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Synthesis, Photophysical and Electrochemical properties of three novel Ru(II) complexes

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ABSTRACT

This paper on three heteroleptic $[(bpy)_2Ru(PEYD)]^{2+}$, $[(bpy)_2Ru(PYIP)]^{2+}$ and $[(bpy)_2Ru(AIYP)]^{2+}$ complexes with perylene, pyrene and anthracene appended 1H-imidazo[4,5-f][1,10]-phenanthroline as the diimine ligands is a further demonstration of the effect of extending the diimine ligands' π -system on the absorption and emission properties.

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KEYWORDS

Ru(II) complex;
Extended π -bond
conjugation;
Absorption and emission
properties.

INTRODUCTION

Tremendous interest has been attracted to ruthenium(II) polypyridyl complexes because of potential applications in molecular electronic devices^[1], as DNA structural probes, new therapeutic agents^[2,3] and photosensitizers in the conversion of solar energy to chemical or electrical energy^[4]. Over the past decade a large amount of data has been accumulated on changes in the electrochemical and photophysical properties of complexes effected by substitution in the 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) rings, or by the replacement of one or two pyridine rings with other nitrogen-containing heterocycles^[5-11]. Based on the earlier studies and recent findings on ruthenium(II) heteroleptic complexes, it is shown that the electrochemical and photophysical properties of ruthenium(II) complexes are not only dependent on the spatial geometry and molecular aggregation in the molecules, but also other factors such as the extended π -conjugation of ligands also play major roles^[12-14]. This paper is dedi-

cated to the synthesis of three Ru(II) complexes with different extended conjugated moieties attached through auxiliary unit.

EXPERIMENTAL

Materials and general physical measurements

KBr, pyrene-1-carbaldehyde, perylene-3-carbaldehyde, anthracene-10-carbaldehyde, 1,10-phenanthroline-5,6-diamine and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ were purchased from *Alfa Aesar* fine chemical Co., LTD and were used without further purification.

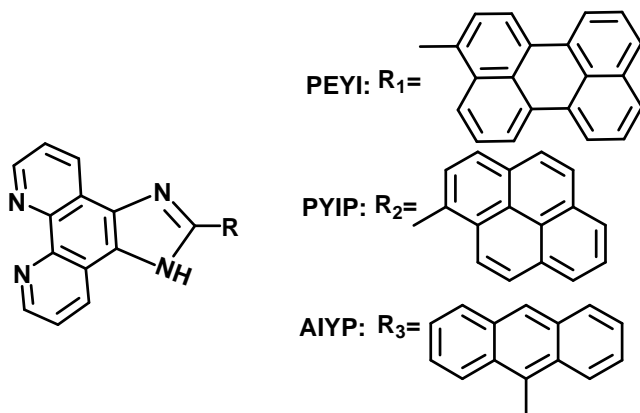
Electronic absorption spectra and fluorescence spectra were determined at room temperature on Varian Cary-100 spectrophotometer and Hitachi F-4500 spectrophotometer, respectively. Elemental analysis was carried out with Carlo Erba Elemental Analyzer 1106. ¹H-NMR spectra were recorded on Bruker DRX-300MHz spectrometer with TMS as internal standard. Infrared spectra were obtained with a Nicolet WQF-200 spectrophotometer with KBr discs. Electrochemi-

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cal experiment was performed on a CHI660B electrochemical system. Electrospray mass spectrometric experiments were performed on a SCIEX TAGA Model 6000E triple quadrupole mass spectrometer.

Synthesis of 2-(perylene-3-yl)-1H-imidazo[4,5-f][1,10]-phenanthroline (PEYI) (Scheme. 1)

