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# Heteroleptic ruthenium(II) polypyridine complexes with a series of substituted 2,2'-bipyridine ligands

Zhi-Min Wang<sup>a</sup>, Su-Mei Shen<sup>b</sup>, Xiu-Yin Shen<sup>c</sup>, Ya-Qin Xu<sup>d</sup>, Ai-Quan Jia<sup>d</sup> and Qian-Feng Zhang<sup>d</sup>

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#### ABSTRACT

Five substituted-2,2'-bipyridine ligands L, (4-(*p*-methylphenyl)-6-phenyl-2,2'-bipyridine (L1), 4-(*p*-bromophenyl)-6-(*p*-bromophenyl)-2,2'-bipyridine (L2), 4-(*p*-bromophenyl)-6-phenyl-2,2'-bipyridine (L3), 4-phenyl-6-(*p*-bromophenyl)-2,2'-bipyridine (L4), and 4-(*p*-fluorophenyl)-6-(*p*-fluorophenyl)-2,2'-bipyridine (L5) were synthesized by stepwise formation. Reaction of *cis*-[RuCl<sub>2</sub>(bpy)<sub>2</sub>]-2H<sub>2</sub>O or *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]-2H<sub>2</sub>O and the substituted-2,2'-bipyridine ligands in the presence of KPF<sub>6</sub> afforded the corresponding cationic polypyridine-ruthenium complexes of the type [(bpy)<sub>2</sub>Ru(L)](PF<sub>6</sub>)<sub>2</sub> (bpy = 2,2'-bipyridine, 1–5) or [(phen)<sub>2</sub>Ru(L)](PF<sub>6</sub>)<sub>2</sub> (phen = 1,10-phenanthroline, 6–10), respectively. All complexes have been spectroscopically characterized by UV-vis, luminescence, and electrogenerated chemiluminescence. The structures of 1·CH<sub>3</sub>COCH<sub>3</sub>, **3**·CH<sub>3</sub>COCH<sub>3</sub>, **5**·2CH<sub>3</sub>COCH<sub>3</sub>, **6**, **8**, **9**, and **10** have been determined by single-crystal X-ray diffraction.

#### **ARTICLE HISTORY**

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#### **KEYWORDS**

Ruthenium complex; 2,2'-Bipyridine; polypyridine; 1,10-phenanthroline; crystal structure



# 1. Introduction

Ruthenium(II) complexes containing polypyridyl chelating ligands have received attention because of their applications in photochemistry, photophysics, and biochemistry [1]. The rich photophysical and

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redox properties associated with these complexes make them potentially useful in areas as diverse as light harvesting, electron transfer, non-linear optics, photovoltaics, self-assembly, and probes for biologically relevant molecules such as DNA [2]. In particular, mononuclear ruthenium(II) complexes of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and diimine analogs continue to be the focus of study [3, 4]. Ruthenium(II) complexes of the [Ru(bpy),]<sup>2+</sup> family are especially interesting due to appropriate modifications in the bulky backbone [5], and the binding mode of the prototype complex  $[Ru(phen)_2]^{2+}$ is still an issue of vigorous debate. The use of these complexes as photosensitizers for the conversion of light (solar) energy to chemical or electrical energy has received attention [6, 7]. Ruthenium polypyridine intercalators like  $[Ru(bpy),(dppz)]^{2+}$  and  $[Ru(phen),(dppz)]^{2+}$  (dppz = dipyrido[3,2-a:2',3'-c]phenazine) have binding affinities of 106–107, which is obviously better than [Ru(bpy)<sub>2</sub>]<sup>2+</sup> having binding affinities of 10<sup>3</sup> [8]. Efficient synthetic routes to heteroleptic bis- and tris-(diimine)ruthenium(II) complexes are important [9, 10]. Several routes for the synthesis of heteroleptic ruthenium(II) polypyridine complexes have previously been reported. Although the synthesis of heteroleptic tris-(diimine)ruthenium(II) complexes with different bidentate dimine ligands was first reported in the early 1980s [11], synthetic methodology to a class of these related complexes has normally involved the use of [Ru(bpy),Cl,]<sup>2+</sup>,  $[Ru(phen)_{2}Cl_{2}^{2+}, or [Ru(L)_{2}Cl_{2}]$  (L = diimine ligand) as the starting reagent [12]. An alternative methodology leading to the formation of heteroleptic bis- and tris-(diimine)ruthenium(II) complexes involves halide bridge splitting combined with other chemical or photochemical reactions [13, 14]; the designed complexes were finally isolated from crystallization with  $PF_6^-$ . It is our longstanding interest to study ruthenium complexes with a variety of donor ligands, and we have reported a series of ruthenium complexes with nitrogen- and sulfur-donor ligands [15–17]. As a part of the program to investigate the synthetic route and photophysical properties with different substituted-2,2'-bipyridine ligands, a series of the heteroleptic ruthenium(II) polypyridine complexes were synthesized and characterized, with substituted-2,2'-bipyridine ligands shown in scheme 1. The UV-vis, luminescence, and electrogenerated chemiluminescence (ECL) of these complexes relative to [Ru(bpy),]<sup>2+</sup> are also reported in this article.

