantiomers. Attempts to resolve each enantiomer employing previous methods [40–42] were not successful.

Reactions of **4** with $Ru(tpy)Cl_3$ [43] in refluxing aq. EtOH, followed by anion exchange with NH_4PF_6, afforded six-coordinate complexes, $[Ru(tpy)(\mathbf{4})](PF_6)_2$ (**7**), and a trace of bis-complex, $[Ru(\mathbf{4b})_2](PF_6)_2$ (**6b**) and $[Ru(\mathbf{4c})_2](PF_6)_2$ (**6c**). Reactions of unsymmetrical *N*,*N*,*N*-tridentate ligands with $RuCl_3 \cdot 3H_2O$ afforded pentaaza-coordinate (N_5) complex, $[Ru(L\text{-}N,N',N'')(L\text{-}N,N')Cl]^+$, and a hexaaza-coordinate (N_6)

complex, $[Ru(L\text{-}N,N',N'')_2]^{2+}$ [21]. Similar result has also been observed in the reaction of *N*,*N*,*C*-tridentate with $Ru(tpy)Cl_3$ to afford a pentaaza-coordinate (N_5) complex, $[Ru(tpy\text{-}N,N',N'')(L\text{-}N,N')Cl]^{+}$, and a hexaaza-coordinate (N_5C) complex, $[Ru(tpy\text{-}N,N',N'')(L\text{-}N,N',C)]^{+}$ [44, 45]. These results strongly support the reaction mechanism shown in scheme 1. However, no evidence of pentaaza-coordinate (N_5) complexes (e.g., **8** and **9**) was found in the reactions with either $RuCl_3$ or $Ru(tpy)Cl_3$. On steric, electronic, and statistical grounds the lone pairs of electrons on N1′ in the distal pyridines should be more nucleophilic than either N1 or N12 of the ligands, thus equatorial attack *via* intermediate **8** of the second ligand is expected to be favored. In addition, pentaaza-coordinate complexes (**8** and/or **9**) would be geometrically and sterically forced to undergo nucleophilic substitution of Cl by the distal N of the ligand giving mixed complex **9**, as shown in scheme 1 and as reported previously [21, 44, 45]. The formation of **6b** and **6c** could be explained by reversible coordination. The release of the tpy from $Ru(tpy)Cl_3$, **8**, and **9** could lead to $Ru(H_2O)_mCl_n$ (where $m+n=6$) [46] and/or $Ru(\mathbf{4})Cl_3$, which then undergo second coordination by **4b** and **4c**, as described previously [47].

Each proton resonance of the ligands and their complexes were assigned based on double-quantum filtered COSY. The ^{1}H NMR spectra of **6** and **7** had a couple of characteristic features, in which the proton resonance pattern of the ligands (**4**) in **6** and **7** are very similar (table 1). Coordination generally depleted electron density on N causing downfield shift of proton resonances. The resonances of H7 were shifted downfield by 0.24–0.32 ppm compared with those of the ligands except **7d**. In addition, H4 is held in the deshielding plane of the distal pyridine and the quinoline rings of the orthogonal ligand, thus downfield-shifted up to 0.55–0.81 ppm except **7e**. On the other hand, H11 of the benzo[*b*]-1,10-phenanthroline moiety resonated at δ 6.59–6.97, upfield by 1.56–2.04 ppm due to the shielding of central pyridine in the orthogonal tpy. Similarly, H6′ of the distal pyridine ring of **4** resonated at δ 6.63–7.36, upfield-shifted by



Scheme 1. Possible reaction mechanism for complex **7**.

1.71–2.00 ppm, and H6′(H6″) of tpy were at δ 7.04–7.25 upfield-shifted by 1.36–1.66 ppm, comparable to 1.36 ppm of $[Ru(tpy)_2]^{2+}$. The chemical shifts of H10 and H5′ were upfield-shifted by 1.0–1.23 ppm due to the same effect, but reduced by distance. Two aliphatic carbons Cα and Cα' of $[Ru(tpy)(\mathbf{4c})]^{2+}$ coincidently resonated at δ 37.64 downfield by 5.16 and 7.17 ppm, respectively, compared with the parent ligand due to the deshielding of orthogonal tpy; Cβ lay was shielded by orthogonal tpy, thus shifted upfield by 6.31 ppm.

