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Aryl-diamide bridged binuclear ruthenium (II) tris(bipyridine) complexes: Synthesis, photophysical, electrochemical and electrochemiluminescence properties

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Abstract

Several new symmetrical aromatic hydrocarbon bridged bipyridine ligands and their binuclear Ru (II) complexes have been designed, synthesized and characterized on the basis of ^{1}H NMR, MS and HRMS. Their absorption and emission properties, electrochemical behaviors and electrochemical luminescence were investigated. All ruthenium complexes show characteristic MLCT absorption and similar redox potential. Among the three complexes reported, **4c** has the best electrochemical luminescence property.
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1. Introduction

The design and synthesis of molecules that have reliable electrogenerated chemiluminescence (ECL) properties are attracting considerable interests [1]. Typically, aromatic hydrocarbons [2] and their derivatives [3] are used either by themselves or by the incorporation to a metal complex [4] as an ECL candidate. One of the most widely used metal complexes is the ruthenium tris(bipyridine) $[Ru(bpy)_3]^{2+}$ [5]. Since the first report by Bard on the electrogenerated chemiluminescence (ECL) of $[Ru(bpy)_3]^{2+}$ [6], the ECL properties of this complex have been studied extensively and widely used in analytical applications, especially in clinical diagnostics [7] and environmental assays [8]. Potential applications also include uses in display devices [9]. Polynuclear system based complexes seem to be the most

potential ECL active substances owing to their multiple redox centers [10]. In recent studies, complexes with two or three ruthenium polypyridyl units connected by a bridging ligand of proporxycarbonyl linker amino acid lysine or the related dipeptide (LysLys) showed that the ECL intensity increases by 30% [11].

On the other hand, significant advances have been achieved recently in the design of electroluminescence molecules of aryl ethylene type [12], e.g., phenylenevinylenes oligomer and phenyl thiophenevinylenes oligomers. Its extension of a π-conjugation system has brought changes in the properties of such assembly, leading to a better electron communications. More importantly, polynuclear ruthenium complex units can be connected through conjugate system by triple bond and aromatic ring [13]. Significant example is the ruthenium tris(bipyridine) bridged with tetraphenylene, which shows fully reversible voltage-dependent switching between green and red light emission [14]. Based on this observation, we would like to examine the EL or ECL for the system of aromatic ring alternatively

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coupled with double or triple bond. However, in some cases, the construction for such molecules encountered great difficulties, although the synthetic methodology has been established, for example, by transition metal catalyzed coupling reaction [15].

We are clearly aware that the amide bond might be a good candidate for the replacement of the double or triple bond, since it has considerable double bond characters due to the conjugation. The lone pair electrons on nitrogen can delocalize into the carbonyl group. In addition, the amide group provides a natural point of attachment to other structure subunit due to the facile synthesis by the connection of acid chloride with amine. However, to the best of our knowledge, amide-containing compounds are quite rare used as ECL material, and there have been very scattered examples containing the amide bond as connections for the construction of substances with electroluminescence properties [16]. To investigate this possibility, we designed a new kind of molecules showed as follows:
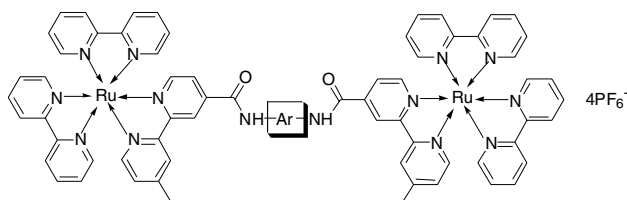
The covalent combination of the aromatic subunits and ruthenium tris(bipyridine) through amide bond will be the substitution of that connected by double or triple bond. We are now interested in the design and synthesis of the amide-bond containing hydrocarbons (analogue of **3** with different central aromatic rings) **3a–3c** as well as their bis-capped ruthenium tris(bipyridine) complexes **4a–4c**. In this work,

an effort has been made to develop this new class of molecule that shows excellent ECL properties, including the design and synthesis.