To the solution of perylene-3-carbaldehyde (560 mg, 2 mmmol) and 1,10-phenanthroline -5,6-diamine (420 mg, 2 mmol) in 25 ml of DMF, sodium metabisulfite (730mg, 3.8 mmol) was added and the obtained mixture was then heated to 105°C for 20 hours. After cooled to room temperature, 100 ml of ethyl acetate was added. The mixture was washed with saturated aqueous NaCl and con-water. The organic layer was dried (MgSO_4) and then concentrated under reduced pressure. Purification by chromatography (silica gel, hexane / acetone = 4:1) gave PEYI (0.84 g, 89%) as pale yellow glassy solid. IR (KBr) ν : 3046, 1668, 1604, 1592, 1508, 1380, 1330, 1214, 1185, 1148, 810, 765, 540 cm^{-1} . EI-MS: m/z 470. $^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{SO}$]: δ , 11.51 (s, 1H), 9.05 (d, 1H), 8.81 (d, 2H), 8.60 (m, 2H), 8.38-8.32 (m, 4 H), 7.99-7.92 (m, 4H), 7.76 (dd, 2H), 7.68 (m, 2H). Anal. Calcd for $\text{C}_{33}\text{H}_{18}\text{N}_4$: C, 84.24; H, 3.86; N, 11.91. Found: C, 84.22; H, 3.87; N, 11.94.

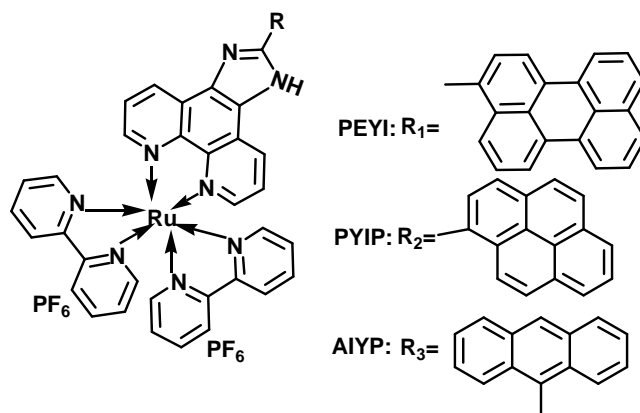


Scheme 1 : The structure of ligands

$[(\text{bpy})_2\text{Ru}(\text{PEYI})] \cdot (\text{PF}_6)_2$ (Scheme. 2)

2-(perylene-3-yl)-1H-imidazo[4,5-f][1,10]-phenanthroline (611 mg, 1.3 mmol) was dissolved in hot 2-methoxyethanol (45mL). $\text{Ru}(\text{bpy})_2 \text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (205 mg, 1 mmol) in 2-methoxyethanol (10mL) was added to the above boiling solution. The obtained solution was then heated at 80 °C for 6 h. After cooled to room

temperature, the formerly formed suspension was filtered and washed with acetonitrile. To the concentrated filtrate, a saturated aqueous NH_4PF_6 solution was added to precipitate the complex. The red–orange product was filtered, washed with water, ethanol and diethylether, and finally dried under vacuum. Yield: 1.05g (93%). It could be recrystallized from a mixture of acetonitrile / methanol / saturated NH_4PF_6 to yield 1.03 g (91%) of brilliant orange flakes. IR(KBr) ν : 3060, 2923, 2852, 1685, 1656, 1616, 1576, 1292, 1205, 1115, 810, 765, 613 cm^{-1} . Positive ion FAB-MS: m/z 1029 $\{\text{M}(\text{PF}_6)\}^+$, 884{M}. $^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{SO}$]: δ , 11.87 (s, 1H), 9.02 (d, 1H), 8.72 (d, 2H), 8.62 (m, 2H), 8.53-8.50 (m, 4H), 8.38-8.31 (m, 4H), 8.12 (dd, 4H), 7.79-7.72 (m, 4H), 7.58 (d, 2H), 7.43 (dd, 2H), 7.38 (dd, 4H), 7.18 (d, 4H). Anal. Calcd for $[(\text{bpy})_2\text{Ru}(\text{PEYI})] \cdot (\text{PF}_6)_2$: C, 54.23; H, 2.92; N, 19.42. Found: C, 54.25; H, 2.94; N, 19.46.



Scheme 2 : The structure of the Ru(II) complexes

2-(Pyren-1-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (PYIP) (Scheme. 1) was prepared by a similar procedure to PEYI. After purification by chromatography, PYIQ was obtained in 89% yield as pale yellow glassy solid. IR(KBr) ν : 3058, 1684, 1661, 1594, 1576, 1560, 1458, 1414, 1316, 1292, 1115, 841, 822, 709, 689, 585 cm^{-1} . EI-MS: m/z 420. $^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{SO}$]: δ , 10.77 (s, 1H), 9.12 (d,1H), 9.01(d, 2H), 8.52-8.50 (m, 2H), 8.42 (d, 1H), 8.31-8.21(m, 5H),8.07 (dd, 2H), 7.60 (d, 2H); Anal. Calcd for $\text{C}_{29}\text{H}_{16}\text{N}_4$: C, 82.84; H, 3.84; N, 13.32; Found: C, 82.81; H, 3.86; N, 13.35.

