

Highly electrochemiluminescent Ru(II) complexes containing 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one ligand

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Abstract

A series of new ruthenium(II) complexes containing 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP) ligand, such as $[\text{Ru}(\text{DTDP})_n(\text{L})_{3-n}]^{2+}$ ($\text{L} = 2,2'$ -bipyridyl (bpy), 4,4'-dimethyl-2,2'-bipyridyl (dmbpy), *o*-phenanthroline (*o*-phen), 5-chloro-*o*-phenanthroline (*o*-phen-Cl), 2,2'-bipyridine-4,4'-dicarboxaldehyde (bpy-(CHO)₂), $n = 1, 2, 3$) were synthesized and examined as ECL materials. All the complexes were characterized in terms of electrochemical redox potential and relative ECL intensity, and were compared to the well-known tris(*o*-phenanthroline) ruthenium(II) complex. Most of the synthesized Ru(II) complexes containing the DTDP ligand exhibited more intense ECL emissions than $[\text{Ru}(\textit{o}\text{-phen})_3]^{2+}$. In particular, the ECL intensities of $[\text{Ru}(\text{DTDP})(\textit{o}\text{-phen})_2]^{2+}$ and $[\text{Ru}(\text{DTDP})(\text{bpy}-(\text{CHO})_2)_2]^{2+}$ were observed to be as high as 9-fold and 20-fold greater, respectively, than the ECL intensity of $[\text{Ru}(\textit{o}\text{-phen})_3]^{2+}$.

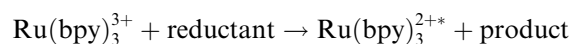
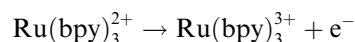
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1. Introduction

Electrochemiluminescence (ECL) emitted by transition metal complexes has been recognized as a powerful method in the analysis of a wide range of compounds such as oxalate, alkylamine, amino acid, NADH, and organic acids [1]. Among the numerous electrogenerated chemiluminescent materials, ECL associated with the tris(2,2'-bipyridyl)ruthenium, $[\text{Ru}(\text{bpy})_3]^{2+}$, system is considered the most intense and best model, thus far [2]. The ECL emission of the $\text{Ru}(\text{bpy})_3^{2+}$ /reductant sys-

tem presumably arises from the energetic electron transfer reaction between electrogenerated $\text{Ru}(\text{bpy})_3^{3+}$ and a strong reducing intermediate that is formed by the one-electron oxidation of the reductant [3], as follows:



In general, the emission of luminescent transition metal complexes always arises from the lowest excited state, which is either a metal-to-ligand charge transfer (MLCT) or localized π - π^* transition. The ECL characteristics of transition metal complexes strongly depend on the conditions in the local environment of

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the complex, such as the d–d state, spin–orbital coupling, pure π – π^* phosphorescence, and the emitting state. The energy gap law states that radiationless processes become more efficient as the emitting state approaches the ground state [4].

In our previous studies, the effects of ligands in a series of ECL ruthenium complexes containing different local environments other than $\text{Ru}(\text{bpy})_3^{2+}$ were reported [5–7]. An interesting relationship between the donor ability of the ligand and the ECL properties of ruthenium(II) complexes was also discussed. As a weak donor ligand, such as *o*-phenanthroline, raises the MLCT band energies of Ru(II) complexes, the ECL intensity of Ru(II) complexes correspondingly increases. In these previous reports, $\text{Ru}(\text{o-phen})_3^{2+}$ produced a more intense ECL emission than $\text{Ru}(\text{bpy})_3^{2+}$ did [6,7].

Several ruthenium(II) complexes containing *o*-phenanthroline and related ligands have been applied to sensitive and selective detection methods, such as pH sensor, DNA binding agent, light switch, and molecular wire [8]. However, only a couple of research groups have described the ECL behavior of $\text{Ru}(\text{o-phen})_3^{2+}$ and its derivatives. Moreover, these previous research studies did not pay much attention to the development of new complexes as alternative ECL materials.

Therefore, we focused on developing a new alternative type of *o*-phenanthroline as a suitable donor ligand in this study. By varying the ligand of the Ru complex, which has unique donor ability, the intensity of the ECL emission can be controlled, as revealed in our previous study. As a potential candidate for the purpose of this study, a new ligand, 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP) was developed and elected as a suitable new ligand for more sensitive ECL Ru(II) complexes, since it was relatively easy to prepare and its donor ability was somehow different from that of the conventional *o*-phenanthroline. Herein, the syntheses and ECL properties of a series of Ru(II) complexes containing the DTDP ligand, which reveals intense ECL emissions, are discussed (see Fig. 1).

2. Results and discussion

2.1. Synthesis

Since *o*-phenanthroline was established in our recent studies as an effective ligand for intense ECL materials, an *o*-phenanthroline alternative, DTDP was synthesized and introduced as the new ligand for Ru complex, in order to develop new ECL Ru(II) complexes. The synthesis of the DTDP ligand was carried out in four steps as shown in Scheme 1, which was appeared in the literature previously [9].