# 2. Experimental

### 2.1. General considerations

Oxygen- or moisture-sensitive reactions were performed in oven-dried glassware attached to a vacuum line using Schlenk techniques. Dry solvents were distilled from suitable desiccants under nitrogen. Commercially available RuCl<sub>3</sub>·3H<sub>2</sub>O (Shanghai Hai Tops Chemistry Co Ltd) was used without purification. 2,2'-Bipyridine (bpy) and 1,10-phenanthroline (phen) were purchased from Alfa Aesar Ltd and used as supplied. *cis*-[RuCl<sub>2</sub>(bpy)<sub>2</sub>]·2H<sub>2</sub>O [18] and *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]·2H<sub>2</sub>O [19] were prepared according to literature methods.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400-MHz Avance NMR spectrometer at 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Positive-ion ESI mass spectra were recorded on a Perkin Elmer Sciex API 365 mass spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. The electrochemiluminescence experiments were carried out by using a chemiluminescence analyzer (Xi'an Remax Electronic Science Tech Co Ltd, China). Solutions used to obtain ECL were  $2.5 \times 10^{-4}$  M ruthenium(II) complexes and 0.05 M tri-*n*-propylamine (TPA) with 0.2 M potassium phosphate (aqueous and mixed 50:50 (v/v) CH<sub>3</sub>CN/H<sub>2</sub>O) as an electrolyte. The photomultiplier tube was biased at 600 V. The ECL cell was placed directly on top of the PMT window and was enclosed in a light-tight box. ECL was measured by cycles from 0 to 2 V versus Ag/AgCl at 0.1 V s<sup>-1</sup> using cyclic voltammetry and the light intensity recorded every 0.1 mV. A glass carbon electrode (3.0 mm diameter) was used as the working electrode after pre-treating with conventional procedure. The counter electrode was a platinum disk (50 mm<sup>2</sup>).



Scheme 1. Synthesis of L1–L5 [20].



Scheme 2. Synthesis of polypyridine ruthenium complexes 1–10.

# 2.2. X-ray diffraction measurements

Crystallographic data and experimental details for  $[(bpy)_2Ru(L1)](PF_6)_2\cdot CH_3COCH_3$  (1·CH<sub>3</sub>COCH<sub>3</sub>),  $[(bpy)_2Ru(L3)](PF_6)_2\cdot CH_3COCH_3$  (3·CH<sub>3</sub>COCH<sub>3</sub>),  $[(bpy)_2Ru(L5)](PF_6)_2\cdot 2CH_3COCH_3$  (5·2CH<sub>3</sub>COCH<sub>3</sub>),  $[(phen)_2Ru(L1)](PF_6)_2$  (6),  $[(phen)_2Ru(L3)](PF_6)_2$  (8),  $[(phen)_2Ru(L4)](PF_6)_2$  (9), and  $[(phen)_2Ru(L5)](PF_6)_2$  (10) are summarized in table (1). Intensity data were collected on a Bruker SMART APEX 2 CCD

