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

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ABSTRACT
This paper on three heteroleptic [(bpy)$_2$Ru(PEYI)]$^{2+}$, [(bpy)$_2$Ru(PYIP)]$^{2+}$ and [(bpy)$_2$Ru (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’s π-system on the 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 dedicated 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)$_2$Cl$_2$·2H$_2$O 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.

$^1$H-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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A solution of perylene-3-carbaldehyde (560 mg, 2 mmol) and 1,10-phenanthroline -5,6-diamine (420 mg, 2 mmol) in 25 ml of DMF, sodium metabisulfite (730 mg, 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 (MgSO₄) 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): v: 3046, 1668, 1604, 1592, 1508, 1380, 1330, 1214, 1185, 1148, 810, 765, 540 cm⁻¹. EI-MS: m/z 470. ¹H-NMR [(CD₃)₂SO]: δ, 11.51 (s, 1H), 9.05 (d, 1H), 8.81 (d, 2H), 8.60 (m, 2H), 8.38-8.32 (m, 4H), 7.99-7.92 (m, 4H), 7.76(dd, 2H), 7.68 (m, 2H). Anal. Calcd for C₃₃H₁₈N₄: C, 84.24; H, 3.86; N, 11.91. Found: C, 84.22; H, 3.87; N, 11.94.

A solution of the former formed suspension was filtered and washed with acetonitrile. To the concentrated filtrate, a saturated aqueous NH₄PF₆ 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: 1.05 g (93%). It could be recrystallized from a mixture of acetonitrile / methanol / saturated NH₄PF₆ to yield 1.03 g (91%) of brilliant orange flakes. IR (KBr): v: 3060, 2923, 2852, 1685, 1656, 1616, 1576, 1292, 1205, 1115, 810, 765, 613 cm⁻¹. Positive ion FAB-MS: m/z 1029 {M(PF₆)⁺}, 884{M}. ¹H-NMR [(CD₃)₂SO]: δ, 11.87 (s, 1H), 9.02 (d, 1H), 8.72 (d, 2H), 8.62 (d, 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 [(bpy)₂Ru(PEYI)]·(PF₆)₂: C, 54.23; H, 2.92; N, 19.42. Found: C, 54.25; H, 2.94; N, 19.46.

2-(perylen-3-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) v: 3058, 1684, 1661, 1594, 1576, 1560, 1458, 1414, 1316, 1292, 1115, 841, 822, 709, 689, 585 cm⁻¹. EI-MS: m/z 420. ¹H-NMR [(CD₃)₂SO]: 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 C₂₉H₁₆N₄: C, 82.84; H, 3.84; N, 13.32; Found: C, 82.81; H, 3.86; N, 13.35.

[(bpy)₂Ru(PYIP)]·(PF₆)₂ (Scheme. 2) was prepared by a similar procedure to [(bpy)₂Ru(PEYI)]·(PF₆)₂. IR(KBr) v: 3102, 3038,
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 spectrum (400–600 nm), characteristics of many other ruthenium(II) polypyridyl complexes, which can be assigned to electronic transitions from the Ru^6-based t_g orbital to the ligand based π* orbital. The absorption wavelength maximum in the visible region of the the complex [(bpy)_2Ru(PyIP)](PF_6)2 was found at 442 nm, which is red-shifted and of lower intensity at 445 nm for [(bpy)_2Ru(AIPY)](PF_6)2 whereas a blue-shift with enhanced intensity at 438 nm was observed for [(bpy)_2Ru(PEYI)](PF_6)2. The molar extinction coefficient of complex [(bpy)_2Ru(PEYI)](PF_6)2 at its maximum (438 nm) in the visible region is 6.92 × 10^4 M^-1 cm^-1, larger than that of [(bpy)_2Ru(PyIP)](PF_6)2 (6.74 × 10^5 M^-1 cm^-1) at 442 nm and [(bpy)_2Ru(AIPY)](PF_6)2 (6.21 × 10^5 M^-1 cm^-1) at 445 nm, respectively. The mixed-ligand nature of complexes [(bpy)_2Ru(PEYI)](PF_6)2, [(bpy)_2Ru(PyIP)](PF_6)2 and [(bpy)_2Ru(AIPY)](PF_6)2 were different to Ru(bpy)_2(phen)PF_6, producing multiple MLCT transitions in the visible, i.e., Ru→bpy, Ru→PyIE, Ru→PyIP and Ru→AIPY 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.
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 $[(bpy)_2Ru(PYIP)]PF_6$ was found at 598 nm, which was blue-shifted and of lower intensity at 594 nm for $[(bpy)_2Ru(AIYP)]PF_6$, whereas a red-shift with enhanced intensity at 610 nm was observed for $[(bpy)_2Ru(PEYI)]PF_6$. It is well known that extending $\pi$-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 $\pi$-systems\[20\]. The photoluminescence quantum yields of $[(bpy)_2Ru(PEYI)]PF_6$, $[(bpy)_2Ru(PYIP)]PF_6$ and $[(bpy)_2Ru(AIYP)]PF_6$ were calculated as 0.32, 0.29 and 0.21, respectively, corresponding to their luminescence lifetimes of 2820, 2510 and 1301 ns, respectively.

Electrochemical study

The CV data of the complexes were summarized in TABLE 1. The reversible one-electron oxidation process I of $[(bpy)_2Ru(PEYI)]PF_6$, $[(bpy)_2Ru(PYIP)]PF_6$ and $[(bpy)_2Ru(AIYP)]PF_6$ 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 ($\eta$) in their dye-sensitized solar cells (DSSCs) is ongoing in our laboratory.

TABLE 1: The electrochemical data for the complexes at $1\times10^{-6}$ M in DMF containing 0.1 M TBAP supporting electrolyte. Step potential = 5 mV, Amplitude = 50 mV vs. Ag|AgCl, Frequency = 10 Hz. Scan rate = 100 mVs$^{-1}$ vs. Ag|AgCl.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Oxidation (I)</th>
<th>Reduction (II)</th>
<th>Reduction (III)</th>
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<tbody>
<tr>
<td>$[(bpy)_2Ru(PEYI)]PF_6$</td>
<td>1.05</td>
<td>-1.22</td>
<td>-1.40</td>
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<tr>
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<td>-1.13</td>
<td>-1.36</td>
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<tr>
<td>$[(bpy)_2Ru(AIYP)]PF_6$</td>
<td>1.31</td>
<td>-0.92</td>
<td>-1.34</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In conclusion, we synthesized three mixed-ligand heteroleptic ruthenium(II) complexes $[(bpy)_2Ru(PEYI)]PF_6$, $[(bpy)_2Ru(PYIP)]PF_6$, $[(bpy)_2Ru(AIYP)]PF_6$, 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 ($\eta$) in their dye-sensitized solar cells (DSSCs) is ongoing in our laboratory.

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