Absorption patterns of **6** and **7** are quite similar (figure 1) with four major ligand-based absorptions and one MLCT (table 2). The UV spectral data of **3**, reported previously as an organic light-emitting device with improved operational stability [48],

Table 1. Chemical shifts of selected H's of **4**[a] and their Ru(II) complexes **6** and **7**.

Compound	H6′ of **4**	H11 of **4**	H7 of **4**	H4 of **4**	H6′(H6″) of tpy
4a	8.75	8.88	8.88	7.65	–
4b	8.63	8.54	8.85	7.96	–
4c	8.61	8.61	8.73	8.06	–
4d	8.70	8.54	8.75	8.11	–
4e[b]	9.22	8.53	9.19	9.19	
$[Ru(\mathbf{4b})_2]^{2+}$	6.63 ($\Delta-2.00$)	6.79 ($\Delta-1.75$)	9.10 ($\Delta+0.28$)	8.77 ($\Delta+0.81$)	–
$[Ru(\mathbf{4c})_2]^{2+}$	6.86 ($\Delta-1.75$)	6.59 ($\Delta-2.02$)	9.02 ($\Delta+0.29$)	8.81 ($\Delta+0.79$)	–
$[Ru(tpy)(\mathbf{4a})]^{2+}$	7.00 ($\Delta-1.75$)	6.84 ($\Delta-2.04$)	9.16 ($\Delta+0.28$)	8.15 ($\Delta+0.50$)	7.21 ($\Delta-1.49$)
$[Ru(tpy)(\mathbf{4b})]^{2+}$	6.77 ($\Delta-1.86$)	6.82 ($\Delta-1.72$)	9.09 ($\Delta+0.24$)	8.57 ($\Delta+0.61$)	7.25 ($\Delta-1.45$)
$[Ru(tpy)(\mathbf{4c})]^{2+}$	6.90 ($\Delta-1.71$)	6.71 ($\Delta-1.90$)	9.06 ($\Delta+0.32$)	8.66 ($\Delta+0.60$)	7.24 ($\Delta-1.46$)
$[Ru(tpy)(\mathbf{4d})]^{2+}$	6.89 ($\Delta-1.81$)	6.69 ($\Delta-1.85$)	9.07 ($\Delta+0.32$)	8.66 ($\Delta+0.55$)	7.15 ($\Delta-1.55$)
$[Ru(tpy)(\mathbf{4e})]^{2+}$	7.36 ($\Delta-1.86$)	6.97 ($\Delta-1.56$)	9.33 ($\Delta+0.14$)	9.14 ($\Delta-0.05$)	7.04 ($\Delta-1.66$)
$[Ru(tpy)_2]^{2+}$[c]	-	-	-	-	7.34 ($\Delta-1.36$)

[a]Data for the ligands were taken from [25].
[b]Each proton refers the same proton as in **4a**–**d** for consistency, as shown in scheme 1, although the numbering pattern is not matched to **4e** based on the IUPAC nomenclature.
[c]H6′ and H6″ of tpy were resonanced at δ 8.70 and data were taken from Thummel *et al.* [33].