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<sup>3</sup> COCH <sub>3</sub> ), [(b	5)](PF <sub>6</sub> ) <sub>2</sub> (1C
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(h)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(h)	$[(PF_6), (9), and [(phen), Ru(LS)](PF_6), (1C)$
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rimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> -CH <sub>3</sub> COCH <sub>3</sub> ), [(b	3)](PF <sub>6</sub> ) <sub>2</sub> (8), [[phen) <sub>2</sub> Ru(L <b>4</b> )](PF <sub>6</sub> ) <sub>2</sub> (9), and [[phen] <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
erimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	[3]](PF <sub>6</sub> ), (8), [(phen),Ru(L4)](PF <sub>6</sub> ), (9), and [(phen),Ru(L5)](PF <sub>6</sub> ), (10
perimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> -CH <sub>3</sub> COCH <sub>3</sub> ), [(b	$(L3)](PF_{6})$ , (8), $[(phen)_{2}Ru(L4)](PF_{6})$ , (9), and $[(phen)_{2}Ru(L5)](PF_{6})_{2}$ (10
sxperimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	$h(L3)](PF_6)_2$ (8), $[(phen)_2Ru(L4)](PF_6)_2$ (9), and $[(phen)_2Ru(L5)](PF_6)_2$ (1C
experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
d experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	$(10^{-1})_{A}$ (10 (2)] (PF <sub>6</sub> ), (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ), (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ), (10)
nd experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	n) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
and experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	len) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
a and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> -CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	hen), Ru(L3)](PF <sub>6</sub> ), (8), [(phen), Ru(L4)](PF <sub>6</sub> ), (9), and [(phen), Ru(L5)](PF <sub>6</sub> ), (10
ata and experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [[phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
data and experimental details for [(bpy) <sub>3</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	$[(phen)_{Ru}(L3)](PF_{6})_{S}(8), [(phen)_{Ru}(L4)](PF_{6})_{S}(9), and [(phen)_{Ru}(L5)](PF_{6})_{S}(10)_{Ru}(L5)](PF_{6})_{S}(10)_{Ru}(L3)_{Ru}(L5)](PF_{6})_{S}(10)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}(L3)_{Ru}($
c data and experimental details for [(bpy/ <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6/2</sub> .CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> -CH <sub>3</sub> COCH <sub>3</sub> ), [(b	), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
iic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
bhic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	(6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
aphic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	), (6), [(phen),Ru(L3)](PF <sub>6</sub> ), (8), [(phen),Ru(L4)](PF <sub>6</sub> ), (9), and [(phen),Ru(L5)](PF <sub>6</sub> ), (1C
raphic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	<sup>2</sup> (6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L <b>4</b> )](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (1C
graphic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6/2</sub> .CH <sub>3</sub> COCH <sub>3</sub> (1.CH <sub>3</sub> COCH <sub>3</sub> ), [(b	PF <sub>6</sub> ), ( <b>6</b> ), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ), ( <b>8</b> ), [(phen) <sub>2</sub> Ru(L <b>4</b> )](PF <sub>6</sub> ), ( <b>9</b> ), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ), ( <b>1</b> C
'ographic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF $_{0,2}$ ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	$(PF_{6})_{2}$ (6), [(phen) <sub>2</sub> Ru(L3)](PF_{6})_{2} (8), [(phen) <sub>2</sub> Ru(L4)](PF_{6})_{2} (9), and [(phen) <sub>2</sub> Ru(L5)](PF_{6})_{2} (10
illographic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	)](PF <sub>6</sub> ), ( <b>6</b> ), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ), ( <b>8</b> ), [(phen) <sub>2</sub> Ru(L <b>4</b> )](PF <sub>6</sub> ), ( <b>9</b> ), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ), ( <b>1</b> C
tallographic data and experimental details for [(bpy) <sub>3</sub> Ru( <b>L1</b> )](PF <sub>8)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	.1)](PF <sub>6</sub> ) <sub>2</sub> (6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
stallographic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6)2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b)	(L1)](PF <sub>6</sub> ), (G), [(phen), Ru(L3)](PF <sub>6</sub> ), (8), [(phen), Ru(L4)](PF <sub>6</sub> ), (9), and [(phen), Ru(L5)](PF <sub>6</sub> ), (1C
rystallographic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)]( $PF_{0,2}$ ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	u(L1)](PF <sub>6</sub> ) <sub>2</sub> (6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L4)](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
Crystallographic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)]( $F_{\beta_2}$ -CH <sub>3</sub> COCH <sub>3</sub> (1-CH <sub>3</sub> COCH <sub>3</sub> ), [(b	Ru(L1)](PF <sub>6</sub> ), (6), [[phen),Ru(L3)](PF <sub>6</sub> ), (8), [[phen),Ru(L4)](PF <sub>6</sub> ), (9), and [[phen],Ru(L5)](PF <sub>6</sub> ), (1C
. Crystallographic data and experimental details for [(bpy) <sub>2</sub> Ru( <b>L</b> 1)](PF $_{0,2}$ ·CH $_3$ COCH $_3$ ( $1$ ·CH $_3$ COCH $_3$ ), [(b	<sup>2</sup> , Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> (6), [(phen) <sub>2</sub> Ru(L3)](PF <sub>6</sub> ) <sub>2</sub> (8), [(phen) <sub>2</sub> Ru(L <b>4</b> )](PF <sub>6</sub> ) <sub>2</sub> (9), and [(phen) <sub>2</sub> Ru(L5)](PF <sub>6</sub> ) <sub>2</sub> (10
1. Crystallographic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)]( $F_{\beta_2}$ , CH <sub>3</sub> COCH <sub>3</sub> (1-CH <sub>3</sub> COCH <sub>3</sub> ), [(b	n),Ru(L1)](PF <sub>6</sub> ), (6), [(phen),Ru(L3)](PF <sub>6</sub> ), (8), [(phen),Ru(L4)](PF <sub>6</sub> ), (9), and [(phen),Ru(L5)](PF <sub>6</sub> ), (1C
e 1. Crystallographic data and experimental details for [(bpy) <sub>2</sub> Ru(L1)](PF $_{0,2}$ ·CH <sub>3</sub> COCH <sub>3</sub> (1·CH <sub>3</sub> COCH <sub>3</sub> ), [(b	en),Ru(L1)](PF <sub>6</sub> ), (6), [(phen),Ru(L3)](PF <sub>6</sub> ), (8), [[phen),Ru(L4)](PF <sub>6</sub> ), (9), and [(phen),Ru(L5)](PF <sub>6</sub> ), (10

