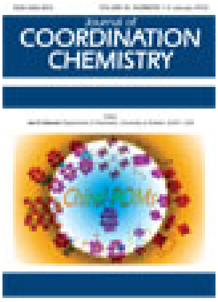

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Synthesis, photophysical, and electrochemical properties of a new family of trinuclear Ru(II) polypyridine complexes

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A series of four tripodal ligands L^{1-4} were prepared by the reaction of 9-(2-hydroxy)phenylimino-4,5-diazafluorene with 1,3,5-*tris*(bromomethyl)benzene, 1,3,5-*tris*(bromomethyl)-2,4,6-trimethylbenzene, *tris*(2-chloroethyl)amine hydrochloride, and pentaerythrityl tetratosylate, respectively, in DMF solution under nitrogen. For each ligand, Ru(II) complexes were prepared by refluxing $Ru(bipy)_2Cl_2 \cdot 2H_2O$ and ligand in 2-methoxyethanol. Photophysical behaviors of these Ru(II) complexes have been investigated by UV-Vis absorption and luminescence spectrometry. They display metal-to-ligand charge transfer absorption at 442 nm in MeCN solution at room temperature and emission at 574 nm in EtOH–MeOH (4 : 1, v/v) glassy matrix at 77 K. Electrochemical studies of the Ru(II) complexes show one Ru(II)-centered oxidation at 1.33 V and three ligand-centered reductions.

Keywords: Tripodal ligand; Ru(II) complex; UV-Vis absorption; Luminescence; Electrochemistry

1. Introduction

Ru(II) polypyridine complexes have attracted much interest in molecular recognition, artificial photosynthesis, DNA intercalation, pH switching, etc. due to their unique combination of chemical stability, redox properties, reactivity, and emission [1]. Polynuclear complexes incorporating Ru(II) polypyridine units have received special attention in connection with development of artificial multicomponent systems for photoinduced electron or energy transfer and other related photonic devices [2]. For instance, $Ru(bipy)_3^{2+}$ and $Os(bipy)_3^{2+}$, covalently attached to the 3′- and 5′-phosphates of two oligonucleotides, are juxtaposed when hybridized contiguously to a fully complementary DNA target. Upon excitation into the metal-to-ligand charge transfer (MLCT) band of $Ru(bipy)_3^{2+}$ leads to resonance energy transfer to the MLCT

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state of $Os(bipy)_3^{2+}$; the system is capable of detecting mutations of DNA [3]. In the design of such polynuclear systems, the bridging ligands used to connect two or more metal polypyridine subunits are crucial because interactions between the bridged units, and thereby the properties of polynuclear complexes, are strongly dependent on the size, shape, and electronic nature of the bridging ligands [4]. A wide range of bridging ligands have been used in recent years and many of them contain 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), or 2,2′ : 6′,2″-terpyridine [5]. Benniston and co-workers prepared a linear 2,2′ : 6′,2″-terpyridine-based trinuclear Ru(II)–Os(II) nanometer-sized complex. This complex comprises two *bis*(2,2′ : 6′,2″-terpyridine)ruthenium(II) terminals connected *via* alkoxy-strapped 4,4′-diethynylated biphenylene units to a central *bis*(2,2′ : 6′,2″-terpyridine) osmium(II) core. Energy transfer occurs with high efficiency from Ru(II) units to the Os(II) center [6]. Cooke *et al.* have shown a new series of supramolecular complexes consisting of Ru(II) polypyridine units bound to dirhodium(II,II) tetracarboxylate cores. Efficient energy transfer from the MLCT triplet state of the Ru-based components to the lowest energy excited state of the dirhodium core takes place at 298 K in MeCN [7]. Much effort has been devoted to the design and synthesis of polypyridine that lead to Ru(II) complexes with interesting photophysical and electrochemical properties. 4,5-Diazafluoren-9-one (dafone) is structurally similar to bipy and phen. However, the rigid structure imposed by the central five-member ring means that the two nitrogen atoms are always held in the same direction to avoid rotational conformation problems. Dafone has a much larger chelate bite compared with bipy and phen (N ··· N: dafone, 3.00 Å; bipy, 2.62 Å; phen, 2.64 Å). As a consequence, Ru(II) complexes including 4,5-diazafluorene have different photophysical and electrochemical properties than $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes [8]. Recently, we described the synthesis, photophysical, and electrochemical properties of trinuclear Ru(II) complexes derived from 4,5-diazafluoren-9-oxime [9] with the goal of synthesizing new 4,5-diazafluoren-9-one based trinuclear Ru(II) complexes with distinct properties. We have now extended this study to the synthesis and characterization of four tripodal ligands and their Ru(II) complexes derived from 9-(2-hydroxy)phenylimino-4,5-diazafluorene. The photophysical and electrochemical properties of these Ru(II) complexes are also presented.