$[(\text{Bpy})_2\text{Ru}(\text{PYIP})] \cdot (\text{PF}_6)_2$ (Scheme. 2) was prepared by a similar procedure to $[(\text{bpy})_2\text{Ru}(\text{PEYI})] \cdot (\text{PF}_6)_2$. IR(KBr) ν :3102, 3038,

2859, 2714, 1680, 1592, 1508, 1540, 1315, 1301, 1199, 1180, 1067, 840, 827, 741, 709 cm^{-1} . Positive ion FAB-MS: m/z 979{ $\text{M}(\text{PF}_6)$ }⁺, 834{M}. ¹H-NMR [CD_3]₂SO]: δ , 11.78 (s, 1H), 9.14 (d, 1H), 9.05 (d, 2H), 8.72 (d, 4H), 8.54-8.51 (m, 2H), 8.43 (d, 1H), 8.32-8.25 (m, 9H), 8.08(dd, 2H), 7.61 (dd, 2H), 7.50 (dd, 4H), 7.12 (d, 4H); Anal. Calcd for [(bpy)₂Ru(PYIP)]·(PF₆)₂: C, 52.37; H, 2.87; N, 9.97. Found: C, 52.39; H, 2.85; N, 9.94

2-(Anthracen-10-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (AIYP) (Scheme. 1) was prepared by a similar procedure to PEYI except that anthracene-10-carbaldehyde was used as the reactant and 2.0 equiv. of diamine and 3.0 equiv of Na₂S₂O₅ were reacted. After purification by chromatography, AIYP was obtained in 84% yield as yellow solid. IR(KBr) ν : 3068, 2923, 2852, 1685, 1635, 1576, 1560, 1458, 1414, 1316, 1205, 1115, 872, 859, 838, 740 cm^{-1} . EI-MS: m/z 396. ¹H-NMR [CD_3]₂SO]: δ , 11.57 (s, 1H), 8.97(d, 2H), 8.80(d, 2H), 8.68(s, 1H), 8.53-8.50(m, 2H), 8.04 (d, 2H), 7.70-7.76 (m, 2H), 7.53 (dd, 2H), 7.43 (d, 2H); Anal. Calcd for C₂₇H₁₆N₄: C, 81.80; H, 4.07; N, 14.13. Found: C, 81.83; H, 4.05; N, 14.11.

[(Bpy)₂Ru(AIYP)]·(PF₆)₂ (Scheme. 2) was prepared by a similar procedure to [(bpy)₂Ru(PEYI)]·(PF₆)₂. IR(KBr) ν : 3106, 2922, 2854, 1668, 1596, 1515, 1464, 1340, 1300, 1242, 872, 740, cm^{-1} . Positive ion FAB-MS: m/z 955 { $\text{M}(\text{PF}_6)$ }⁺, 810{M}. ¹H-NMR [CD_3]₂SO]: δ , 11.52 (s, 1H), 8.94 (d, 2H), 8.86 (d, 2H), 8.56 (s, 1H), 8.50 (d, 4H), 8.43-8.40 (m, 2H), 8.30(dd, 4H), 8.04 (d, 2H), 7.71-7.67(m, 2H), 7.53(dd, 2H), 7.47(d, 2H), 7.26(dd, 4H), 7.14(d, 4H); Anal. Calcd for [(bpy)₂Ru(AIYP)]·(PF₆)₂: C, 51.33; H, 2.93; N, 10.19. Found: C, 51.35; H, 2.96; N, 10.21.