<b>Table 1.</b> Crystallographic [(phen) <sub>2</sub> Ru(L1)](PF <sub>6</sub> ) <sub>2</sub> (6)	: data and experimental c , [(phen) <sub>2</sub> Ru(L <b>3</b> )](PF <sub>6</sub> ) <sub>2</sub> ( <b>1</b>	details for [(bpy) <sub>2</sub> Ru( <b>L1</b> )](P <b>B</b> ), [(phen) <sub>2</sub> Ru( <b>L4</b> )](PF <sub>6)2</sub> ( <b>5</b>	F <sub>6</sub> ) <sub>2</sub> ·CH <sub>3</sub> COCH <sub>3</sub> ( <b>1</b> ·CH <sub>3</sub> COC <b>9</b> ), and [(phen) <sub>2</sub> Ru( <b>L5</b> )](PF	$F_{6,2}^{3}$ , [(bpy) <sub>2</sub> Ru( <b>L3</b> )](PF <sub>6</sub> ) $F_{6,2}^{3}$ ( <b>10</b> ).	2.cH3cocH3 ( <b>3</b> .cH3cocH3	), [(bpy) <sub>2</sub> Ru( <b>L5</b> )](PF <sub>6</sub> ) <sub>2</sub> ·2CF	I <sub>3</sub> COCH <sub>3</sub> ( <b>5</b> ·2CH <sub>3</sub> COCH <sub>3</sub> ),
Compound	1.CH <sub>3</sub> COCH <sub>3</sub>	3-CH <sub>3</sub> COCH <sub>3</sub>	5.2CH <sub>3</sub> COCH <sub>3</sub>	6	8	6	10
Empirical formula Formula weight	C <sub>46</sub> H <sub>40</sub> N <sub>6</sub> OF <sub>12</sub> P <sub>2</sub> Ru 1083.85	C <sub>45</sub> H <sub>37</sub> N <sub>6</sub> OBrF <sub>12</sub> P <sub>2</sub> Ru 1148.73	C <sub>48</sub> H <sub>42</sub> N <sub>6</sub> O <sub>2</sub> F <sub>14</sub> P <sub>2</sub> Ru 1163.89	C <sub>47</sub> H <sub>34</sub> N <sub>6</sub> F <sub>12</sub> P <sub>2</sub> Ru 1073.81	C <sub>46</sub> H <sub>31</sub> N <sub>6</sub> BrF <sub>12</sub> P <sub>2</sub> Ru 1138.69	C <sub>46</sub> H <sub>30</sub> N <sub>6</sub> Br <sub>2</sub> F <sub>12</sub> P <sub>2</sub> Ru 1217.59	C <sub>46</sub> H <sub>30</sub> N <sub>6</sub> F <sub>14</sub> P <sub>2</sub> Ru 1095.77
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	25.014(4)	24.955(6)	13.84(3)	18.188(12)	18.014(3)	18.394(3)	17.624(6)
b (Å)	14.405(2)	14.229(3)	25.26(5)	17.424(12)	13.295(2)	13.315(2)	13.167(5)
c (Å)	25.990(4)	26.678(6)	14.30(3)	15.290(10)	41.603(6)	42.314(17)	42.582(14)
β (°)			98.09(3)	108.858(8)	92.888(2)	91.032(2)	94.587(4)
V (Å <sup>3</sup> )	9365(2)	9473(4)	4955(16)	4585(5)	9951(3)	10,362(3)	9849(6)
Space group	Pbca	Pbca	P2 <sub>1</sub> /c	P2,/c	C2/c	C2/c	C2/c
Z	8	8	4	4	8	8	8
$D_{Calcd}$ (g cm <sup>-3</sup> )	1.537	1.611	1.560	1.555	1.520	1.561	1.478
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
F (0 0 0)	4384	4592	2352	2160	4528	4800	4384
μ(Mo-Ka) (mm <sup>-1</sup> )	0.494	1.332	0.480	0.502	1.266	1.988	0.475
Total refln.	56,303	55,900	10,872	27,976	30,370	31,760	30,096
Independent refln.	10,771	10,801	7218	10,407	11,324	11,784	11,252
Parameters	616	623	618	614	613	622	622
Rint	0.1022	0.0918	0.0946	0.0466	0.0594	0.0687	0.0389
$R1^{a}$ , $wR2^{b}$ ( $l > 2\sigma(l)$ )	0.0744, 0.1645	0.0622, 0.1335	0.0552, 0.0890	0.0554, 0.1428	0.0607, 0.1483	0.0599, 0.1376	0.0685, 0.1862
R1, wR2 (all data)	0.1149, 0.2229	0.0964, 0.1801	0.0832, 0.1226	0.0874, 0.1637	0.1149, 0.1703	0.1333, 0.1609	0.1016, 0.2062
Gof	0.956	0.967	0.611	1.051	0.904	0.883	0.949
${}^{a}R1 =   F_{o}  -  F_{c}  / F_{o} .$ ${}^{b}wR2 = [w( F_{o}^{2}  -  F_{c}^{2} )^{2}/w.$ ${}^{c}cccc - r_{w}( E^{-1} -  E^{-1}E^{-1}/w.)$	$ F_{o}^{2} ^{1/2}$ .						
$dot = [w(y] + 0] =  y ^{0}$	bs 7 'V param / J						