2. Experimental

2.1. *Materials*

2,2′-Bipyridine, 1,10-phenanthroline, 2-aminophenol, p-toluenesulfonyl chloride, 1,3,5-*tris*(bromomethyl)benzene, pentaerythritol, *tris*(2-chloroethyl)amine hydrochloride, mesitylene, ammonium hexafluorophosphate, hydrated ruthenium trichloride, MeCN, CH_2Cl_2, EtOH, MeOH, and DMF were purchased from the Tianji Chemical Reagent Factory. All solvents and raw materials were of analytical grade and used as received, with the exception of MeCN, which was filtered over activated alumina and distilled from P_2O_5 immediately prior to use. Tetrabutylammonium perchlorate (TBAP) [10], 4,5-diazafluoren-9-one [11], 9-(2-hydroxy)phenylimino-4,5-diazafluorene [12], 1,3,5-*tris*(bromomethyl)-2,4,6trimethylbenzene [13], pentaerythrityl tetratosylate [14], and $Ru(bipy)_2Cl_2 \cdot 2H_2O$ [15] were synthesized according to literature procedures.

2.2. *Physical measurements*

Liquid chromatography-mass spectrometry (LC-MS) spectra were recorded on a Bruker Daltonics Esquire 6000 mass spectrometer. ^{1}H NMR spectra were performed on a Mercury Plus 300 spectrometer using TMS as internal standard. Elemental analyses were obtained using a Perkin-Elmer 240C analytical instrument, absorption spectra on a Varian Cary-100 UV-Visible spectrophotometer, and emission spectra with a Hitachi F-4500 spectrophotometer. Emission quantum yields were calculated relative to Ru(bipy)$_3^{2+}$ ($\Phi_{\text{std}} = 0.376$) in an EtOH–MeOH (4 : 1, v/v) glassy matrix and the uncertainty in quantum yields was 15% [16]. Electrochemical measurements were carried out at room temperature using a CHI 660B electrochemical workstation. Cyclic voltammetry and differential pulse voltammetry were performed in MeCN and DMF solutions by using a microcell equipped with a platinum disc working electrode, a platinum auxiliary electrode, and a saturated potassium chloride calomel reference electrode with 0.1 mol L^{-1} TBAP as supporting electrolyte. All samples were purged with nitrogen prior to measurement.

2.3. *Preparations*

1,3,5-Tris[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]benzene (L^1): A mixture of 1,3,5-*tris*(bromomethyl)benzene (213 mg, 0.60 mmol), 9-(2-hydroxy)phenylimino-4,5-diazafluorene (571 mg, 2.09 mmol), and K_2CO_3 (306 mg, 2.22 mmol) in DMF (20 mL) was heated to 80°C for 24 h under nitrogen. The solution was poured into 200 mL of water after cooling to room temperature. A red precipitate was formed and collected by filtration. The precipitate was chromatographed on silica, eluted first with CH_2Cl_2–ethyl acetate (1 : 1, v/v) to remove impurities, then with CH_2Cl_2–EtOH (25 : 1, v/v) affording the desired product as a red solid. Yield: 189 mg (33.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (s, 6H), 6.58 (s, 3H), 6.86–6.99 (m, 12H), 7.08 (t, $J = 6.9$ Hz, 3H), 7.16–7.23 (m, 6H), 8.30 (dd, $J = 7.2$, 1.2 Hz, 3H), 8.54 (dd, $J = 3.3$, 2.4 Hz, 3H), 8.70 (d, $J = 4.2$ Hz, 3H). LC-MS: *m*/*z* 934.5 $(M + H)^+$, 956.2 $(M + Na)^+$.

1,3,5-Tris[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-2,4,6-trimethylbenzene (L^2): L^2 was prepared by the same process as described for L^1, except that 1,3,5-*tris*(bromomethyl)-2,4,6-trimethylbenzene (243 mg, 0.61 mmol) was used instead of 1,3,5-*tris*(bromomethyl)benzene to react with 9-(2-hydroxy)phenylimino-4,5-diazafluorene (592 mg, 2.17 mmol). Yield: 216 mg (36.1%) of a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (s, 9H), 4.58 (s, 6H), 6.67 (d, $J = 7.5$ Hz, 3H), 6.79 (d, $J = 7.2$ Hz, 3H), 6.92 (dd, $J = 8.1$, 5.1 Hz, 3H), 6.98-7.06 (m, 6H), 7.18 (t, $J = 7.8$ Hz, 3H), 7.26–7.30 (m, 3H), 8.07 (d, $J = 7.5$ Hz, 3H), 8.55 (d, $J = 5.4$ Hz, 3H), 8.75 (d, $J = 4.5$ Hz, 3H). LC-MS: *m*/*z* 976.3 $(M + H)^+$, 998.2 $(M + Na)^+$.