2. Results and discussion

2.1. Synthesis and characterization

In connection with our studies on the synthesis of tris(bipyridine) ruthenium complexes, we need to prepare the key ligand **3a**, **3b** and **3c**. The synthesis of our three target ligands was carried out as outlined in Scheme 1. 1,4-Phenylenediamine reacted with 4′-methyl-2,2′-bipyridi-nyl- 4-carbonyl chloride (prepared from 4,4′-dimethyl-2, 2′-bypyridine) [17] in the presence of Et₃N to form phe-nyl-centered bipyridine ligand **3a** in good yield. The other two ligands **3b** and **3c** were prepared in the similar manner. These compounds proved extremely insoluble in even the most polar aprotic solvents, making both purification and characterization difficult. Therefore for these three ligands, it is rather difficult to perform their ^{13}C NMR. Nevertheless, the structures of the three aryl diamides were well confirmed by ^{1}H NMR. It was worth mentioning that the experiment condition for the synthesis of the ligands was vital. Higher temperature or longer reaction time yielded other by-products.

With the three ligands in hand, the preparation of tris(bipyridine) ruthenium complexes were accomplished quite easily. The ligands were refluxed in EtOH–H₂O (1:1) with Ru(bpy)₂Cl₂ and the binuclear complexes were purified by column chromotography to give the orange-colored product in good yield. The structures of these compounds were confirmed by ^{1}H, ^{13}C NMR, MS and each proton was well assigned by ^{1}H-^{1}H COSY. Compound **4a** showed an ESI^{+}-MS molecular ion at m/z 1328.28, consistent with the formula C₇₀H₅₆N₁₄O₂Ru₂. The strong UV
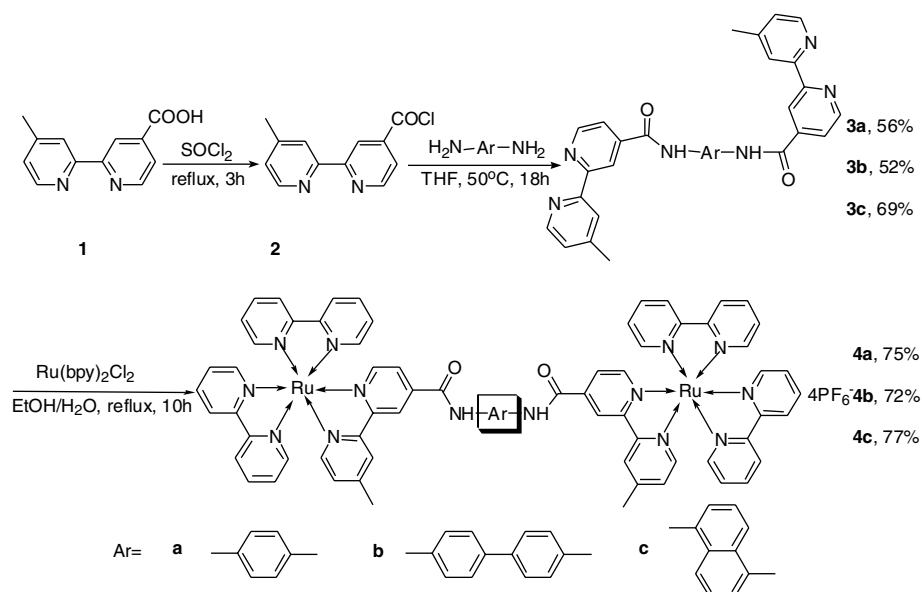
Scheme 1. Synthetic route for ligands **3a–3c** and metal complexes **4a–4c**.

absorption maximum at 460 nm indicated the presence of $[Ru(bpy)_3]^{2+}$ (Fig. 1). In the ^{1}H NMR spectrum for complex **4a**, the chemical shift for each proton in bpy ligand (designated as b) follows the general trend order as reported in the literature [18]: H_{b3} (8.50) > H_{b4} (8.06) > H_{b6} (*ca.* 7.72) > H_{b5} (7.4). Those in amide bpy ligand (designated as a) are easy for assignment based on the peak split. The proton on the central phenyl was observed in δ 7.82, reflecting the strong unshielding effect compared to the average value (7.26). ^{1}H NMR experiments indicated that the presence of amides at δ 9.34. The ^{1}H NMR data of **4b** and **4c** showed a strong resemblance with those of **4a**, providing evidence for the presence of $Ru(bpy)_3$ unit. Clear differences in the ^{1}H NMR spectra of these compounds were only evident in the low field region for different central aromatic moieties (phenyl, biphenyl, and naphthalyl).