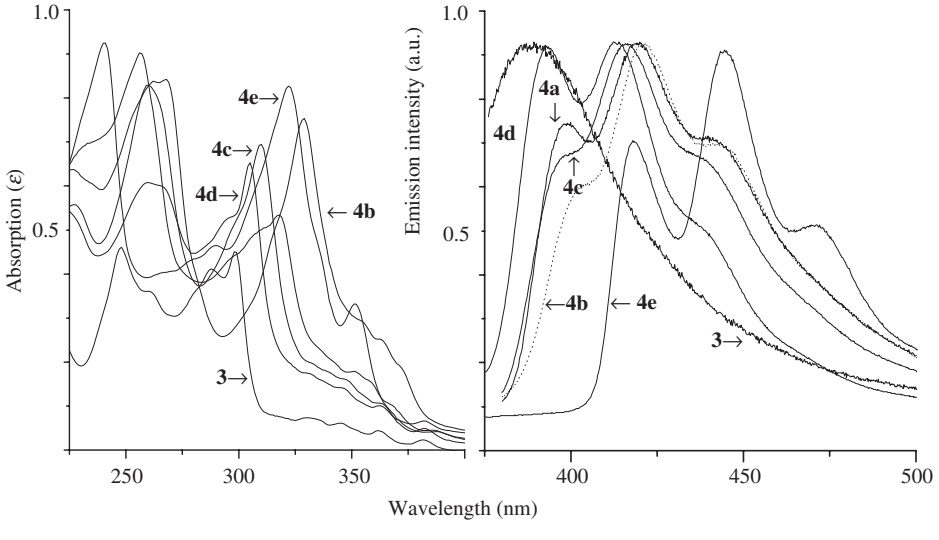


Figure 1. Absorption (left) and emission (right) spectra of **3** and ligands (**4**) in deaerated CH_3CN at 298 K.

Table 2. UV-Vis absorption spectral data for **4**, **6**, and **7** (CH_3CN).

Compound	λ_{max} nm ($\log \varepsilon$, $cm^{-1} M^{-1}$)					$\lambda_{emission}$		
4a	256 (5.03)	297 (4.71)	318 (4.80)	355 (4.59)[a]		398	418	441
4b	268 (5.02)	315 (4.78)	329 (4.97)	365 (4.48)[a]		402	420	442
4c	260 (5.02)	297 (4.80)	310 (4.94)	347 (4.31)[a]		397	414	437
4d	260 (4.88)	294 (4.81)	305 (4.91)	334 (4.31)[a]		392	413	437
4e	241 (5.06)	290 (4.76)	322 (5.01)	351 (4.62)[a]		417	444	471
3	247 (4.76)	261 (4.64)	287 (4.70)	298 (4.75)		388		
$[Ru(\mathbf{4b})_2]^{2+}$	244 (4.83)	272 (4.78)	323 (4.77)	370 (4.50)	495 (4.17)	418		
$[Ru(\mathbf{4c})_2]^{2+}$	247 (4.82)	272 (4.73)	327 (4.79)	372 (4.35)	507 (4.12)	410	430	
$[Ru(tpy)(\mathbf{4a})]^{2+}$	241 (4.74)	266 (4.73)	310 (4.74)	368 (4.18)	481 (4.14)	448		
$[Ru(tpy)(\mathbf{4b})]^{2+}$	245 (4.83)	270 (4.81)	312 (4.86)	366 (4.36)	487 (4.28)	410		
$[Ru(tpy)(\mathbf{4c})]^{2+}$	245 (4.83)	270 (4.81)	313 (4.86)	367 (4.35)	487 (4.28)	410		
$[Ru(tpy)(\mathbf{4d})]^{2+}$	244 (4.85)	271 (4.83)	312 (4.84)	368 (4.34)	486 (4.25)	410	446	
$[Ru(tpy)(\mathbf{4e})]^{2+}$	238 (4.95) 478 (4.29)	271 (4.78)	309 (4.86)	331 (4.89)	355 (4.51)	410	444	
$[Ru(tpy)_2]^{2+}$ [b]	240 (4.49) 475 (4.21)	270 (4.63)	280 (4.46)	310 (4.85)	330 (4.52)	No emission		

[a]Data were taken from [25].
[b]Data were taken from [33].

were presented for comparison. As is typical for Ru(II) complexes, strong absorption in the ultraviolet (UV) and near-UV regions is attributable to ligand-centered (LC) π–π^* transitions [49]. In the homoleptic bis-complexes $[Ru(\mathbf{4})_2]^{2+}$ and the heteroleptic complexes $[Ru(tpy)(\mathbf{4})]^{2+}$, LC π–π^* transitions resulted in four major absorption maxima in the regions 238–247, 266–272, 309–327, 355–372 nm corresponding to those of $[Ru(tpy)_2]^{2+}$. The broad absorptions at 478–507 nm in the complexes are typical of Ru(II) complexes and correspond to $Ru(d_\pi) \rightarrow ligand(\pi^*)$ MLCT, an approximate 3–32 nm shift to lower energy for the two complexes compared with that of $[Ru(tpy)_2]^{2+}$ [33]. Such bathochromatic shift may be explained by the stabilization of the metal t_{2g} orbital, caused by the additional fused benzene ring that enables the delocalization of charge and, thus, the MLCT absorption shifts to lower energy [50–52].