2,2′,2″-Tris[2-(4,5-diazafluoren-9-ylimino)phenoxyethyl]amine (L^3): L^3 was prepared by the same process as described for L^1, except that *tris*(2-chloroethyl)amine hydrochloride (169 mg, 0.71 mmol) was used instead of 1,3,5-*tris*(bromomethyl)benzene to react with 9-(2-hydroxy)phenylimino-4,5-diazafluorene (676 mg, 2.48 mmol). Yield: 268 mg (41.3%) of a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (t, $J = 5.0$ Hz, 6H), 3.43 (t, $J = 5.0$ Hz, 6H), 6.57 (d, $J = 8.4$ Hz, 3 H), 6.87–6.95 (m, 9H), 7.00 (t, $J = 7.5$ Hz, 3H), 7.11 (t, $J = 7.5$ Hz, 3H), 7.28 (t, $J = 3.9$ Hz, 3H), 8.19 (dd, $J = 7.8$, 1.2 Hz, 3H), 8.59 (dd, $J = 4.5$, 1.2 Hz, 3H), 8.75 (dd, $J = 6.3$, 4.8 Hz, 3H). LC-MS: *m*/*z* 915.4 $(M + H)^+$, 938.2 $(M + Na)^+$.

1,1′,1″-Tris[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1‴-(p-tosyloxymethyl)-methane (L^4): L^4 was prepared by the same process as described for L^1, except that pentaerythrityl tetratosylate (716 mg, 0.95 mmol) was used instead of 1,3,5-*tris*(bromomethyl)benzene to react with 9-(2-hydroxy)phenylimino-4,5-diazafluorene (855 mg, 3.13 mmol). Yield: 153 mg (15.3%) of a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.39 (s, 6H), 3.58 (s, 2H), 6.18–6.21 (m, 3H), 6.80–6.87 (m, 9H), 6.96–7.03 (m, 8H), 7.25–7.28 (m, 2H), 7.36 (dd, $J = 7.8$, 5.4 Hz, 3H), 8.08 (dd, $J = 7.5$, 1.8 Hz, 3H), 8.50 (t, $J = 3.2$ Hz, 3H), 8.79 (dd, $J = 4.5$, 1.5 Hz, 3H). LC-MS: m/z 1056.2 $(M + H)^+$.

$[(bipy)_6Ru_3L^1](PF_6)_6$ (Ru-L^1): A mixture of L^1 (76 mg, 0.085 mmol) and $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (147 mg, 0.28 mmol) in 2-methoxyethanol (20 mL) was heated to 120°C for 12 h under nitrogen to give a clear deep red solution, then solvent was evaporated under reduced pressure. The residue was purified twice by column chromatography on neutral alumina, eluted first with MeCN–EtOH (10 : 1, v/v) to remove impurities, then with MeCN–EtOH (2 : 1, v/v) affording $[(bipy)_6Ru_3L^1]Cl_6$, which was then dissolved in a minimum of water followed by dropwise addition of saturated aqueous NH_4PF_6 until no more precipitate formed. The precipitate was recrystallized from MeCN–Et_2O (vapor diffusion method) yielding a red solid. Yield: 91 mg (36.7%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.93 (s, 6H), 7.02–7.15 (m, 12H), 7.22 (t, $J = 8.4$ Hz, 3H), 7.28 (s, 3H), 7.35 (t, $J = 8.4$ Hz, 3H), 7.37–7.58 (m, 15H), 7.62 (d, $J = 5.4$ Hz, 3H), 7.73 (d, $J = 5.1$ Hz, 3H), 7.83 (dd, $J = 9.9$, 5.4 Hz, 6H), 8.07 (d, $J = 5.1$ Hz, 3H), 8.08–8.21 (m, 15H), 8.44 (d, $J = 7.5$ Hz, 3H), 8.81 (t, $J = 8.4$ Hz, 12H). LC-MS: m/z 869.4 $(M–3PF_6)^{3+}$, 615.8 $(M–4PF_6)^{4+}$. Elemental anal. Found: C, 47.54; H, 2.77; N, 9.47. Calcd for $C_{120}H_{87}F_{36}N_{21}O_3P_6Ru_3$: C, 47.35; H, 2.88; N, 9.66.