As shown in Scheme 2, a series of novel ruthenium(II) complexes, $[\text{Ru}(\text{DTDP})_n(\text{L})_{3-n}]^{2+}$ ($\text{L} = 2,2'$ -bipyridyl (bpy), 4,4'-dimethyl-2,2'-bipyridyl (dmbpy), *o*-phenanthroline (*o*-phen), 5-chloro-*o*-phenanthroline (*o*-phen-Cl), 2,2'-bipyridine-4,4'-dicarboxaldehyde (bpy-(CHO)₂), $n = 1, 2, 3$) was obtained through the sequential reaction of $[\text{RuCl}_2(\textit{p-cymene})]_2$ with DTDP or an elected ligand in ethanol, H₂O, or H₂O/EtOH. When 2 equiv of DTDP or the elected ligand was applied to $[\text{RuCl}_2(\textit{p-cymene})]_2$ in the EtOH solution at room temperature, $[\text{RuCl}_2(\textit{p-cymene})(\text{DTDP})]$ or $[\text{RuCl}_2(\textit{p-cymene})\text{L}]$ was obtained quite selectively. After refluxing $[\text{RuCl}_2(\textit{p-cymene})(\text{DTDP})]$ or $[\text{RuCl}_2(\textit{p-cymene})\text{L}]$ with 2 equiv of the alternative ligand in an aqueous solution followed by NH_4PF_6 treatment, **5–14** were obtained respectively in reasonable yields (Table 1). A symmetrical complex such as **15**, was obtained by refluxing $[\text{RuCl}_2(\textit{p-cymene})]_2$ with 6 equiv of DTDP in aqueous EtOH ($v/v = 2:1$) followed by NH_4PF_6 treatment.

2.2. Electrochemical and ECL characteristics

2.2.1. Electrochemical and ECL properties of Ru(II) containing a series of 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one

At first, the electrochemical and ECL properties of Ru(II) complexes containing mono DTDP ligand, $[\text{Ru}(\text{DTDP})\text{L}_2]^{2+}$, were studied. The cyclic voltammograms of all the ruthenium(II) complexes containing mono DTDP were obtained in a 50 mM phosphate

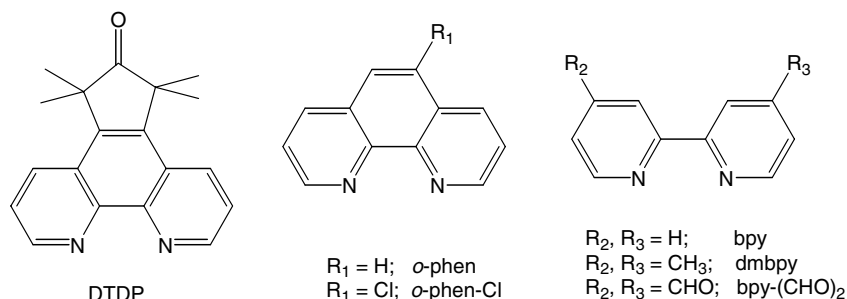
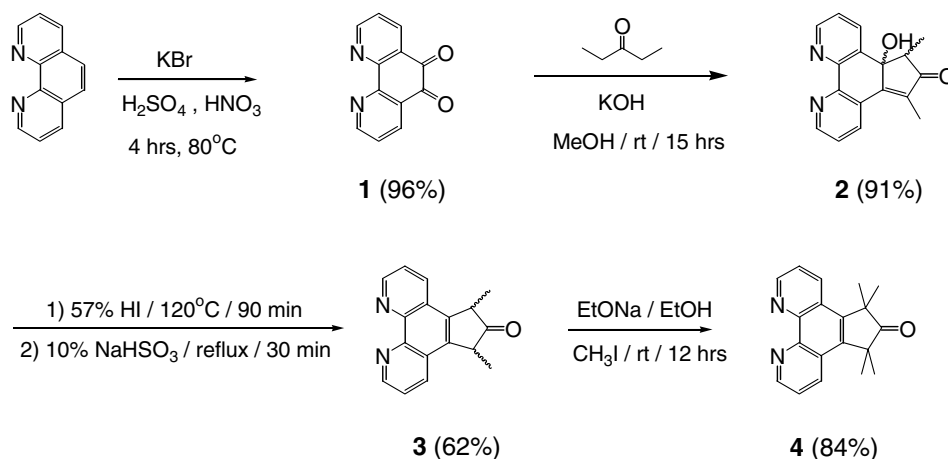
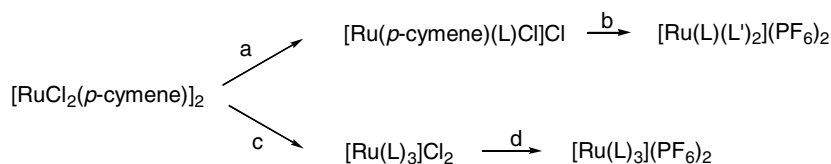


Fig. 1. Chemical structure of ligands used in this study.