The solution photoluminescences of ligands (**4**) and complexes (**6** and **7**) were studied in CH_3CN (8×10^{-6} M) and are presented in table 2 and figure 1. All the ligands could be excited by 351–365 nm light to show three major emission wavelengths, 392–417, 418–444, and 437–471 nm. The observed emission wavelength is highly dependent on the length of the methylene bridge connecting C3 of bphen and C3 of pyridine. Each of the emission maxima is bathochromatically shifted from the complex with the most distorted ligand (**4d**) to the complex with fully aromatized planar ligand (**4e**), indicating that the higher degree of conjugation as well as planarity results in a significant decrease in the energy of the emission maximum. The parent non-bridged ligand lies between the tri- and tetra-methylene-bridged ligands, as expected from the dihedral angle between the two aromatic planes. The Ru complexes showed one or two emission maxima in contrast to $[Ru(tpy)_2]^{2+}$, which does not show any emission at room temperature [50, 53, 54]. The complex **7e** with fully aromatic planar ligand and **7d** most distorted showed two clear emission maxima at 410 and 444–446 nm while the others were at 410 nm except the complex **7a** at 448 nm.

In conclusion, homo- and heteroleptic Ru complexes of a series of 3,3′-polymethylene-2-(pyrid-2′-yl)benzo[*b*]-1,10-phenanthrolines, $[Ru(\mathbf{4})_2]^{2+}$ and $[Ru(tpy)(\mathbf{4})]^{2+}$ were prepared and characterized by spectroscopic methods. Reactions of the

parent non-bridged ligand (**4a**), tetramethylene-bridged ligand (**4d**), and fully aromatized ligand (**4e**) with $RuCl_3$ afforded a messy mixture while reactions of **4b** and **4c** afforded bis-complexes, $[Ru(\mathbf{4})_2]^{2+}$. Reactions of **4** with $Ru(tpy)Cl_3$ afforded $[Ru(tpy)(\mathbf{4})]^{2+}$. Ru complexes showed four major absorption maxima for LC π–π^* transitions and one $Ru(d_\pi) \rightarrow$ ligand(π^*) MLCT absorption. The ligands showed three major emission maxima, in which the emission wavelength is highly dependent on the length of the methylene bridge connecting C3 of benzo[*b*]-1,10-phenanthroline and C3 of pyridine. Each emission maximum is bathochromatically shifted from the complex with the most distorted ligand (**4d**) to the complex with fully aromatized planar ligand (**4e**), indicating lower energy photoluminescence. Ru complexes showed one or two emission maxima at room temperature. The complexes with fully aromatic ligand, $[Ru(tpy)(\mathbf{4e})]^{2+}$, and the most distorted ligand, $[Ru(tpy)(\mathbf{4d})]^{2+}$, showed two emission maxima at 410 and 444–446 nm while the others had one. Resolution of the enantiomers of $[Ru(\mathbf{4b/c})_2]^{2+}$ and $[Ru(tpy)(\mathbf{4d})]^{2+}$ as well as studies on the biological properties of the Ru(II) complexes are in progress.

3. Experimental

Melting points were determined using a Fischer–Jones melting points apparatus and are not corrected. UV spectra were recorded on a JASCO-V550 spectrophotometer, and emission spectra on an F-4500 Fluorescence Spectrophotometer, Rigong International, Japan. NMR spectra were obtained using a Bruker-250 spectrometer 250 MHz for ^1H NMR and 62.5 MHz for ^{13}C NMR and are reported as parts per million from the internal standard tetramethylsilane (TMS). Chemicals and solvents were of commercial reagent grade and used without purification. The starting 4-aminoacridine-3-carbaldehyde [24] and $Ru(tpy)Cl_3$ [43] were prepared by using previously reported methods. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on an LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer.