$[(bipy)_6Ru_3L^2](PF_6)_6$ (Ru-L^2): Ru-L^2 was prepared by the same process as described for Ru-L^1, except that L^2 (86 mg, 0.088 mmol) was used instead of L^1 to react with $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (182 mg, 0.35 mmol) affording a red solid. Yield: 89 mg (32.7%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.04 (s, 9H), 4.98 (s, 6H), 7.05–7.14 (m, 9H), 7.36–7.40 (m, 9H), 7.51–7.58 (m, 15H), 7.66 (d, $J = 5.4$ Hz, 3H), 7.72 (d, $J = 5.7$ Hz, 3H), 7.83 (t, $J = 6.6$ Hz, 6H), 8.06–8.21 (m, 18H), 8.33 (d, $J = 7.5$ Hz, 3H), 8.79–8.84 (m, 12H). LC-MS: m/z 883.7 $(M–3PF_6)^{3+}$, 626.2 $(M–4PF_6)^{4+}$, 472.3 $(M–5PF_6)^{5+}$. Elemental anal. Found: C, 48.06; H, 3.17; N, 9.67. Calcd for $C_{123}H_{93}F_{36}N_{21}O_3P_6Ru_3$: C, 47.87; H, 3.04; N, 9.53.

$[(bipy)_6Ru_3L^3](PF_6)_6$ (Ru-L^3): Ru-L^3 was prepared by the same process as described for Ru-L^1, except that L^3 (92 mg, 0.10 mmol) was used instead of L^1 to react with $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (186 mg, 0.36 mmol) affording a red solid. Yield: 117 mg (38.4%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.59 (s, 6H), 3.74 (s, 6H), 6.80–6.82 (m, 3H), 6.96–7.01 (m, 3H), 7.08–7.14 (m, 6H), 7.37 (t, $J = 6.3$ Hz, 3H), 7.52–7.59 (m, 18H), 7.64 (d, $J = 5.7$ Hz, 3H), 7.75 (d, $J = 5.4$ Hz, 3H), 7.86 (dd, $J = 10.5$, 5.4 Hz, 6H), 8.10–8.22 (m, 18H), 8.30–8.34 (m, 3H), 8.79 (d, $J = 8.1$ Hz, 6H), 8.85 (d, $J = 8.1$ Hz, 6H). LC-MS: m/z 1367.0 $(M–2PF_6)^{2+}$, 864.1 $(M–3PF_6)^{3+}$, 611.0 $(M–4PF_6)^{4+}$. Elemental anal. Found: C, 46.59; H, 3.16; N, 10.03. Calcd for $C_{117}H_{90}F_{36}N_{22}O_3P_6Ru_3$: C, 46.45; H, 3.00; N, 10.19.

$[(bipy)_6Ru_3L^4](PF_6)_6$ (Ru-L^4): Ru-L^4 was prepared by the same process as described for Ru-L^1, except that L^4 (83 mg, 0.079 mmol) was used instead of L^1 to react with $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (148 mg, 0.28 mmol) affording a red solid. Yield: 87 mg (34.9%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.17 (s, 3H), 3.49 (s, 6H), 3.63 (s, 2H), 6.80–7.04 (m, 6H), 6.97–7.07 (m, 9H), 7.18–7.32 (m, 5H), 7.40–7.61 (m, 15H), 7.67 (t, $J = 6.3$ Hz, 3H), 7.79–7.84 (m, 9H), 7.99–8.06 (m, 3H), 8.09–8.22 (m, 17H), 8.28 (t, $J = 6.3$ Hz, 3H), 8.79–8.85 (m, 12H). LC-MS: m/z 911.0 $(M - 3PF_6)^{3+}$, 646.1 $(M–4PF_6)^{4+}$, 487.7 $(M–5PF_6)^{5+}$. Elemental anal. Found: C, 46.86; H, 3.18; N, 9.50. Calcd for $C_{123}H_{93}F_{36}N_{21}O_6P_6Ru_3S$: C, 46.66; H, 2.96; N, 9.29.