2.2. Electronic absorption and emission spectra

Absorption and emission spectra were measured in CH_3CN and shown in Fig. 1. $[Ru(bpy)_3]^{2+}$ was used as reference, which showed two bands at 454 and 248 nm for the MLCT absorption, and one band at 286 nm for the ligand centered $\pi–\pi^*$ absorption [17]. The absorption spectra for the three target binuclear ruthenium complexes **4a**, **4b** and **4c** were quite similar to that of the reference $[Ru(bpy)_3]^{2+}$, with a broad band at 460 nm and an observable band at 244 nm for $d\pi$ (Ru) $\rightarrow \pi^*$(bpy) metal to ligand charge transfer ([1]MLCT) and an intense ligand centered $\pi–\pi^*$ absorption at 288 nm. These similar maximal absorptions indicate the absence of a strong electronic interaction between the two $[Ru(bpy)_3]^{2+}$ units. It was noted that the more extended conjugation for the three complexes leads to almost no shift of the MLCT band (see Table 1).

The emission spectra of **4a**, **4b** and **4c** are shown in Fig. 1b. All of these three complexes exhibited almost the same emission maxima, centered at 642, 638 and 636 nm.

Table 1
The absorption spectra for the three ruthenium complexes in CH_3CN

Complexes	Absorption			Emission	Φ
	λ_{max}/nm			λ_{max}/nm	
$Ru(bpy)_3 2PF_6$	245	283	454	618	0.062
4a	244	288	458	642	0.053
4b	244	288	459	638	0.081
4c	242	288	458	636	0.058

This indicates that the [3]MLCT excited state is almost the same for the three complexes and have the same energy level, no matter what kind of linkage existed in the molecules. The average value of *ca.* 640 nm for the emission maxima is red shifted by only *ca.* 20 nm from that of the $[Ru(bpy)_3]^{2+}$ that it is derived from. The small difference in emission properties of these three complexes and that of its parent core molecule might be caused by the lack of delocalization across the amide bond connecting the two parts of the $[Ru(bpy)_3]^{2+}$ moiety. The twisting around the central connecting bond made the full delocalization of the molecular orbitals over the entire molecule not possible. This small difference may also reflect the strong electron accepting nature of the amide bonds. The luminescence quantum yields for **4a** and **4c** are lower than that of the reference $[Ru(bpy)_3]^{2+}$, while for **3b** is higher to the reference complex. A large strokes shift of *ca.* 170 nm was observed between the absorption and emission spectra maxima (see Fig. 1(b)).

2.3. Electrochemistry

The redox behavior of the three different aromatic amide bridged homo-binuclear complexes **4a**, **4b** and **4c** was determined by cyclic voltammetry (CV) in MeCN ($c = 10^{-4}$ M) using tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting salt (see Fig. 2). All electrochemical data for the three ruthenium complexes were recorded in Table 2. The oxidation potentials of **4a**, **4b**
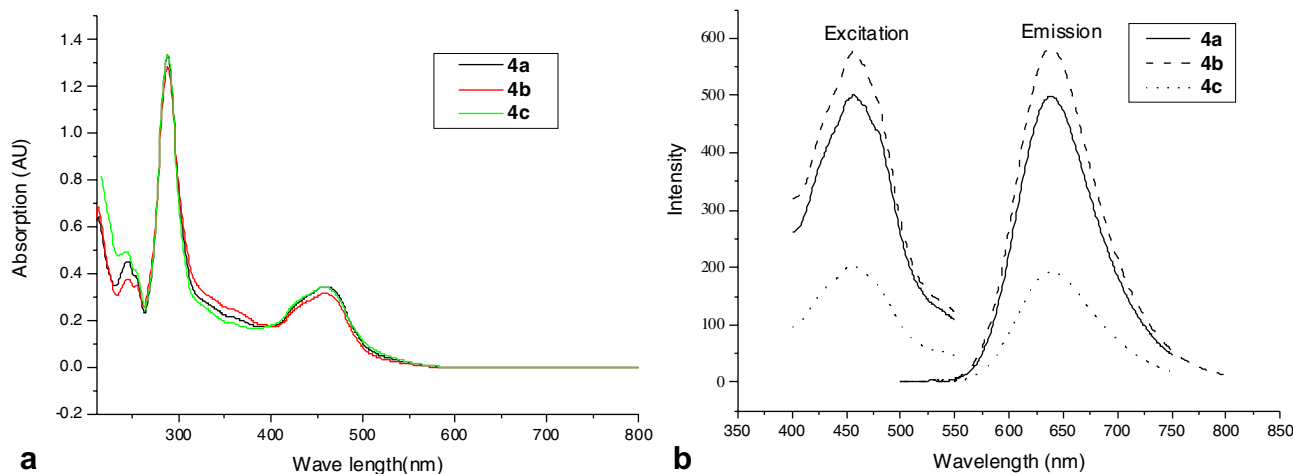