3.1. *Reaction of 4b with $RuCl_3 \cdot 3H_2O$*

General procedure: A mixture of $RuCl_3 \cdot 3H_2O$ (52 mg, 0.2 mmol) and **4b** (67 mg, 0.2 mmol), and Et_3N (three drops) in EtOH : H_2O (3 : 1, 12 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered to remove insoluble materials. NH_4PF_6 (23.2 mg. 0.2 mmol) in water (5 mL) was added to the filtrate and the solvent was evaporated to dryness. The resulting residue was chromatographed on Al_2O_3 (30 g) eluting with CH_3CN : toluene (1 : 1). The early fractions [R_f = 0.50 (toluene : CH_3CN = 1 : 1)] gave $[Ru(\mathbf{4b})_2](PF_6)_2$ (**6b**) as purple needles [R_f = 0.6, CH_3CN : toluene (1 : 1)] (45 mg, 57%); m.p. > 310°C. ^1H NMR (CD_3CN, 250 MHz) δ 9.09 (s, 2H, H7), 8.77 (s, 2H, H4), 8.41 (AB quartet, 4H, H5 and H6), 8.04 (d, 2H, J = 8.5 Hz, H4′), 7.57 (d, 2H, J = 8.0 Hz, H8), 7.47 (t, 2H, J = 8.0 Hz, H9), 7.26 (td, 2H, J = 8.3, 1.2 Hz, H10), 6.91 (dd, 2H, J = 8.5, 5.2 Hz, H5′), 6.79 (d, 2H, J = 8.8 Hz, H11), 6.63 (d, 2H, J = 5.2 Hz, H6′), 3.78 (t, 4H, J = 7.5 Hz),

3.43 (t, 4H, $J = 7.5$ Hz). ESI mass for $[RuC_{46}H_{30}N_6]^+$: 768.16. Found: 768.44. Elemental analysis for $C_{46}H_{30}F_{12}N_6P_2Ru$: C, 52.25 (Calcd 52.23); H, 2.87 (Calcd 2.86); N, 7.98 (Calcd 7.95).

$[Ru(\mathbf{4c})_2](PF_6)_2$ (**6c**): Purple solid (78%) [$R_f = 0.63$, CH_3CN : toluene (2 : 3)] ^{1}H NMR (CD_3CN, 250 MHz) δ 9.02 (s, 2H, H7), 8.81 (s, 2H, H4), 8.32 (AB quartet, 4H, H5 and H6), 8.00 (d, 2H, $J = 9.5$ Hz, H4′), 7.52 (d, 2H, $J = 7.5$ Hz, H8), 7.44 (td, 2H, $J = 8.0$, 1.2 Hz, H9), 7.20 (td, 2H, $J = 8.3$, 1.2 Hz, H10), 6.86–6.79 (m, 2H, H5′ and H6′), 6.59 (d, 1H, J = 9.3 Hz, H11), 3.37 (t, 4H, $J = 6.7$ Hz), 3.28 (t, 4H, $J = 6.7$ Hz), 2.14 (m, 4H). ESI mass Calcd for $[RuC_{48}H_{34}N_6]^+$: 796.19. Found: 796.43. Elemental analysis for $C_{48}H_{34}F_{12}N_6P_2Ru$: C, 53.21 (Calcd 53.09); H, 3.14 (Calcd 3.16); N, 7.78 (Calcd 7.74).