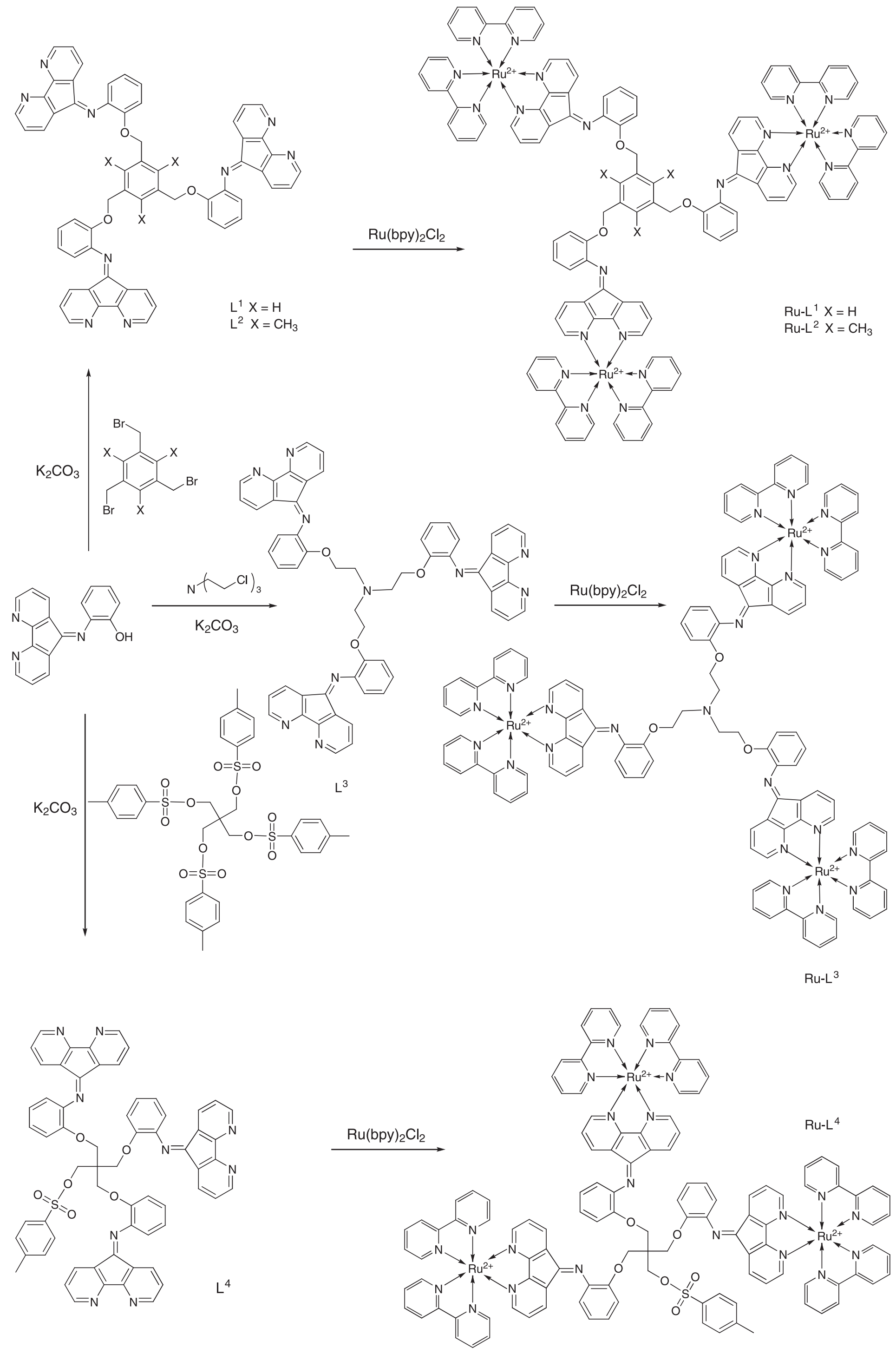
3. Results and discussion

3.1. *Synthesis*

The outline of the synthesis of the four tripodal ligands $L^{1–4}$ and their Ru(II) complexes $[(bipy)_6Ru_3L^{1–4}](PF_6)_6$, abbreviated as Ru-$L^{1–4}$, is presented in scheme 1. The starting compound **9**-(2-hydroxy)phenylimino-4,5-diazafluorene was synthesized from 4,5-diazafluoren-9-one according to literature procedure [12]. L^1, L^2, and L^3 were prepared in good yields by the reaction of 9-(2-hydroxy)phenylimino-4,5-diazafluorene with 1,3,5-*tris*(bromomethyl)benzene, 1,3,5-*tris*(bromomethyl)-2,4,6-trimethylbenzene, and *tris*(2-chloroethyl)amine hydrochloride, respectively, in DMF. Initial attempt to prepare the polypodal ligand of 9-(2-hydroxy)phenylimino-4,5-diazafluorene with pentaerythrityl tetratosylate under the same experimental conditions did not afford tetrapodal diimine ligand, but instead afforded the tripodal ligand L^4. It may be noted that the reaction conditions, namely temperature, duration of reaction, and Lewis base, are very important. High temperature and NaOH resulted in the formation of a tetrapodal diimine ligand [17]. The Ru(II) complexes were prepared by refluxing $Ru(bipy)_2Cl_2 \cdot 2H_2O$ and the ligands in 2-methoxyethanol solution, and isolated as their PF_6^- salts. These compounds were characterized by ^{1}H NMR, MS, and elemental analyses.