Scheme 1. Synthesis of 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1] phenanthren-2-one (DTDP).



L or L' = bpy, dmbpy, bpy-(CHO)₂, *o*-phen, *o*-phen-Cl, DTDP

a) 2L/EtOH, rt, 2 h. b) 2L'/H₂O, reflux, then NH₄PF₆. c) 6L/EtOH:H₂O (1:2), reflux. d) NH₄PF₆.

Scheme 2. Synthesis of Ru(II) complexes.

Table 1
Syntheses of Ru(II) complexes containing DTDP ligand(s)

Entry	[Ru(L) _n (L') ₂](PF ₆) ₂	Yield (%) ^a
1	[Ru(DTDP) ₂ (bpy)](PF ₆) ₂ (5)	57
2	[Ru(DTDP)(bpy) ₂](PF ₆) ₂ (6)	72
3	[Ru(DTDP) ₂ (<i>o</i> -phen)](PF ₆) ₂ (7)	67
4	[Ru(DTDP)(dmbpy) ₂](PF ₆) ₂ (8)	63
5	[Ru(DTDP) ₂ (bpy-(CHO) ₂)](PF ₆) ₂ (9)	40
6	[Ru(DTDP)(bpy-(CHO) ₂) ₂](PF ₆) ₂ (10)	55
7	[Ru(DTDP) ₂ (<i>o</i> -phen)](PF ₆) ₂ (11)	68
8	[Ru(DTDP)(<i>o</i> -phen) ₂](PF ₆) ₂ (12)	55
9	[Ru(DTDP) ₂ (<i>o</i> -phen-Cl)](PF ₆) ₂ (13)	60
10	[Ru(DTDP)(<i>o</i> -phen-Cl) ₂](PF ₆) ₂ (14)	65
11	[Ru(DTDP) ₃](PF ₆) ₂ (15)	64

^a Isolated yield.

buffer at pH 7 with a small amount of acetonitrile (less than 20% (v/v)). The cyclic voltammograms showed a quasi-reversible one electron process for Ru(II)/Ru(III) oxidation–reduction, with half-wave potentials in the range of 1.08 V < E_{1/2} < 1.18 V vs. Ag/AgCl (3 M NaCl) (E_{1/2} = (E_{pa} + E_{pc})/2).

ECL experiments were carried out in Ru(II) complex solutions containing tripropylamine as a co-reactant in the FIA system. ECL emissions were obtained for each of the complexes upon sweeping the potential sufficiently positive to oxidize both the complex and tripro-

pylamine (TPA). The results indicated that the ECL intensities of [Ru(DTDP)L₂]²⁺ increased in the following order: L = bpy-(CHO)₂ > *o*-phen > bpy > *o*-phen-Cl > dmbpy, which showed similar tendency compared to our previous study [7]. In addition, the ECL intensities of [Ru(DTDP)L₂]²⁺ were found to be stronger than those of the reference compound, [Ru(*o*-phen)₃]²⁺ (Table 2).

Surprisingly, the ECL intensities of [Ru(DTDP)(*o*-phen)₂]²⁺ and [Ru(DTDP)(bpy-(CHO)₂)₂]²⁺ were observed to be higher by 923% and 2010%, respectively, than that of [Ru(*o*-phen)₃]²⁺. These highly luminescent materials can be used not only for ECL-based sensors but also for light-emitting devices.

A pH study was carried out to determine the pH effect on the [Ru(DTDP)L₂]²⁺-TPA system. The study revealed that the ECL intensity of the [Ru(DTDP)L₂]²⁺-TPA system was greatly affected by the pH of the buffer solution. The pH response of the [Ru(DTDP)(*o*-phen)₂]²⁺ and [Ru(DTDP)(bpy-(CHO)₂)₂]²⁺ was exhibited almost the same trend. The background-corrected ECL signals of TPA with [Ru(DTDP)(*o*-phen)₂]²⁺ increased significantly from pH 3.0 up to pH 7.0, but slightly decreased at a higher pH. The ECL intensity obtained at pH 7 was 3000-fold greater than the ECL intensity emitted at pH 3.0. This trend is similar to the results observed in the solution-phase

Table 2
Electrochemical and ECL properties of Ru (II) complexes containing DTDP ligand(s)