Figure 1. Molecular structure of the cation in  $[(bpy)_2 Ru(L1)](PF_6)_2$ -CH<sub>3</sub>COCH<sub>3</sub> (1-CH<sub>3</sub>COCH<sub>3</sub>). Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.



Figure 2. Molecular structure of the cation in  $[(bpy)_2Ru(L3)](PF_6)_2$ -CH<sub>3</sub>COCH<sub>3</sub> (3-CH<sub>3</sub>COCH<sub>3</sub>). Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.

diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. The collected frames were processed with SAINT [21]. The data were corrected for absorption using SADABS [22]. Structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [23, 24]. All non-hydrogen atoms except for the lattice solvent molecules were refined anisotropically. The positions of all hydrogens were generated geometrically ( $C_{sp3}$ -H = 0.96 Å and  $C_{sp2}$ -H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen before the final cycle of least-squares refinement. Solvent molecules such as acetone in **5**·2CH<sub>3</sub>COCH<sub>3</sub> were isotropically refined or without hydrogens due to heavy disorder, which probably resulted in the relatively high *R* values in the final refinement.

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**Figure 3.** Molecular structure of the cation in  $[(bpy)_2Ru(L5)](PF_6)_2 \cdot 2CH_3COCH_3 (5 \cdot 2CH_3COCH_3)$ . Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.