Rillema and co-workers reported the electronic and ^{1}H NMR properties of a series of polypyridyl ligands derived from 4,5-diazafluoren-9-one [12]. Due to sp^2 hybridization of the nitrogen in the bridge, the structure of the phenylimino-4,5-diazafluorene group is asymmetric, the protons in the two pyridine units of each 4,5-diazafluorene group are non-equivalent. As shown for L^2 (figure S1), the chemical shifts for the α, β, and γ protons are 8.75, 7.18, and 8.07 ppm, respectively; the chemical shifts for the α', β', and γ' protons are 8.55, 7.06, and 7.30 ppm, respectively.

Elemental analyses are consistent with the formation of trinuclear systems. Octahedral metal centers with bidentate ligands generally show stereoisomerism. The number of stereoisomeric possibilities in polynuclear complexes increases exponentially with the number of metal centers. Although ^{1}H NMR spectra of some Ru(II) polypyridine complexes have been clearly described [18], in most cases, the ^{1}H NMR spectra of polynuclear Ru(II) complexes are complicated. The protons in the two pyridine units of each 4,5-diazafluorene group of Ru-$L^{1–4}$ are unequal; therefore, the ^{1}H NMR spectra of the complexes are complicated and the assignment of the proton signals is difficult. The structures of trinuclear Ru(II) complexes are further established by LC-MS spectra. This technique has proven to be very helpful for identifying polynuclear transition metal complexes with high molecular masses [19]. The data with the assignments of the peaks are given in section 2. Usually, the mass is calculated from a series of multiply charged ions obtained by successive loss of counteranions. LC-MS spectra for the complexes exhibit some expected peaks due to $(M–nPF_6)^{n+}$.



Scheme 1. Synthesis of tripodal ligands L^{1-4} and corresponding Ru(II) complexes Ru-L^{1-4}.

Figure S2 shows the LC-MS spectrum of Ru-L^2. Clearly, the main peak at *m*/*z* 626.2 is assigned to $(M\text{–}4PF_6)^{4+}$ and the other two peaks at *m*/*z* 883.7 and 472.3 are assigned to $(M\text{–}3PF_6)^{3+}$ and $(M\text{–}5PF_6)^{5+}$, respectively. The measured molecular weights are consistent with expected values.

3.2. *Absorption spectra*

Absorption spectra of the ligands are studied in $CHCl_3$ and their Ru(II) polypyridine complexes are studied in MeCN solution. The concentration of all samples is 10^{-5} mol L^{-1}. The spectra are shown in figure 1 with the data summarized in table 1. Absorptions of the ligands can be assigned to ligand-centered intraligand $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions. Assignments of the absorptions of Ru-$L^{1–4}$ were made on the basis of well-documented optical transitions of analogous Ru(II) polypyridine complexes [20]. Absorption spectra of the complexes show three well-resolved bands. Those at *ca* 285 and 236 nm can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions centered on 2,2′-bipyridine. The lowest energy band at 442 nm is attributed to MLCT transition, which consists of overlapping $d\pi(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{bipy})$ and $d\pi(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{L})$ components. The lowered symmetry removes the degeneracy of the π^* levels, which results in the appearance of a non-symmetrical MLCT band. The MLCT absorption maxima of the complexes are blue-shifted by 8 nm compared with that of $\mathrm{Ru(bipy)}_3^{2+}$ [21], suggesting that the donor properties of the ligands are weaker than that of 2,2′-bipyridine. The extinction coefficients of the MLCT bands of Ru-$L^{1–4}$ are larger than those of trinuclear Ru(II) complexes containing 2,2′-bipyridine or 1,10-phenanthroline, but smaller than those of trinuclear Ru(II) complexes containing 2,2′ : 6′,2″-terpyridine [22].