Fig. 1. (a) UV–vis absorption spectra of complexes **4a**, **4b** and **4c** in CH_3CN. (b) Excitation and emission spectra of complexes **4a**, **4b** and **4c** in CH_3CN (10^{-5} M) at 25 °C (λ_{ex} = 457 nm, λ_{em} = 639 nm).
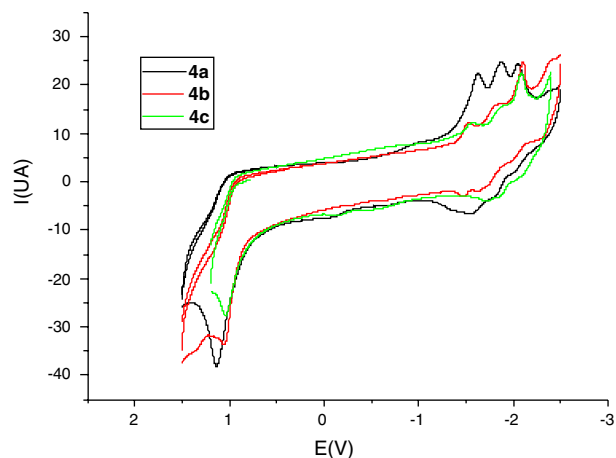
Fig. 2. Cyclic voltammogram of complex **4**, 0.1 mM in 0.05 M of *n*-Bu$_4$NPF$_6$/CH$_3$CN at a scan rate of 100 mV/s.

Table 2
Electrochemical data for three ruthenium complexes

Complexes	E_p (V)			
	Oxidation	Reduction		
Ru(bpy)$_3$·(2PF$_6$)[a] [19]	+1.35	−1.32	−1.51	−1.76
Ru(bpy)$_3$·(2PF$_6$)	+0.95	−1.67	−1.88	−2.15
4a	+1.04	−1.53	−1.73	−2.04
4b	+1.03	−1.52	−1.72	−2.04
4c	+1.01	−1.62	−1.85	−2.14

[a] Measured with SCE as reference electrode, otherwise with Ag/AgNO$_3$ as reference electrode.

and **4c** occurred in a single irreversible two electron step at potentials E_p = +1.04, +1.03, and +1.01 V *vs.* Ag/Ag$^+$ electrode, respectively, with the peak current for the oxidation being noticeably larger than that for the reduction. The cyclic voltammogram of these ruthenium binuclear complexes show only a single oxidation wave, suggesting further relatively little or weak interaction between the two ruthenium centers. The oxidation potential of the present binuclear ruthenium complex is more positive than that obtained for the reference [Ru(bpy)$_3$]$^{2+}$(E_p = +0.95 V), which indicates that binuclear ruthenium complex is more difficult to be oxidized. In the cathodic region, complex **4a** exhibited three quasi-reversible reduction wave at −1.53, −1.73, and −2.04 V. Complex **4b** has also three peaks at almost the same to that of **4a**, while for **4c**, the reduction potential moved more negatively at −1.62, −1.85 and −2.14 V, respectively.

2.4. Electrochemiluminescence

ECL emission spectra were recorded in the presence of TPA with the sample concentration of 0.1 mM (see Fig. 3). All the ECL data of the three ruthenium complexes are shown in Table 3. The pulsed voltage was used from the first negative to first positive peak potentials. Ru(bpy)$_3^{2+}$ was used as the reference for the measuring the relative ECL efficiency (Φ_{ECL}). All three complexes **4a**, **4b** and **4c**
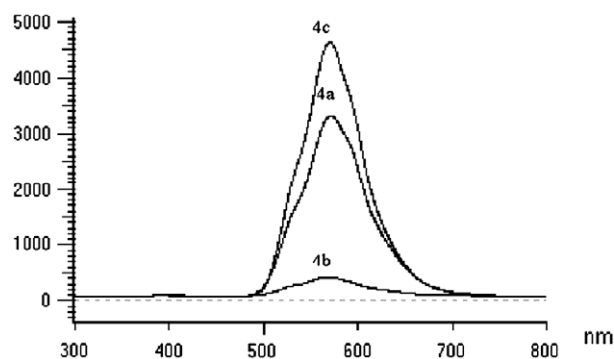

Fig. 3. Electrochemiluminescence spectra of complexes **4a**–**4c** in MeCN (1.22×10^{-4} mol/L) at room temperature.