3.2. *Reactions of 4 with Ru(tpy)Cl$_3$*

General procedure: A mixture of $Ru(tpy)Cl_3$ (44 mg, 0.1 mmol), **4a** [55] (31 mg, 0.1 mmol), and Et_3N (three drops) in EtOH : H_2O (3 : 1, 12 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered to remove insoluble materials. NH_4PF_6 (11.6 mg. 0.1 mmol) in water (5 mL) was added to the filtrate and the solvent was evaporated to dryness. The resulting residue was chromatographed on Al_2O_3 (30 g) eluting with CH_3CN : toluene (1 : 1). The latter fractions [$R_f = 0.4$, CH_3CN : toluene (1 : 1)] afforded $[Ru(tpy)(\mathbf{4a})](PF_6)_2$ (**7a**) as purple needles (45 mg, 61%): m.p. > 310°C. ^{1}H NMR (CD_3CN, 250 MHz) δ 9.16 (s, 1H, H7 of **4a**), 8.99–8.88 (m, 4H, H3 and H5 of tpy, H3 and H3′ of **4a**), 8.57 (t, 2H, $J = 8.0$ Hz, H4′ and H4″ of tpy), 8.48 (m, 2H, H4 and H4′ of **4a**), 8.37 (AB quartet, 2H, H5 and H6 of **4a**), 8.15 (d, 1H, $J = 7.8$ Hz, H8 of **4a**), 7.90 (t, 1H, $J = 7.9$ Hz, H4 of tpy), 7.81 (t, 2H, $J = 7.9$ Hz, H3′ and H3″ of tpy), 7.57 (t, 1H, $J = 8.4$ Hz, H9 of **4a**), 7.48 (t, 1H, $J = 8.4$ Hz, H10 of **4a**), 7.21 (dd, 2H, $J = 5.1$, 0.9 Hz, H6′ and H6″ of tpy), 7.22 (d, 1H, $J = 5.1$, 0.9 Hz, H6′ of **4a**), 7.00–6.93 (m, 3H, H5′ and H5″ of tpy, H5′ of **4a**), 6.84 (d, 1H, $J = 8.4$ Hz, H11 of **4a**). ^{13}C NMR (CD_3CN, 62.5 MHz) δ 159.5, 158.7, 156.5, 155.1, 154.2, 153.3, 152.9, 150.9, 148.2, 139.7, 139.0, 138.9, 137.5, 134.54, 134.49, 133.1, 131.4, 131.1, 129.9, 129.5, 128.9, 128.7, 128.2, 126.7, 125.6, 125.5, 125.4, 124.7, 123.3. ESI mass Calcd for $[C_{36}H_{24}N_6Ru]^+$: 641.69. Found: 641.65. Elemental analysis for $C_{36}H_{24}F_{12}N_6P_2Ru$: C, 46.82 (Calcd 46.41); H, 2.61 (Calcd 2.60); N, 9.00 (Calcd 9.02).

3.3. *[Ru(tpy)(4b)](PF$_6$)$_2$ (7b)*

Red-purple needles (67%) [$R_f = 0.4$, CH_3CN : toluene (1 : 1)]: m.p. > 300°C. ^{1}H NMR (CD_3CN, 250 MHz) δ 9.09 (s, 1H, H7 of **4b**), 8.89 (d, 2H, $J = 8.2$ Hz, H3 and H5 of tpy), 8.57 (s, 1H, H4 of **4b**), 8.55 (t, 1H, $J = 8.2$ Hz, H4 of tpy), 8.48 (d, 1H, $J = 8.3$ Hz, H4′ of **4b**), 8.29 (AB quartet, 2H, H5 and H6 of **4b**), 8.11 (d, 2H, $J = 8.3$ Hz, H3′ and H3″ of tpy), 7.81 (td, 2H, $J = 8.3$, 1.2 Hz, H4′ and H4″ of tpy), 7.65 (d, 1H, $J = 8.1$, 0.9 Hz, H8 of **4b**), 7.53 (td, 1H, $J = 8.1$, 0.9 Hz, H9 of **4b**), 7.46 (td, 1H, $J = 8.1$, 0.9 Hz, H10 of **4b**), 7.25 (dd, 2H, $J = 5.5$, 1.2 Hz, H6′ and H6″ of tpy), 7.07 (dd, 1H, $J = 8.3$, 5.5 Hz, H5′ of **4b**), 7.00 (dd, 2H, $J = 8.3$, 5.5 Hz, H5′ and H5″ of tpy), 6.82 (d, 1H, $J = 8.1$ Hz, H11 of **4b**), 6.77 (dd, 1H, $J = 5.5$, 1.0 Hz, H6′ of **4b**), 3.70 (t, 2H, $J = 5.8$ Hz), 3.40 (t, 2H, $J = 5.8$ Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.7, 158.4, 156.5, 155.0, 154.2, 153.2,

150.6, 150.4, 146.7, 144.1, 142.6, 142.1, 139.6, 139.0, 137.3, 136.5, 133.3, 132.3, 131.5, 131.2, 129.8, 129.5, 128.7, 128.3, 127.3, 126.3, 125.6, 125.5, 124.4, 35.64, 34.91. ESI mass Calcd for $[C_{38}H_{26}N_6Ru]^+$: 667.72. Found 667.43. Elemental analysis for $C_{38}H_{26}F_{12}N_6P_2Ru$: C, 45.89 (Calcd 47.66); H, 2.67 (Calcd 2.74); N, 8.32 (Calcd 8.78).

The early fractions [$R_f = 0.60$ (CH_3CN : toluene = 2 : 3)] gave Ru(**4b**)$_2(PF_6)_2$, of which the spectral data were identical to those described above.