Entry	Ru(II) cpd	UV (nm) ^a	E_{pa} (V) ^b	E_{pc} (V) ^b	ΔE_p (mV) ^b	ECL (%) ^c
1	[Ru(DTDP)(bpy-(CHO) ₂) ₂](PF ₆) ₂ (10)	485	1.18	1.10	180	2010
2	[Ru(DTDP)(<i>o</i> -phen) ₂](PF ₆) ₂ (12)	448	1.16	0.98	180	923
3	[Ru(DTDP) ₂ (<i>o</i> -phen)](PF ₆) ₂ (11)	450	1.10	0.97	130	213
4	[Ru(DTDP) ₂ (bpy)](PF ₆) ₂ (5)	450	1.18	0.96	220	183
5	[Ru(DTDP)(bpy) ₂](PF ₆) ₂ (6)	449	1.16	1.10	60	174
6	[Ru(DTDP)(<i>o</i> -phen-Cl) ₂](PF ₆) ₂ (14)	450	1.38	1.24	140	150
7	[Ru(DTDP) ₂ (<i>o</i> -phen-Cl)](PF ₆) ₂ (13)	450	1.11	0.98	130	117
8	[Ru(DTDP)(dmbpy) ₂](PF ₆) ₂ (8)	456	1.13	1.00	130	108
9	[Ru(DTDP) ₂ (dmbpy)](PF ₆) ₂ (7)	456	1.08	0.99	90	100
10	[Ru(DTDP) ₃](PF ₆) ₂ (15)	451	1.13	0.98	150	96
11	[Ru(DTDP) ₂ (bpy-(CHO) ₂)](PF ₆) ₂ (9)	443	1.18	0.98	200	90

^a In acetone.

^b Measured in acetonitrile/H₂O at pH 7 containing 50 mM phosphate buffer as a supporting electrolyte at a glassy carbon electrode vs. Ag/AgCl (3 M NaCl).

^c ECL relative to [Ru(*o*-phen)₃](PF₆)₂(100%).

Ru(bpy)₃²⁺-TPA system. As it can be expected from the ECL mechanism of the [Ru(DTDP)L₂]²⁺-TPA system, TPA should be oxidized first before it reacts with the oxidized [Ru(DTDP)L₂]³⁺ species. Therefore, ECL intensity for TPA is dependent upon the degree of oxidation, i.e. anodic current of TPA in cyclic voltammograms. The effect of pH on the anodic peak current of TPA was quite similar to the pH effect on the ECL intensity. The anodic peak current increased significantly from pH 4.0 up to pH 7.0 and slightly decreased at higher pH. In addition, [Ru(DTDP)L₂]³⁺ species is most stable at pH 6–7 as reported previously for Ru(bpy)₃³⁺ species by the Bard and his co-workers [10]. Therefore, as the pH increases, some decomposition of [Ru(DTDP)L₂]³⁺ species would be expected, leading to a diminished ECL reagent available for ECL reaction, which resulted in decreased ECL intensity because the ECL intensity is strongly dependent upon the amount of [Ru(DTDP)L₂]³⁺ species concentration.

For the extension of the above study on the Ru(II) complexes containing mono DTDP ligand, the electrochemical and ECL properties of Ru(II) complexes containing a couple of DTDP ligands, [Ru(DTDP)₂L]²⁺, were studied. The half-wave potentials ($E_{1/2}$) of the Ru(II)/Ru(III) oxidation–reduction on [Ru(DTDP)₂L]²⁺ were seen in the range of 1.04 V < $E_{1/2}$ < 1.08 V vs. Ag/AgCl (3 M NaCl). The oxidation potentials on [Ru(DTDP)₂L]²⁺ were shifted cathodically by around 80 mV compared to those obtained with [Ru(DTDP)L₂]²⁺. In addition, the ECL intensities of [Ru(DTDP)₂L]²⁺ were stronger than that of reference compound of [Ru(*o*-phen)₃]²⁺ except [Ru(DTDP)₂(bpy-(CHO)₂)₂]²⁺ (Table 2, entry 11). The ECL intensities of [Ru(DTDP)₂L]²⁺ exhibited a different tendency from those of [Ru(DTDP)L₂]²⁺, that is, L = *o*-phen > bpy > *o*-phen-Cl > dmbpy > bpy-(CHO)₂. Although the ECL intensities of [Ru(DTDP)L₂]²⁺ seemed to be consistent with the donor ability of α -diimine ligands, the ECL

intensity observed with [Ru(DTDP)₂(bpy-(CHO)₂)₂]²⁺ was found to be somehow independent of the donor ability of ligand.

A pH study was also carried out to determine the pH effect on the [Ru(DTDP)₂(*o*-phen)]²⁺-TPA system. The results showed that ECL intensity for the [Ru(DTDP)₂(*o*-phen)]²⁺-TPA system was also greatly affected by the pH of the buffer solution. The pH response trend observed in the [Ru(DTDP)₂(*o*-phen)]²⁺ was the almost same as that seen in the [Ru(DTDP)(*o*-phen)₂]²⁺, in which the maximum ECL intensity was obtained at pH 7. From the above pH studies for the [Ru(DTDP)L₂]²⁺-TPA and [Ru(DTDP)₂(*o*-phen)]²⁺-TPA systems, it can be rationalized that a series of Ru(II) complexes containing the DTDP ligand exhibits the same pH response trend for TPA as in the Ru(bpy)₃²⁺-TPA system because the ECL mechanism for the two systems is identical.