Table 3
ECL data for three ruthenium complexes

Complexes	ECL λ_{max}/nm	ECL	ECL (a.u.)	ECL (times)
[(bpy)$_3$Ru(2PF$_6$)	595	202	404	1
4a	569	3327	3327	8.2
4b	570	447	447	1.1
4c	570	4627	4627	11.5

exhibited ECL emission centered around 570 nm with different intensities. The ECL emissions of the three complexes have the same shapes, but different maxima compared to their fluorescence spectra with red-shifted by *ca*. 65 nm. Since there existed little interaction between the two equal ruthenium tris(bipyridine) subunits based on the UV–vis spectra and cyclic voltammograms studies, we calculated the efficiency by comparing the number of ruthenium tris(bipyridine) containing in the molecules. Thus, the actual efficiency is half of that by measuring. The relative emission intensities behaves in the following order: **4c** > **4a** > **4b**, respectively, 4, 0.5 and 6 times than that of the reference compound. The reason is not clear, but it seemed that this related to the polarity and the conjugation of the whole molecules. The reaction mechanism is quite certain that electrochemically oxidized Ru (III) reacted with radical Pr$_2$N$^-$CH$_2$CH$_2$CH$_3$ which was obtained from Pr$_2$N$^+$CH$_2$CH$_2$CH$_3$ radical cation. The [Ru(bpy)$_3$]$^{3+}$ was reduced to Ru(II) with concomitant formation of Pr$_2$N$^+$=CHEt and then to give out the emission to the ground state.

As a reference compound, Ru(bpy)$_3^{2+}$ has been already widely used in analytical aspects, including the detection of biological agents, metal cations and DNA mutations because of its low-lying metal-to-ligand charge transfer (MLCT) excited states, high emission quantum yield and long excited-stated lifetimes. A comparison of the emission intensities of **4a**–**4c** with the reference complex Ru(bpy)$_3^{2+}$ proves that **4c** is the most ECL-active complex with the rigidity and planarity of the bridging aromatic unit, which contributes much to the ECL efficiency. Thus much attention will be paid to its potential applications in above-mentioned areas. The stronger intensity of **4c** compared

to the reference Ru(bpy)$_3^{2+}$ means the higher sensitivity and lower detection limit, which could provide quickly access to a wide range of analytical applications. The PF$_6^-$ counter ions in these complexes could be exchanged with Cl$^-$ to improve the solubility in aqueous solution. This work is in progress.

In conclusion, the aryl-diamide centered binuclear ruthenium (II) tris(bipyridine) complexes **4a**, **4b** and **4c** are obtainable from readily available 4-methyl-2,2′-bipyridinyl-4-carboxylic acid aromatic diamine *via* the amidation. ECL studies showed that **4c** has much higher emission intensity than the reference. The combination of amide bond and central aromatic ring seems to be responsible for the high efficiency of ECL. Based on these results, work will be extended in our laboratory to the same kind of molecules that have thiophene analogue as the bridges.

3. Experimental section

General: ^{1}H NMR at 400 MHz and ^{13}C NMR were recorded on a Varian spectrometer. FT-NMR instrument. UV–vis absorption spectra were recorded on a model 8452A Hewlett–Packard diode array spectrophotometer referenced against a solvent blank (CH$_3$CN). Electrochemistry was performed with a CH Instrument Model 660. All experiments were performed with the protection of Argon with Bu$_4$NPF$_6$ as supporting electrolyte, glassy-carbon as working electrode and Ag/AgNO$_3$ electrode as reference. The eluents for the column chromatography was selected with the polarity to ensure all R_f values kept at *ca.* 0.2 for the better separation.

All reagents from commercial sources were used without further purification except for the following: THF and Et$_3$N were distilled from sodium. *p*-Phenylenediamine, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 4,4′-diphenylenediamine, 1,5-naphthalenediamine, hydrated ruthenium trichloride, and ammonium hexafluorophosphate were purchased from Chinese Chemicals Corporation. 4′-Methyl-2,2′-bipyridyl-4-carbaldehyde [20] and *cis*-[Ru(bpy)$_2$Cl$_2$] · 2H$_2$O [21] were prepared according to the literature procedures. The serial numbers of complexes **4a**, **4b** and **4c** are shown in Fig. 4.