3.4. *[Ru(tpy)(4c)](PF$_6$)$_2$ (7c)*

Red-purple needles (72%) [$R_f = 0.5$, CH_3CN : toluene (2 : 3)]: m.p. > 300°C. ^{1}H NMR (CD_3CN, 250 MHz) δ 9.06 (s, 1H, H7 of **4c**), 8.89 (d, 2H, $J = 8.2$ Hz, H3 and H5 of tpy), 8.66 (s, 1H, H4 of **4c**), 8.55 (t, 1H, $J = 8.2$ Hz, H4 of tpy), 8.46 (d, 1H, $J = 8.3$ Hz, H4′ of **4c**), 8.29 (d, 1H, $J = 9.0$ Hz, H5/H6 of **4c**), 8.21 (d, 1H, $J = 9.0$ Hz, H6/H5), 8.11 (d, 2H, $J = 8.3$ Hz, H3′ and H3″ of tpy), 7.80 (td, 2H, $J = 8.3$, 1.5 Hz, H4′ and H4″ of tpy), 7.65 (d, 1H, $J = 8.0$ Hz, H8 of **4c**), 7.57 (td, 1H, $J = 8.3$, 1.0 Hz, H9 of **4c**), 7.43 (td, 1H, $J = 8.3$, 1.0 Hz, H10 of **4c**), 7.24 (dd, 2H, $J = 5.5$, 0.9 Hz, H6′ and H6″ of tpy), 7.05–6.95 (m, 3H, H5′ of **4c**, and H5′ and H5″of tpy), 6.90 (dd, 1H, $J = 5.5$, 1.2 Hz, H6′ of **4c**), 6.71 (d, 1H, $J = 8.3$ Hz, H11 of **4c**), 3.71 (t, 2H, $J = 5.8$ Hz), 3.35 (t, 2H, $J = 5.8$ Hz), 2.41–2.33 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.71, 158.42, 156.47, 154.97, 154.21, 153.11, 150.59, 150.39, 146.68, 144.11, 142.56, 142.06, 139.63, 138.96, 137.30, 136.50, 133.29, 132.26, 131.49, 131.20, 129.78, 129.45, 128.86, 128.32, 127.34, 126.29, 125.61, 125.45, 124.39, 37.64 (two C's), 23.91. ESI mass Calcd for $[C_{39}H_{28}N_6Ru]^+$: 681.75. Found 681.75. Elemental analysis for $C_{45}H_{30}F_{12}N_6P_2Ru$: C 48.15 (Calcd 48.21); H, 2.93 (Calcd 2.90); N, 8.09 (Calcd 8.65).

The early fractions [$R_f = 0.63$ (CH_3CN : toluene = 2 : 3)] gave Ru(**4c**)$_2(PF_6)_2$, of which the spectral data were identical to those described above.