Finally, electrochemical and ECL properties of Ru(II) complexes containing tris (DTDP), [Ru(DTDP)₃]²⁺, were studied. The electrochemical characteristics of [Ru(DTDP)₃]²⁺ were similar with those of [Ru(DTDP)₂L]²⁺. Unexpectedly, the ECL intensity of [Ru(DTDP)₃]²⁺ was slightly weaker than that of [Ru(*o*-phen)₃]²⁺. However, [Ru(DTDP)₃]²⁺ can still be utilized as an effective ECL material.

2.2.2. Analytical applications of Ru(II) complexes with 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one ligand

Since the ECL intensities of [Ru(DTDP)(*o*-phen)₂]²⁺ and [Ru(DTDP)(bpy-(CHO)₂)₂]²⁺ were observed to be higher by 923% and 2010%, respectively, than that of [Ru(*o*-phen)₃]²⁺, the working curves for TPA using the [Ru(DTDP)(*o*-phen)₂]²⁺ and [Ru(DTDP)(bpy-(CHO)₂)₂]²⁺ were constructed in a flow injection system. As expected, the detection limits for TPA with [Ru(DTDP)(*o*-phen)₂]²⁺ and [Ru(DTDP)(bpy-

$(\text{CHO})_2]^{2+}$ were recorded at 0.05 μM , which is slightly better than that observed with $[\text{Ru}(o\text{-phen})_3]^{2+}$ (LOD = 0.1 μM).

$\text{Ru}(\text{bpy})_3^{2+}$ ECL has become popular for the detection of proteins and oligonucleotides in immunoassays and DNA probe assays. The Bard group carried out a preliminary ECL immunoassay using a Ru-chelate with an *N*-hydroxysuccinimide residue (Ru-chelate), which enabled protein or DNA to be labeled [10]. Further studies on new Ru-chelate labels have also been reported by other research groups [5,11,12].

To utilize the highly luminescent ruthenium complexes containing DTDP as an ECL label, new ruthenium(II) complexes containing 4-carboxymethyl-4'-methyl-2,2'-bipyridyl (mbpy- $\text{CH}_2\text{CO}_2\text{H}$) ligand in the above $[\text{Ru}(\text{DTDP})\text{L}_2]^{2+}$ can be synthesized. In this case, the carboxylic acid group of the ligand can be coupled with an amino group of a protein or DNA through a conventional coupling reaction, such as the 1,3-dicyclohexylcarbodiimide (DCC) reaction [13]. Further studies are underway in this direction.

3. Conclusion

A series of new electrochemiluminescent ruthenium(II) complexes containing DTDP (**5–15**) were synthesized in reasonable yields. The relationship between the observed ECL intensities and ligand properties of such Ru(II) complexes was investigated. The study revealed that intense ECL emissions were observed in all novel Ru(II) complexes containing the DTDP ligand. Most of the Ru(II) complexes containing DTDP, except **9** and **15**, showed more intense ECL emissions than $[\text{Ru}(o\text{-phen})_3]^{2+}$ did. The ECL intensities of $[\text{Ru}(\text{DTDP})(o\text{-phen})_2]^{2+}$ and $[\text{Ru}(\text{DTDP})(\text{bpy}-(\text{CHO})_2)]^{2+}$ were 9-fold and 20-fold higher, respectively, than the ECL intensity of $[\text{Ru}(o\text{-phen})_3]^{2+}$. These highly electrochemiluminescent Ru(II) complexes can be utilized not only as an excellent ECL materials but also as an intense light emitting material. These results lead to the conclusion that the proper combination of DTDP with other ligands that possess suitable donor ability can produce more effective ECL materials.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out under a dry nitrogen atmosphere unless otherwise stated. Solvents were purchased and dried by the standard method. Most of the chemical reagents were purchased from Aldrich Chemical Co. and used as received without further purification in most cases. DTDP (**4**) [9] and

$[\text{RuCl}_2(p\text{-cymene})]_2$ [14] were prepared by known methods in the literature.

^1H NMR spectra were recorded on a 300 MHz Jeol instrument. Chemical shifts are reported in ppm relative to residual solvent as an internal standard. GC/MS was recorded on a HP 6890 mass spectrometer and FAB mass was recorded on a JMS-DX303 (JEOL Co.). Infrared spectra (IR) were recorded on a Nicolet 205 FT-IR and UV spectra were recorded on a Shimadzu UV-240 or a Sinco S-3100. Flow injection analysis (FIA) was performed with the ECL detection system described previously [5].