3.1. Bis(4′-methyl-2,2′-bipyridinyl-4-carboxamide)-N,N′-(1,4-phenylene) (3a)

A solution of 4′-methyl-2,2′-bipyridinyl-4-carboxylic acid (214 mg, 1 mmol) in SOCl$_2$ (10 mL) was refluxed for 2 h. After removing excess of SOCl$_2$ by distillation under reduced pressure and dried in vacuum at 70 °C for 1 h the residue was dissolved in dry THF (2 mL) and then added dropwise to the mixture of TEA (150 mg, 1.5 mmol) and *p*-phenylenediamine (54 mg, 0.5 mmol) in anhydrous THF (20 mL) under vigorously stirring within 5 min. The reaction mixture was left to react for 18 h under Argon at 50 °C, and then filtered on a frit. The white precipitate was washed with THF (3 × 10 mL), water (3 × 10 mL) and dried over 70 °C under vacuum. White powder was obtained (140 mg, 56%). ^{1}H NMR (CD$_3$)$_2$SO δ 2.45 (s, 6H), 7.36 (d, 2H, J = 4.8 Hz), 7.83 (s, 4H), 7.93 (d, 2H, J = 8.8 Hz), 8.30 (s, 2H), 8.62 (d, 2H, J = 4.8 Hz), 8.86 (m, 4H), 10.73 (s, 2H); MS m/z: [M + H]$^+$ 501.5.
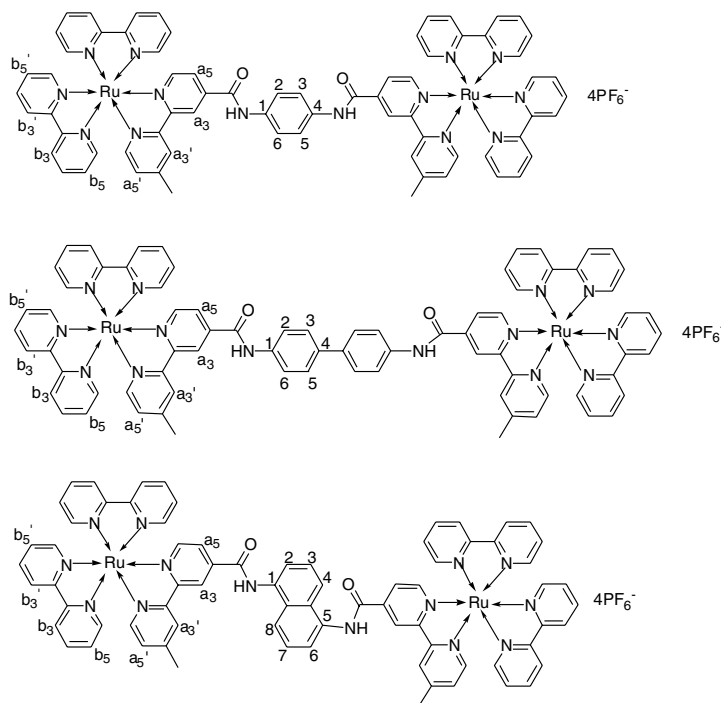

Fig. 4. Serial numbers of complexes **4a**, **4b** and **4c**.

3.2. Bis(4'-methyl-2,2'-bipyridinyl-4-carboxamide)-N,N'-(4,4'-biphenylene) (3b)

This ligand was prepared following the same procedure as described for the preparation of **3a** using 4'-methyl-2,2'-bipyridinyl-4-carboxylic acid (214 mg, 1 mmol), 4, 4'-diphenylenediamine (92 mg, 0.5 mmol) and 3 eq. of TEA to give a white solid (150 mg, 52%). ^{1}H NMR $(CD_3)_2SO$ δ 2.46 (s, 6H), 7.37 (d, $J = 4.0$ Hz, 2H), 7.75 (d, $J = 8.8$ Hz, 4H), 7.93 (d, $J = 8.8$ Hz, 4H), 7.96 (d, $J = 2.0$ Hz, 2H), 8.32 (s, 2H), 8.63 (d, $J = 4.8$ Hz, 2H), 8.88 (s, 2H), 8.90 (d, $J = 5.6$ Hz, 2H), 10.81 (s, 2H) MS m/z: $[M + H]^+$ 577.3 TOF MS EI[+]: 576.2269.