**Figure 4.** Molecular structure of the cation in  $[(phen)_2 Ru(L1)](PF_6)_2$  (6). Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.

# 3. Results and discussion

The syntheses of **L1–L5** and polypyridine ruthenium complexes **1–10** are illustrated in schemes 1 and 2, respectively. The ligands investigated in this study have a bidentate 4'-phenyl-6'-phenyl-2,2'-bipyridine framework substituted in the 4'-position with the phenyl rings bearing different *para* R substituents. The synthesis of these five ligands was based on a literature method [25]. Interaction of *cis*-[RuCl<sub>2</sub>(b-py)<sub>2</sub>]-2H<sub>2</sub>O or *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]·2H<sub>2</sub>O and the substituted-2,2'-bipyridine ligands in the presence of KPF<sub>6</sub> in ethanol/water afforded the corresponding cationic polypyridine-ruthenium complexes, [(bpy)<sub>2</sub>Ru(**L**)] (PF<sub>6</sub>)<sub>2</sub> (bpy = 2,2'-bipyridine, **1–5**, SI) and [(phen)<sub>2</sub>Ru(**L**)](PF<sub>6</sub>)<sub>2</sub> (phen = 1,10-phenanthroline, **6–10**, SI). The two chlorides in *cis*-[RuCl<sub>2</sub>(bpy)<sub>2</sub>]·2H<sub>2</sub>O or *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]·2H<sub>2</sub>O or *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]·2H<sub>2</sub>O and the corresponding cationic polypyridine-ruthenium complexes, [(bpy)<sub>2</sub>Ru(**L**)] (PF<sub>6</sub>)<sub>2</sub> (bpy = 2,2'-bipyridine, **1–5**, SI) and [(phen)<sub>2</sub>Ru(**L**)](PF<sub>6</sub>)<sub>2</sub> (phen = 1,10-phenanthroline, **6–10**, SI). The two chlorides in *cis*-[RuCl<sub>2</sub>(bpy)<sub>2</sub>]·2H<sub>2</sub>O or *cis*-[RuCl<sub>2</sub>(phen)<sub>2</sub>]·2H<sub>2</sub>O were extracted by KPF<sub>6</sub> and the cationic ruthenium was then attacked by **L** to form six-nitrogen coordinated complexes in relatively good yields.



**Figure 5.** Molecular structure of the cation in  $[(phen)_2 Ru(L3)](PF_6)_2$  (8). Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.



**Figure 6.** Molecular structure of the cation in  $[(phen)_2 Ru(\mathbf{L4})](PF_6)_2(\mathbf{9})$ . The  $[PF_6]^-$  are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

Structures of  $1 \cdot CH_3 COCH_3$ ,  $3 \cdot CH_3 COCH_3$ ,  $5 \cdot 2CH_3 COCH_3$ , 6, 8, 9, and 10 have been established by X-ray crystallography. Structures of the cationic part of these Ru(II) polypyridine complexes are shown in figures (1–7). The rutheniums are all in octahedral coordination environment containing two 2,2'-bpy or phen units and one substituted-2,2'-bipyridine ligand. The characteristic bond lengths and angles of these Ru(II) polypyridine complexes are summarized in table (2). The Ru–N(bpy) bond lengths in  $1 \cdot CH_3 COCH_3$ ,  $3 \cdot CH_3 COCH_3$ , and  $5 \cdot 2CH_3 COCH_3$  are 2.032(7)-2.075(6) Å, which agree well with those in [Ru(bpy)<sub>2</sub>(pbnHH)]<sup>2+</sup> (pbn =  $2 - (2 \cdot pyridyl)$ benzo[b]-1,5-naphthyridine) (av. 2.060(2) Å) [26]. The Ru–N(phen) bond lengths in 6, 8, 9, and 10 are from 2.056(6) to 2.083(4) Å, slightly longer than the Ru–N(bpy) bond distances in  $1 \cdot CH_3 COCH_3$ ,  $3 \cdot CH_3 COCH_3$ , and  $5 \cdot 2CH_3 COCH_3$ . The bond lengths of Ru–N(5) in the seven new complexes are all shorter than that of Ru–N(6), i.e. Ru–N (the substituted pyridine), probably due to steric hindrance. The N(bpy)–Ru–N(bpy) bond angles from  $77.5(2)^{\circ}$  to  $79.6(3)^{\circ}$ in  $1 \cdot CH_3 COCH_3$ ,  $3 \cdot CH_3 COCH_3$ , and  $5 \cdot 2CH_3 COCH_3$  are near to those of N(phen)–Ru–N(phen) from  $79.3(2)^{\circ}$ to  $79.95(13)^{\circ}$  in 6, 8, 9 and 10.