4.2. Experimental conditions

In the FIA experiments, the dual platinum electrode was polished prior to each experiment with 0.05 μm alumina, sonicated, and rinsed with methanol followed by water. The flow cell was assembled and placed in the FIA system. The buffered carrier stream flow rate was 2.0 mL/min. The working electrode was held at a potential of +1.3 V (vs. the Ag quasi-reference electrode). Ru(II) complex solution and tripropylamine (TPA) solutions were prepared in the same 50 mM pH 7.0 phosphate buffer. TPA solutions (1.0 mM) were mixed with 1.0 mM Ru(II) complex solutions (1:1 v/v). A mixture of Ru(II) complex and TPA was injected and passed through the cell. Blank injections were made in all studies. Blanks were prepared by mixing the given concentration of Ru(II) complex solution and the same buffer (1:1 v/v). Corrected ECL signals were obtained by subtracting the ECL signals for blank solutions from the observed ECL signals for TPA. For all studies, the ECL signal was calculated on the basis of the maximum peak height. In the pH study, solutions of each $[\text{Ru}(\text{DTDP})_n(\text{L})_{3-n}]^{2+}$ compound were prepared at different pH values covering a range from 4 to 10. In order to cover wide range of pH values, it was necessary to use three different buffer systems. Buffer solutions used in these studies were acetate buffer (pH 4.0–5.0), phosphate buffer (pH 6.0–8.0), and borate buffer (pH 9.0–10.0). One millimolar TPA and each 1.0 mM $[\text{Ru}(\text{DTDP})_n(\text{L})_{3-n}]^{2+}$ solution were prepared in the 100 mM buffer solution. Each $[\text{Ru}(\text{DTDP})_n(\text{L})_{3-n}]^{2+}$ solution was mixed with TPA solution (1:1 v/v). Mixture was injected and passed through the flow cell. The carrier stream was delivered at a flow rate of 2.0 mL/min.

4.3. Syntheses

4.3.1. General procedure for the preparation of $[\text{Ru}(\text{L})(\text{L}')_2](\text{PF}_6)_2$ ($\text{L}, \text{L}' = \text{DTDP}, \text{bpy}, \text{dmbpy}, o\text{-phen}, o\text{-phen-Cl}, \text{bpy}-(\text{CHO})_2$)

A solution of $[\text{RuCl}_2(p\text{-cymene})]_2$ (55.1 mg, 0.09 mmol) and L (0.18 mmol) in ethanol (5 mL) was

stirred for 2 h. Then, L' (0.36 mmol) and distilled water (10 mL) was added to the solution, which was then refluxed for an additional 24 h. The reaction was monitored by TLC. After cooling to r.t., ethanol was removed under reduced pressure and the residue was treated with a saturated aqueous solution of NH_4PF_6 , which gave a red precipitate. The solid was filtered and recrystallized from acetonitrile/ethyl acetate. Dark red crystals were obtained in 40–72% yield.

4.3.2. $[\text{Ru}(\text{DTDP})_2(\text{bpy})](\text{PF}_6)_2$ (**5**)

Yield: 57%. UV (Acetone): 330, 450 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.62 (s, 6H), 1.67 (s, 6H), 1.69 (s, 6H), 1.73 (s, 6H), 7.38–7.42 (m, 2H), 7.69–7.74 (m, 2H), 7.93–7.99 (m, 4H), 8.12–8.23 (m, 4H), 8.49–8.51 (m, 2H), 8.80–8.83 (m, 2H), 8.98–9.12 (m, 4H). FAB MS m/z : 982 ($\text{M} - \text{PF}_6^-$) $^+$, 836 ($\text{M} - 2\text{PF}_6^- - \text{H}^+$) $^{2+}$, 681 ($\text{Ru}(\text{DTDP})_2$) $^+$, 546 ($\text{Ru}(\text{DTDP})(\text{bpy})$) $^+$. IR (KBr): 3116, 2974, 1751, 1605, 1466, 1244, 833 cm^{-1} .

4.3.3. $[\text{Ru}(\text{DTDP})(\text{bpy})_2](\text{PF}_6)_2$ (**6**)

Yield: 72%. UV (Acetone): 332, 449 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.65 (s, 6H), 1.71 (s, 6H), 7.31–7.36 (m, 2H), 7.56–7.61 (m, 2H), 7.81–7.94 (m, 4H), 8.08–8.24 (m, 6H), 8.41–8.43 (m, 2H), 8.76–8.82 (m, 4H), 9.05–9.08 (m, 2H). FAB MS m/z : 993 (M^+), 849 ($\text{M} - \text{PF}_6^- + \text{H}^+$) $^+$, 703 ($\text{M} - 2\text{PF}_6^-$) $^{2+}$, 547 ($\text{Ru}(\text{DTDP})(\text{bpy})$) $^+$, 413 ($\text{Ru}(\text{bpy})_2$) $^+$, 257 ($\text{Ru}(\text{bpy})$) $^+$. IR (KBr): 3117, 2974, 2933, 2871, 1749, 1608, 1466, 1426, 1244, 837 cm^{-1} .