3.5. *[Ru(tpy)(4d)](PF$_6$)$_2$ (7d)*

Red-purple needles (96%) [$R_f = 0.45$, CH_3CN : toluene (1 : 1)]: m.p. 270°C (dec). ^{1}H NMR (CD_3CN, 250 MHz) δ 9.07 (s, 1H, H7 of **4d**), 8.86 (d, 2H, $J = 8.4$ Hz, H3 and H5 of tpy), 8.66 (s, 1H, H4 of **4d**), 8.53 (t, 1H, $J = 8.4$ Hz, H4 of tpy), 8.45 (d, 2H, $J = 8.4$ Hz, H3′ and H3″ of tpy), 8.28 (d, 1H, $J = 9.0$ Hz, H5/H6 of **4d**), 8.21 (d, 1H, $J = 9.0$ Hz, H6/H5 of **4d**), 8.11 (d, 1H, $J = 8.4$ Hz, H8 of **4d**), 7.80 (td, 2H, $J = 8.4$, 1.2 Hz, H4′ and H4″ of tpy), 7.63 (d, 1H, $J = 8.3$ Hz, H4′ of **4d**), 7.56 (td, 1H, $J = 8.3$, 0.9 Hz, H9 of **4d**), 7.43 (td, 1H, $J = 8.3$, 0.9 Hz, H10 of **4d**), 7.15 (dd, 2H, $J = 5.5$, 1.2 Hz, H6′ and H6″ of tpy), 7.05 (dd, 1H, $J = 8.0$, 5.5 Hz, H5′ of **4d**), 7.00 (ddd, 2H, 1H, $J = 8.4$, 5.5, 1.2 Hz, H5′ and H5″of tpy), 6.89 (dd, 1H, $J = 5.5$, 1.2 Hz, H6′ of **4d**), 6.70 (d, 1H, $J = 8.3$ Hz, H11 of **4d**), 3.55 (br s, 2H), 3.19 (br s, 2H), 2.02 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.81, 158.68, 156.67, 154.71, 153.94, 152.83, 150.86, 150.44, 146.49, 142.85, 142.49, 142.22, 139.55, 138.91, 137.63, 137.25, 134.27, 132.78, 131.50, 131.07, 129.73, 129.34, 128.82, 128.39, 127.57, 126.20, 125.54, 125.43, 124.40, 34.63, 33.78, 25.86, 24.69. ESI mass Calcd for $[C_{40}H_{30}N_6Ru]^+$: 695.78. Found: 695.42. Elemental analysis for $C_{40}H_{30}F_{12}N_6P_2Ru$: C, 48.78 (Calcd 48.74); H, 3.04 (Calcd 3.07); N, 8.62 (Calcd 8.53).

3.6. *[Ru(tpy)(4e)](PF$_6$)$_2$ (7e)*

Red-purple needles (72%) [$R_f = 0.5$, CH_3CN : toluene (1 : 1)]: m.p. = 360°C (dec). ^{1}H NMR (CD_3CN, 250 MHz) δ 9.33 (s, 1H, H7 of **4e**), 9.14 (s, 1H, H4 of **4e**), 8.94 (d, 2H, $J = 8.2$ Hz, H3 and H5 of tpy), 8.61 (t, 1H, $J = 8.2$ Hz, H4 of tpy), 8.60 (d, 1H, $J = 9.0$ Hz, H5/H6 of **4e**), 8.50 (d, 1H, $J = 9.3$ Hz, Hα of **4e**), 8.49 (d, 2H, $J = 8.0$ Hz, H3′ and H3″ of tpy), 8.43 (dd, 1H, $J = 8.1$, 1.1 Hz, H4′ of **4e**), 8.35 (d, 1H, $J = 9.3$ Hz, Hβ of **4e**), 8.26 (d, 1H, $J = 9.0$ Hz, H6/H5 of **4e**), 8.16 (d, 1H, $J = 8.3$ Hz, H8 of **4e**), 7.80 (td, 2H, $J = 8.0$, 1.5 Hz, H4′ and H4″ of tpy), 7.65 (td, 1H, $J = 8.3$, 1.0 Hz, H9 of **4e**), 7.56 (td, 1H, $J = 8.3$ Hz, H10 of **4e**), 7.45 (dd, 1H, $J = 8.1$, 5.0 Hz, H5′ of **4e**), 7.36 (dd, 1H, $J = 5.0$, 1.1 Hz, H6′ of **4e**), 7.04 (dd, 2H, $J = 4.7$, 0.9 Hz, H6′ and H6″ of tpy), 6.97 (d, 1H, $J = 8.3$ Hz, H11 of **4e**), 6.71 (ddd, 2H, $J = 8.0$, 4.7, 1.3 Hz, H5′ and H5″ of tpy). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.89, 156.60, 154.56, 154.28, 153.28, 153.18, 151.31, 150.70, 148.54, 146.31, 139.24, 138.97, 137.78, 137.23, 134.31, 132.23, 131.92, 131.30, 130.82, 130.33, 130.28, 130.17, 129.74, 129.23, 129.02, 128.02, 127.52, 127.31, 125.38, 125.33, 125.05. ESI mass Calcd for $[C_{38}H_{24}N_6Ru]^+$: 665.71. Found 665.50. Elemental analysis for $C_{38}H_{24}F_{12}N_6P_2Ru$: C, 48.66 (Calcd 47.76); H, 2.54 (Calcd 2.53); N, 8.82 (Calcd 8.79).

Acknowledgment

Financial support from Korean Research Foundation Grant (KRF-2008-521-E00189) is gratefully acknowledged.

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