3.3. Bis(4'-methyl-2,2'-bipyridinyl-4-carboxamide)-N,N'-(1,5-naphthylene) (3c)

This ligand was prepared as the same procedure for the preparation of **3a** outlined above using 4'-methyl-2,2'-bipyridinyl-4-carboxylic acid (214 mg, 1 mmol), 1,5-naphthalenedimine (79 mg, 0.5 mmol) and 3 eq. of TEA to give a white solid (190 mg, 69%). ^{1}H NMR $(CD_3)_2SO$ δ 2.46 (s, 6H), 7.37 (d, $J = 4.0$ Hz, 2H), 7.64–7.68 (m, 4H), 8.01 (d, $J = 8.8$ Hz, 2H), 8.07–8.09 (m, 2H), 8.34 (s, 2H), 8.63 (d, $J = 4.4$ Hz, 2H), 8.93 (d, $J = 4.0$ Hz, 2H), 9.01 (s, 2H), 10.98 (s, 2H) MS m/z: $[M + H]^+$ 551.7 TOF MS EI[+]: 550.2116.

3.4. Bis(2,2'-bipyridine)-ruthenium-bis(4'-methyl-2,2'-bipyridinyl-4-carboxamide)-N,N'-(1,4-phenylene)-ruthenium-bis(2,2'-bipyridine) hexafluorophosphate (4a)

Bis-2,2'-bipyridyl ruthenium dichloride (55 mg, 0.11 mmol) and **3a** (25 mg, 0.05 mmol) were refluxed in the solution of EtOH and H_2O (20 mL, 1:1) under argon for 10 h. The color of the solution turned red. The solvent was removed by rotary evaporation and the residue was purified by column chromatography packed with silica gel, with acetonitrile–water–saturated KNO_3(100:10:1) as eluent. The solvent was removed by rotary evaporation and the residue was re-dissolved in a minimum volume (5 mL) of acetonitrile, and the precipitation appeared by addition of saturated NH_4PF_6. The precipitation was filtered off and dried in vacuum to give the red solid (71 mg, 75%). ^{1}H NMR (CD_3CN) δ 2.56 (s, 6H, –CH_3), 7.28 (d, 2H, $J = 5.2$ Hz, Ha_5), 7.38–7.42 (m, 8H, Hb_5, $Hb_{5'}$, Hb_5, $Hb_{5'}$), 7.56 (d, 2H, $J = 6.0$ Hz, Ha_6), 7.70–7.74 (m, 8H, Hb_6, $Hb_{6'}$, Hb_6, $Hb_{6'}$), 7.78 (dd, 2H, $J = 7.2$ Hz, $J = 1.6$ Hz, $Ha_{5'}$), 7.82 (s, 4H, H_2, H_6, H_3, H_5), 7.91 (d, 2H, $J = 6.0$ Hz, $Ha_{6'}$), 8.06 (ddd, 8H, $J = 8.0$ Hz, $J = 8.0$ Hz, $J = 1.2$ Hz, Hb_4, $Hb_{4'}$, Hb_4, $Hb_{4'}$), 8.50 (d, 8H, $J = 8.0$ Hz, Hb_3, $Hb_{3'}$, Hb_3, $Hb_{3'}$), 8.56 (s, 2H, Ha_3), 8.92 (s, 2H, $Ha_{3'}$), 9.34 (s, 2H, N–H); ^{13}C NMR (CD_3CN) δ 20.51, 121.45, 121.96, 124.54, 125.06, 125.80, 127.86, 129.01, 135.12, 138.13, 143.01, 150.99, 151.79, 151.99, 152.66, 156.20, 156.80, 157.02,

157.24, 158.05, 162.31.TOF MS ES[+] Calc. 1328.2798, $M^{4+}/4$ (m/z) 332.0706; Measured. 1328.2824.