4.3.4. $[\text{Ru}(\text{DTDP})_2(\text{dmbpy})](\text{PF}_6)_2$ (**7**)

Yield: 67%. UV (Acetone): 330, 456 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.64 (s, 6H), 1.69 (s, 6H), 1.71 (s, 6H), 1.75 (s, 6H), 2.53 (s, 6H), 7.25 (d, $J = 5.3$ Hz, 2H), 7.70–7.75 (m, 4H), 7.99 (dd, $J = 5.1, 8.4$ Hz, 2H), 8.22 (d, $J = 5.1$ Hz, 2H), 8.51 (d, $J = 5.1$ Hz, 2H), 8.68–8.72 (m, 2H), 8.99 (d, $J = 8.4$ Hz, 2H), 9.11 (d, $J = 8.6$ Hz, 2H). FAB MS m/z : 1012 ($\text{M} - \text{PF}_6^- + 2\text{H}^+$) $^+$, 836 ($\text{M} - 2\text{PF}_6^- + 2\text{H}^+$) $^{2+}$, 683 ($\text{Ru}(\text{DTDP})_2 + 2\text{H}^+$) $^+$, 575 ($\text{Ru}(\text{DTDP})(\text{dmbpy})$) $^+$. IR (KBr): 3113, 2973, 1750, 1621, 1429, 842 cm^{-1} .

4.3.5. $[\text{Ru}(\text{DTDP})(\text{dmbpy})_2](\text{PF}_6)_2$ (**8**)

Yield: 63%. UV (Acetone): 331, 456 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.57 (s, 6H), 1.62 (s, 6H), 2.38 (s, 6H), 2.48 (s, 6H), 7.06 (d, $J = 5.7$ Hz, 2H), 7.33 (d, $J = 5.3$ Hz, 2H), 7.50 (d, $J = 5.7$ Hz, 2H), 7.78–7.84 (m, 4H), 8.31 (d, $J = 5.3$ Hz, 2H), 8.57 (d, $J = 13.4$ Hz, 2H), 8.94 (d, $J = 8.1$ Hz, 2H). FAB MS m/z : 1051 ($\text{M} + 2\text{H}^+$) $^+$, 906 ($\text{M} - \text{PF}_6^- + 2\text{H}^+$) $^+$, 760 ($\text{M} - 2\text{PF}_6^- + \text{H}^+$) $^{2+}$, 576 ($\text{Ru}(\text{DTDP})(\text{dmbpy}) + \text{H}^+$) $^+$, 470 ($\text{Ru}(\text{dmbpy})_2 + \text{H}^+$) $^+$. IR (KBr): 3086, 2982, 2932, 2878, 1750, 1620, 1481, 1427, 1242, 850 cm^{-1} .

4.3.6. $[\text{Ru}(\text{DTDP})_2(\text{bpy}-(\text{CHO})_2)](\text{PF}_6)_2$ (**9**)

Yield: 40%. UV (Acetone): 330, 443 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.54 (s, 6H), 1.58 (s, 6H), 1.62 (s, 6H), 1.64 (s, 6H), 7.60–7.70 (m, 4H), 7.81–7.89 (m, 2H), 8.13–8.23 (m, 4H), 8.41–8.48 (m, 2H), 8.92–9.08 (m, 4H), 9.25–9.31 (m, 2H), 10.12 (s, 2H). FAB MS m/z : 894 ($\text{M} - 2\text{PF}_6^-$) $^{2+}$, 683 ($\text{Ru}(\text{DTDP})_2 + 2\text{H}^+$) $^+$. IR (KBr): 3116, 2966, 2939, 2869, 1708, 1609, 1432, 1259, 837 cm^{-1} .

4.3.7. $[\text{Ru}(\text{DTDP})(\text{bpy}-(\text{CHO})_2)_2](\text{PF}_6)_2$ (**10**)

Yield: 55%. UV (Acetone): 332, 485 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.56 (s, 6H), 1.62 (s, 6H), 7.61–7.67 (m, 2H), 7.81–7.87 (m, 4H), 8.36–8.42 (m, 4H), 9.02–9.05 (m, 2H), 9.27–9.31 (m, 3H), 10.10 (s, 2H), 10.18 (s, 2H). FAB MS m/z : 962 ($\text{M} - \text{PF}_6^-$) $^+$, 817 ($\text{M} - 2\text{PF}_6^-$) $^{2+}$, 605 ($\text{Ru}(\text{DTDP})(\text{bpy}-(\text{CHO})_2) + 2\text{H}^+$) $^+$. IR (KBr): 3089, 2973, 2932, 2868, 1750, 1707, 1614, 1426, 1197, 841 cm^{-1} .