3.3. *Emission behavior*

Ru-$L^{1–4}$ are non-emissive in MeCN at room temperature upon excitation into the MLCT band. The emission properties of Ru(II) polypyridine complexes generally

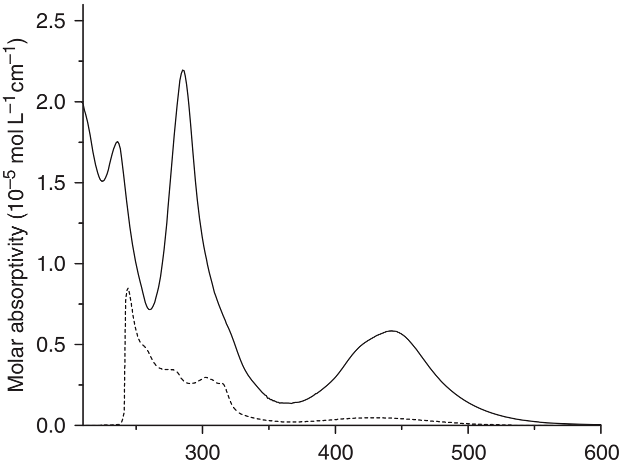


Figure 1. Absorption spectra of Ru-L^1 (10^{-5} mol L^{-1}, (—), typical for Ru-$L^{1–4}$) in MeCN and L^1 (10^{-5} mol L^{-1}, (---), typical for $L^{1–4}$) in $CHCl_3$ solution.

Table 1. Photophysical data of ligands and their Ru(II) polypyridine complexes.[a]

Compound	λ_{max}, nm (10^4 ε, $(\mathrm{mol\,L^{-1}})^{-1}\mathrm{cm}^{-1}$)			λ_{max} (nm)	Φ
L^1	429 (0.47)	302 (2.96)	244 (8.48)		
L^2	428 (0.48)	302 (2.78)	244 (8.07)		
L^3	428 (0.37)	302 (2.61)	244 (7.96)		
L^4	427 (0.36)	302 (2.66)	244 (10.04)		
Ru-L^1	443 (5.84)	285 (21.95)	236 (17.53)	573	0.085
Ru-L^2	442 (5.29)	285 (20.25)	235 (16.67)	574	0.088
Ru-L^3	443 (5.63)	286 (21.21)	236 (16.53)	574	0.090
Ru-L^4	442 (5.44)	285 (20.55)	235 (16.25)	575	0.081

[a]Emission quantum yields are calculated relative to $\mathrm{Ru(bipy)_3^{2+}}$ ($\Phi_{std} = 0.376$) in an EtOH–MeOH (4 : 1, v/v) glassy matrix at 77 K, the uncertainty in quantum yields is 15%.

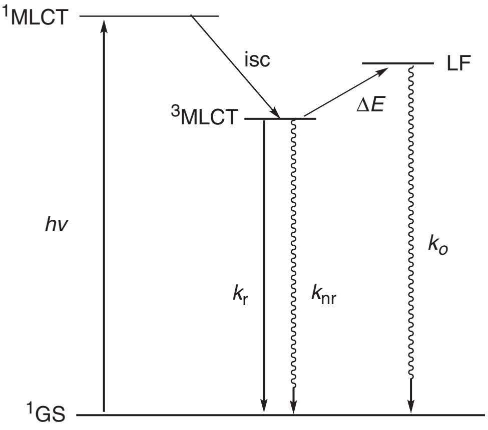


Figure 2. Energy state diagram based on the Crosby–Meyer model.

follow the energy gap law [23]. The ^{3}MLCT state is reasonably long-lived and is thought to be deactivated by radiative decay, k_r, radiationless decay, k_{nr}, and thermal population of a higher lying excited state, $k_o\exp(-\Delta E/RT)$. For the last process, the thermally accessible excited state has been designated as a ligand field (LF) excited state. The energy of this presumed LF state should depend on the LF strength. Emission intensities follow the model shown in figure 2 originally proposed by Crosby, Meyer, and others [24]. The values of ΔE for the diimine complexes containing diazafluorene are substantially lower than the corresponding value for $\mathrm{Ru(bipy)_3^{2+}}$. These results are consistent with ligand field theory. Diazafluorene derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series [25]. Hence, substitution of diazafluorene derivatives for 2,2′-bipyridine results in a decreased ligand field and therefore, a lower LF excited state energy. Since the ^{3}MLCT excited state is not significantly affected, the variation in the LF state dictates the energy gap [26]. Consequently, population of the LF state is very efficient for these complexes at room temperature and they are essentially non-emissive at room temperature. However, energy transfer is inhibited at 77 K, so they show vibrational components similar to that of $\mathrm{Ru(bipy)_3^{2+}}$ in EtOH–MeOH (4 : 1, v/v) glassy matrix at 77 K (figure 3) [27].