3.5. Bis(2,2'-bipyridine)-ruthenium-bis(4'-methyl-2,2'-bipyridinyl-4-carbox amide)-N,N'-(1,4-biphenylene)-ruthenium-bis(2,2'-bipyridine) hexafluorophosphate (4b)

The procedure for the preparation of compound **4b** was the same as that of compound **4a** from bis-2,2'-bipyridyl ruthenium dichloride (55 mg, 0.11 mmol) and **3b** (29 mg, 0.05 mmol) to give compound **4b** after purified with acetonitrile–water–saturated KNO_3 (100:10:0.8) as an orange-red solid (71 mg, 72%). ^{1}H NMR (CD_3CN) δ 2.55 (s, 6H, –CH_3), 7.28 (d, 2H, $J = 5.6$ Hz, $Ha_{5'}$), 7.38–7.43 (m, 8H, Hb_5, $Hb_{5'}$, Hb_5, $Hb_{5'}$), 7.57 (d, 2H, $J = 6.0$ Hz, $Ha_{6'}$), 7.78 (d, 2H, $J = 6.4$ Hz, Ha_5), 7.70–7.75 (m, 12H, Hb_6, $Hb_{6'}$, Hb_6, $Hb_{6'}$, H_3, H_5), 7.85 (d, 4H, $J = 8.4$ Hz, H_2, H_6), 7.91 (d, 2H, $J = 6.0$ Hz, Ha_6), 8.07 (t, 8H, $J = 8.0$ Hz, Hb_4, $Hb_{4'}$, Hb_4, $Hb_{4'}$), 8.50 (d, 8H, $J = 8.0$ Hz, Hb_3, $Hb_{3'}$, Hb_3, $Hb_{3'}$), 8.56 (s, 2H, $Ha_{3'}$), 8.90 (s, 2H, Ha_3), 9.24 (s, 2H, N–H); ^{13}C NMR (CD_3CN) δ 20.51, 121.29, 121.99, 124.54, 125.05, 125.81, 127.36, 127.85, 129.02, 136.87, 137.62, 138.13, 143.03, 150.99, 151.09, 151.79, 151.99, 152.68, 156.20, 157.02, 157.23, 158.27, 162.42; TOF MS ES[+] Calc. 1404.3084, $M^{4+}/4$ (m/z) 351.0771; Measured. 1401.3084.

3.6. Bis(2,2'-bipyridine)-ruthenium-bis(4'-methyl-2,2'-bipyridinyl-4-carboxamide)-N,N'-(1,5-naphthylene)-ruthenium-bis(2,2'-bipyridine) hexafluorophosphate (4c)

The procedure for the preparation of compound **4c** was the same as that of compound **4a** from bis-2,2'-bipyridyl ruthenium dichloride (55 mg, 0.11 mmol) and **3c** (28 mg, 0.05 mmol) to give compound **4c** after purified with acetonitrile–water–saturated KNO_3 (100:10:0.6) as an orange-red solid (77 mg, 77 %). ^{1}H NMR (CD_3CN) δ 2.56 (s, 6H, –CH_3), 7.29 (d, 2H, $J = 5.2$ Hz, $Ha_{5'}$), 7.40–7.45 (m, 8H, Hb_5, $Hb_{5'}$, Hb_5, $Hb_{5'}$), 7.59 (d, 2H, $J = 6.0$ Hz, $Ha_{6'}$), 7.63 (dd, 2H, $J = 8.4$ Hz, $J = 8.4$ Hz, H_3, H_7), 7.74 (d, 8H, $J = 5.6$ Hz, Hb_6, $Hb_{6'}$, Hb_6, $Hb_{6'}$), 7.79 (d, 2H, $J = 5.2$ Hz, H_4, H_8), 7.86 (d, 2H, $J = 4.8$ Hz, Ha_5), 7.97 (d, 2H, $J = 6.0$ Hz, Ha_6), 8.02–8.10 (m, 10H, Hb_4, $b_{4'}$, Hb_4, $Hb_{4'}$, H_2, H_6), 8.51 (d, 8H, $J = 8.0$ Hz, Hb_3, $Hb_{3'}$, Hb_3, $Hb_{3'}$), 8.57 (s, 2H, $Hb_{3'}$), 8.98 (s, 2H, Ha_3), 9.35 (s, 2H, N–H).^{13}C NMR (CD_3CN) δ 20.51, 122.18, 122.48, 124.57, 125.18, 125.86, 126.30, 127.90, 129.05, 130.13, 133.26, 138.15, 142.63, 151.01, 151.11, 151.82, 152.01, 156.21, 157.03, 157.26, 158.38, 163.69, TOF MS ES[+] Calc. 1378.2954, $M^{4+}/4$ (m/z) 344.5722; Measured. 1378.2888.

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