RESULTS AND DISCUSSION

Electronic absorption spectroscopy

The UV-Vis absorbance spectra of the complexes, which were recorded at room temperature in DMF were shown in Figure 1. There were broad and intense metal-to-ligand charge (MLCT) absorption bands in the complexes throughout the visible region of the spec-

trum (400-600 nm), characteristics of many other ruthenium(II) polypyridyl complexes, which can be assigned to electronic transitions from the Ru^{II} based t_{2g} orbital to the ligand based π^* orbital. The absorption wavelength maximum in the visible region of the the complex [(bpy)₂Ru(PYIP)]·(PF₆)₂ was found at 442 nm, which is red-shifted and of lower intensity at 445 nm for [(bpy)₂Ru(AYIP)]·(PF₆)₂, whereas a blue-shift with enhanced intensity at 438 nm was observed for [(bpy)₂Ru(PEYI)]·(PF₆)₂. The molar extinction coefficient of complex [(bpy)₂Ru(PEYI)]·(PF₆)₂ at its maximum (438nm) in the visible region is $6.92 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, larger than that of [(bpy)₂Ru(PYIP)]·(PF₆)₂ ($6.74 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) at 442 nm and [(bpy)₂Ru(AYIP)]·(PF₆)₂ ($6.21 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) at 445 nm, respectively. The mixed-ligand nature of complexes [(bpy)₂Ru(PEYP)]·(PF₆)₂, [(bpy)₂Ru(PYIP)]·(PF₆)₂ and [(bpy)₂Ru(AYIP)]·(PF₆)₂ were different to Ru(bpy)₃]²⁺(PF₆)₂^[16], producing multiple MLCT transitions in the visible, *i.e.*, Ru→bpy, Ru→PYIE, Ru→PYIP and Ru→AYIP with broad absorption at 344, 362 and 358 nm. These features have been found as a means of improving light absorption cross-sections at higher energy in similar complexes^[17]. The intense absorption bands in the UV region around 280-330 nm were assigned to the intraligand π - π^* transitions of the ligands. The lower-energy absorption in complexes were enhanced due to extending the π -conjugation of the ligands, which lowers the energy of the π^* orbital of the ligands.

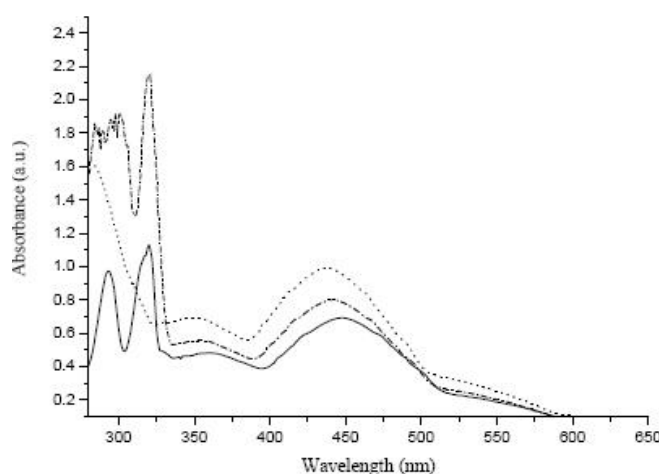


Figure 1 : Comparison of the UV-Vis absorption spectrum of [(bpy)₂Ru(PEYI)]·(PF₆)₂ (dot line) with [(bpy)₂Ru(PYIP)]·(PF₆)₂ (dash dot line) and [(bpy)₂Ru(AIYP)]·(PF₆)₂ (solid line) at a concentration of $1 \times 10^{-5} \text{ M}^{-1}$ in DMF solution showing effect of extended π -conjugation.

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The emission spectrum

The emission spectrum of complexes was shown in Figure 2. Upon excitation into the ¹LC and ¹MLCT bands, ($\lambda_{exc} = 440$ nm), the complexes displayed appreciable luminescence at room temperature. The emission wavelength maximum of complex [(bpy)₂Ru(PYIP)]·(PF₆)₂ was found at 598 nm, which was blue-shifted and of lower intensity at 594 nm for [(bpy)₂Ru(AYIP)]·(PF₆)₂, whereas a red-shift with enhanced intensity at 610 nm was observed for [(bpy)₂Ru(PEYI)]·(PF₆)₂. It is well known that extending π -conjugation of the ligands is useful for the study of electron transport at the molecular scale and the use of fused-ring systems is a powerful and practical approach^[18, 19]. The intense emission in the complexes is a significant contribution to the excited state from an interaction between the metal *d*-orbital and the ligand π -systems^[20]. The photoluminescence quantum yields of [(bpy)₂Ru(PEYI)]·(PF₆)₂, [(bpy)₂Ru(PYIP)]·(PF₆)₂ and [(bpy)₂Ru(AYIP)]·(PF₆)₂ were calculated as 0.32, 0.29 and 0.21, respectively, corresponding to their luminescence lifetimes of 2820, 2510 and 1301 ns, respectively.