4.3.8. $[\text{Ru}(\text{DTDP})_2(o\text{-phen})](\text{PF}_6)_2$ (**11**)

Yield: 68%. UV (Acetone): 329, 450 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.68 (s, 12H), 1.75 (s, 12H), 7.77–7.84 (m, 6H), 8.33–8.44 (m, 8H), 8.80 (d, $J = 8.3$ Hz, 2H), 9.09 (d, $J = 8.3$ Hz, 4H). FAB MS m/z : 1006 ($\text{M} - \text{PF}_6^-$) $^+$, 860 ($\text{M} - 2\text{PF}_6^- - \text{H}^+$) $^+$, 680 ($\text{Ru}(\text{DTDP})_2 - \text{H}^+$) $^+$, 572 ($\text{Ru}(\text{DTDP})(o\text{-phen}) + \text{H}^+$) $^+$. IR (KBr): 3107, 2977, 2938, 2881, 1751, 1464, 1427, 841 cm^{-1} .

4.3.9. $[\text{Ru}(\text{DTDP})(o\text{-phen})_2](\text{PF}_6)_2$ (**12**)

Yield: 55%. UV (Acetone): 329, 448 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.68 (s, 6H), 1.75 (s, 6H), 7.77–7.84 (m, 6H), 8.35–8.44 (m, 10H), 8.79 (ddd, $J = 1.3, 2.6, 8.2$ Hz, 4H), 9.67 (d, $J = 8.6$ Hz, 2H). FAB MS m/z : 897 ($\text{M} - \text{PF}_6^-$) $^+$, 751 ($\text{M} - 2\text{PF}_6^-$) $^{2+}$, 571 ($\text{Ru}(\text{DTDP})(o\text{-phen})$) $^+$, 460 ($\text{Ru}(o\text{-phen})_2 - \text{H}^+$) $^+$, 391 ($\text{Ru}(\text{DTDP})$) $^+$. IR (KBr): 3106, 2977, 2939, 1749, 1426, 1240, 839 cm^{-1} .

4.3.10. $[\text{Ru}(\text{DTDP})_2(o\text{-phen-Cl})](\text{PF}_6)_2$ (**13**)

Yield: 60%. UV (Acetone): 329, 450 nm. ^1H NMR (300 MHz, acetone- d_6): δ 1.64 (s, 12H), 1.71 (s, 12H), 7.75–7.89 (m, 6H), 8.32–8.40 (m, 6H), 8.58–8.59 (m, 1H), 8.69–8.72 (m, 1H), 8.88–8.91 (m, 1H), 9.02–9.05 (m, 4H). FAB MS m/z : 1042 ($\text{M} - \text{PF}_6^- + \text{H}^+$) $^+$, 897 ($\text{M} - 2\text{PF}_6^- + \text{H}^+$) $^{2+}$, 683 ($\text{Ru}(\text{DTDP})_2 + \text{H}^+$) $^+$, 607 ($\text{Ru}(\text{DTDP})(o\text{-phen-Cl}) + \text{H}^+$) $^+$. IR (KBr): 3104, 2982, 2937, 2874, 1750, 1465, 1426, 1248, 835 cm^{-1} .

4.3.11. $[\text{Ru}(\text{DTDP})(o\text{-phen-Cl})_2](\text{PF}_6)_2$ (**14**)

Yield: 65%. UV (Acetone): 450 nm. ^1H NMR (300 MHz, Acetonitrile- d_3): δ 1.65 (s, 6H), 1.72 (s, 6H), 7.57–7.77 (m, 7H), 7.97–8.10 (m, 5H), 8.42 (d, $J = 1.4$), 8.52 (dd, $J = 1.5, 9.7$ Hz, 2H), 8.80–8.85 (m, 4H). FAB MS m/z : 965 ($\text{M} - \text{PF}_6^-$) $^+$, 820 ($\text{M} - 2\text{PF}_6^-$) $^{2+}$, 606

(Ru(DTDP)(5-chloro-*o*-phen))⁺. IR (KBr) 3108, 2973, 2938, 1734, 1621, 1426, 1242, 845, 724 cm⁻¹.

4.3.12. Preparation of [Ru(DTDP)₃](PF₆)₂ (**15**)

A solution of DTDP (87.0 mg, 0.3 mmol) and [RuCl₂(*p*-cymene)]₂ (30.0 mg, 0.05 mmol) in 15 mL of ethanol–water (1:2) mixture was refluxed for 24 h. After cooling, the solvent was removed under reduced pressure and was treated with a saturated aqueous NH₄PF₆ solution to give a red precipitate. Dark red crystal was obtained in 64% yield from recrystallization in acetone/ethyl acetate. UV (Acetone): 328, 451 nm. ¹H NMR (300 MHz, acetone-d₆): δ 1.68 (s, 18H), 1.75 (s, 18H), 7.81 (dd, *J* = 5.1, 8.5 Hz, 6H), 8.37 (dd, *J* = 1.1, 5.1 Hz, 6H), 9.08 (dd, *J* = 1.1, 8.5 Hz, 6H). FAB MS *m/z*: 1116 (M – PF₆⁻)⁺, 971 (M – 2PF₆⁻)²⁺, 681 (Ru(DTDP)₂)⁺. IR (KBr): 3107, 2974, 1751, 1428, 1253, 846 cm⁻¹.

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