**Figure 7.** Molecular structure of the cation in  $[(phen)_2 Ru(L5)](PF_6)_2$  (**10**). Thermal ellipsoids are shown at the 40% probability level. The  $[PF_6]^-$  are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for 1·CH<sub>3</sub>COCH<sub>3</sub>, 3·CH<sub>3</sub>COCH<sub>3</sub>, 5·2CH<sub>3</sub>COCH<sub>3</sub>, 6, 8, 9, and 10.

Complex	Ru–N (bpy/phen)	Ru–N(L)	N(bpy/phen)–Ru–N(bpy/phen)	N(L)-Ru-N(L)
[(bpy),Ru(L1)](PF,), 1	2.063(6)	2.039(6)	77.5(2)	79.0(2)
	2.075(6)	2.107(5)	78.5(2)	
	2.061(6)			
	2.055(5)			
[(bpy) <sub>2</sub> Ru( <b>L3</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>3</b>	2.065(5)	2.040(5)	78.2(2)	78.51(19)
2 02	2.061(5)	2.118(5)	78.4(2)	
	2.057(5)			
	2.053(5)			
[(bpy) <sub>2</sub> Ru( <b>L5</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>5</b>	2.034(7)	2.026(8)	79.6(3)	78.3(3)
	2.041(7)	2.112(7)	78.9(3)	
	2.049(7)			
	2.032(7)			
[(phen) <sub>2</sub> Ru( <b>L1</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>6</b>	2.063(3)	2.057(3)	79.56(13)	78.46(12)
	2.077(3)	2.119(3)	79.95(13)	
	2.067(3)			
	2.081(3)			
[(phen) <sub>2</sub> Ru( <b>L3</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>8</b>	2.068(5)	2.054(5)	79.3(2)	78.45(18)
	2.072(5)	2.123(4)	79.9(2)	
	2.062(5)			
	2.072(5)			
[(phen) <sub>2</sub> Ru( <b>L4</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>9</b>	2.056(6)	2.043(5)	79.5(2)	78.6(2)
	2.076(5)	2.114(5)	79.5(2)	
	2.062(5)			
	2.062(5)			
[(phen) <sub>2</sub> Ru( <b>L5</b> )](PF <sub>6</sub> ) <sub>2</sub> <b>10</b>	2.060(5)	2.053(4)	79.58(17)	78.91(15)
	2.083(4)	2.119(4)	79.89(17)	
	2.072(4)			
	2.066(4)			

The UV–Vis absorption spectra of new Ru(II)-bpy and Ru(II)-phen complexes, together with  $[Ru(bpy)_3]$ (PF<sub>6</sub>)<sub>2</sub>, in CH<sub>3</sub>CN at room temperature are shown in figure 8(a) and (b), respectively. Complexes **1–5** have similar spectra, while the spectra of **6–10** are also very close. The UV-vis absorption spectra of **1–5** are dominated by two intense absorption bands at 198 and 290 nm, and a comparatively less intense band at 450 nm. The former is assigned to a typical spin-allowed  ${}^{1}\pi{-}\pi^{*}$  transition of the ligands and the latter to metal-to-ligand charge transfer (MLCT). These spectra are similar to that of  $[Ru(bpy)_3](PF_6)_2$ . For **6–10**, the two absorption bands of  ${}^{1}\pi{-}\pi^{*}$  transition are at 198 and 267 nm and the MLCT transition at 450 nm.



Figure 8. (a) The UV-vis absorption spectra of 1-5 and  $[Ru(bpy)_3](PF_6)_2$  in  $CH_3CN$  solution. (b) The UV-vis absorption spectra of 6-10 and  $[Ru(bpy)_3](PF_6)_2$  in  $CH_3CN$  solution.



Figure 9. (a) Luminescence emission spectra of 1-5 in CH<sub>3</sub>CN solution. (b) Luminescence emission spectra of 6-10 in CH<sub>3</sub>CN solution ( $\lambda_{ex} = 460$  nm).