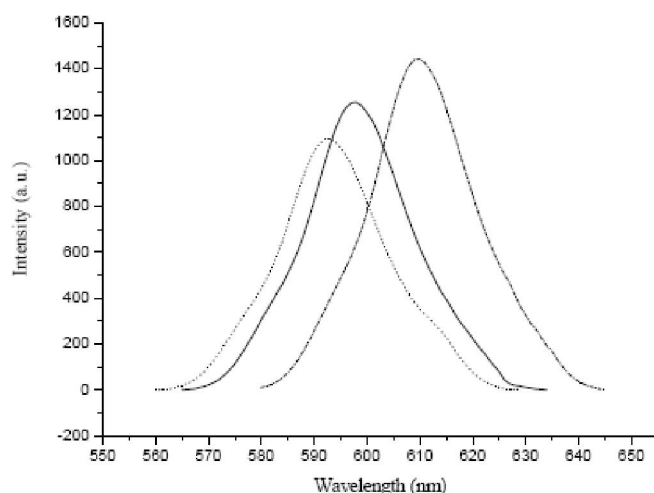


Figure 2 : Comparison of the emission spectrum of [(bpy)₂Ru(PYIP)]·(PF₆)₂ (dash dot line) with [(bpy)₂Ru(PEYI)]·(PF₆)₂ (solid line) and [(bpy)₂Ru(AYIP)]·(PF₆)₂ (dot line) at a concentration of 1×10^{-5} M⁻¹ in DMF solution showing effect of extended π -conjugation.

Electrochemical study

The CV data of the complexes were summarized in TABLE 1. The reversible one-electron oxidation process I of [(bpy)₂Ru(PYIP)]·(PF₆)₂ was found at $E_{1/2} = +1.22$ V, which was negative-transfer at +1.05 V for

[(bpy)₂Ru(PEYI)]·(PF₆)₂, whereas positive-transfer at +1.31 V was observed for [(bpy)₂Ru(AYIP)]·(PF₆)₂, which was assigned to the metal centre Ru(III)/Ru(II) wave couples^[21]. A irreversible wave of the complex [(bpy)₂Ru(PYIP)]·(PF₆)₂ was observed for processes II at -1.13 V, which is negative-transfer at -1.22 V for [(bpy)₂Ru(PEYI)]·(PF₆)₂, whereas positive-transfer at -0.92 V was observed for [(bpy)₂Ru(AYIP)]·(PF₆)₂. The more positive reduction potential may be assigned to the contribution from ligands due to extending the π -conjugation of the ligands being responsible for lowering the LUMO levels. The irreversible wave for processes III was assigned to electron injection into the LUMO+1 levels of bpy.

TABLE 1 : The electrochemical data for the complexes at 1×10^{-6} M in DMF containing 0.1 M TBAP supporting electrolyte. Step potential = 5 mV, 1amplitude = 50 mV vs. Ag|AgCl, frequency = 10 Hz. Scan rate = 100 m Vs⁻¹ vs. Ag|AgCl.

Complex	Oxidation	Reduction	Reduction
	(I)	(II)	(III)
[(bpy) ₂ Ru(PEYI)]·(PF ₆) ₂	1.05	-1.22	-1.40
[(bpy) ₂ Ru(PYIP)]·(PF ₆) ₂	1.22	-1.13	-1.36
[(bpy) ₂ Ru(AYIP)]·(PF ₆) ₂	1.31	-0.92	-1.34

CONCLUSIONS

In conclusion, we synthesized three mixed-ligand heteroleptic ruthenium(II) complexes [(bpy)₂Ru(PEYI)]·(PF₆)₂, [(bpy)₂Ru(PYIP)]·(PF₆)₂ and [(bpy)₂Ru(AYIP)]·(PF₆)₂, with broad spectral bandwidth and visible light absorption at 445, 442 and 438. Three ruthenium(II) complexes in DMF solution exhibit strong emission bands centered at 610, 598, and 594 nm, respectively, indicating that they are red and orange light-emitting materials. Particularly for these molecules, further work to establish the solar-to-electrical energy conversion efficiency (σ) in their dye-sensitized solar cells (DSSCs) is ongoing in our laboratory.

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