Figure 10. (a) ECL intensities of 1-5. (b) ECL intensities of 6-10.

The room temperature PL spectra of **1–10** in CH<sub>3</sub>CN solution are illustrated in figure (9). Complexes all emit weak luminescence because of the rotation of diphenyl rotors of the substituted-2,2'-bipyridine ligands in solution. Complexes **1–5** emit orange luminescence (see figure 9(a)) with emission wavelengths between 600 and 607 nm, red shifted compared to that of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (598 nm) because the substituted-2,2'-bipyridine ligands have larger conjugation than 2,2'-bipyridine. There is no obvious change caused by different substituents on phenyl groups. When 2,2'-bipyridine was replaced by more conjugated 1,10-phenanthroline, the emission wavelength of **6–10** (see figure 9(b)) red shifted to 610 nm.

The potential-ECL intensity curves of **1–10** are shown in figure (10). The peak potentials between 1.27 and 1.40 V are assigned to electrooxidation of ruthenium(II) complexes. In general, the ECL comes from the radiation transition of triplet state <sup>3</sup>MLCT [27]. Like the weak luminescence, the ECL intensities of **1–10** are also weak (below 2500) compared to  $[Ru(bpy)_3](PF_6)_2$  (*ca.* 20,000 under the same conditions). For **1–5**, the brominated complexes **2–4** have stronger ECL intensity than other complexes. For **6–10**, the intensity difference is not obvious except that **9** has slightly stronger luminescence.

In summary, a series of new substituted-2,2'-bipyridine ligands have been synthesized and used to prepare the corresponding bpy- and phen-Ru(II)-polypyridine cationic complexes with defined structures. The UV-vis, luminescence, and ECL properties of the ruthenium complexes were investigated. No obvious change was observed in optical properties caused by different substituents on phenyl rings. The PL spectra show that  $[(bpy)_2Ru(L)](PF_6)_2$  and  $[(phen)_2Ru(L)](PF_6)_2$  with more conjugated ligand system led to red shift compared to  $[Ru(bpy)_3](PF_6)_2$ . As a matter of fact, the IR spectrum obtained for some  $[Ru(L)_3]^{2+}$  (where L = bpy, 2,2'-bipyrimidine (bmp), 2,2'-bipyrazine (bpz), and phen) displays characteristic peaks from 1100 to 1800 cm<sup>-1</sup>. It is thus understood that the vibrational frequencies observed for  $[Ru(L)_3]^{2+}$  arise exclusively in the ligand part of the complex [28]. Recent report of similar Ru(II) complexes,  $[Ru(bpy)_2(pipz)]^{2+}$  and  $[Ru(phen)_2(pipz)]^{2+}$  (pipz = 2-pyridine-1H-imidazo[4,5-b]phenazine), involved in DNA binding properties is quite interesting, as both complexes are efficient DNA photocleavers [29], which should draw us to further explore the photo-chemistry and -biochemistry properties of the present bpy- and phen-Ru(II)-polypyridine cationic complexes.

# Supplementary material

Crystallographic data for [(bpy)<sub>2</sub>Ru(**L**)](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>COCH<sub>3</sub> (1·CH<sub>3</sub>COCH<sub>3</sub>), [(bpy)<sub>2</sub>Ru(**L3**)](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>COCH<sub>3</sub> (**3**-CH<sub>3</sub>COCH<sub>3</sub>), [(bpy)<sub>2</sub>Ru(**L5**)](PF<sub>6</sub>)<sub>2</sub>·2CH<sub>3</sub>COCH<sub>3</sub> (**5**-2CH<sub>3</sub>COCH<sub>3</sub>), [(phen)<sub>2</sub>Ru(**L1**)](PF<sub>6</sub>)<sub>2</sub> (**6**), [(phen)<sub>2</sub>Ru(**L3**)](PF<sub>6</sub>)<sub>2</sub> (**8**), [(phen)<sub>2</sub>Ru(**L4**)](PF<sub>6</sub>)<sub>2</sub> (**9**), and [(phen)<sub>2</sub>Ru(**L5**)](PF<sub>6</sub>)<sub>2</sub> (**10**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 1401755-1401761, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1233-336-033; E-mail: deposit@ccdc.cam.ac.uk].

# Disclosure statement

No potential conflict of interest was reported by the authors.

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