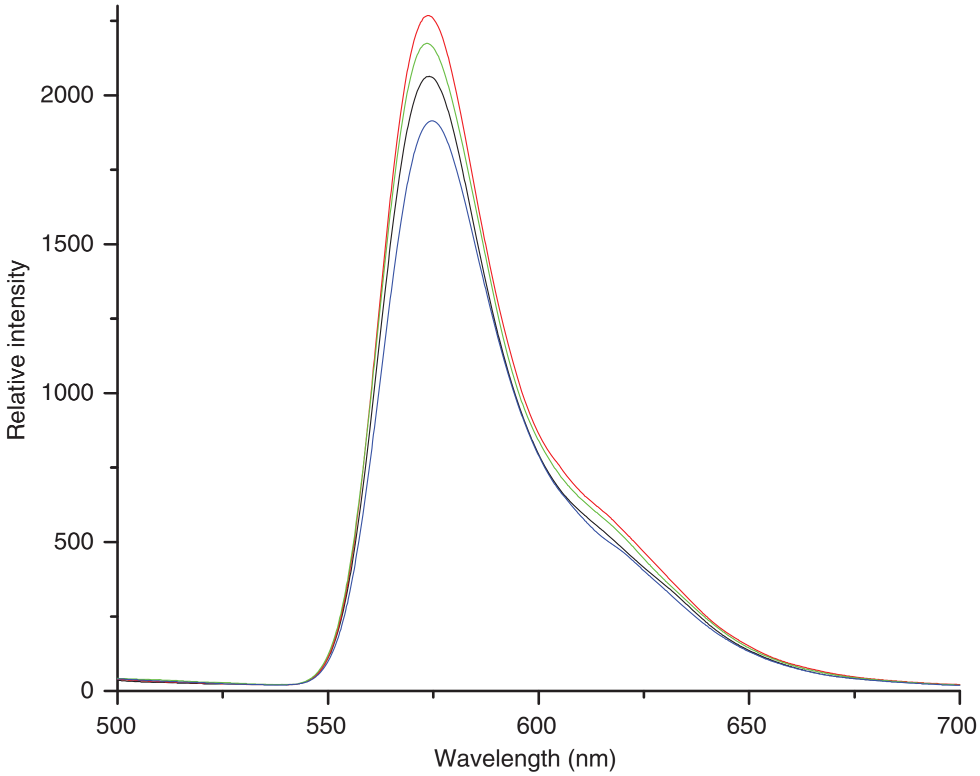


Figure 3. Luminescence spectra of Ru-L^1 (green), Ru-L^2 (black), Ru-L^3 (red), and Ru-L^4 (blue) in EtOH–MeOH (4 : 1, v/v) glassy matrix at 77 K.

The complexes (10^{-5} mol L^{-1}) exhibit characteristic emission at 574 nm in EtOH–MeOH glassy matrix at 77 K with an excitation wavelength at 436 nm (table 1).

3.4. *Electrochemistry*

Electrochemical behaviors of the complexes have been studied in DMF and MeCN solutions with 0.1 mol L^{-1} TBAP as supporting electrolyte. Reduction processes of the complexes are not well-behaved in MeCN solution due to adsorption of the reduced species onto the surface of the platinum electrode. In DMF solution, the complexes display clear reduction processes, but do not exhibit oxidative waves due to the insufficient anodic window of the solvent. So, the reduction processes were recorded in DMF and oxidation processes in MeCN (table 2).

Ru-L^1 exhibits a Ru(II)-centered reversible oxidation couple at 1.33 V (figure 4). This potential is slightly more positive (by 50 mV) than that of Ru(bipy)$_3^{2+}$ (+1.28 V *vs.* SCE) [28], but slightly more negative (by 60 mV) than that of the parent complex [(bipy)$_2$Ru(dafone)]$^{2+}$ [25], which indicates that L^1 is a stronger π-acceptor than bipy but a weaker π-acceptor than dafone. In this study, the complexes show a single wave in cyclic voltammetry and a single peak without broadening in differential

Table 2. Redox potentials of the Ru(II) polypyridine complexes.[a]

	$E_{1/2}$ (V) (ΔE_p, mV)			
Complex	Oxidation	Reduction		
Ru-L^1	1.33 (61)	−0.84	−1.41 (90)	−1.67 (82)
Ru-L^2	1.33 (64)	−0.84	−1.41 (120)	−1.67 (84)
Ru-L^3	1.34 (67)	−0.86	−1.42 (97)	−1.68 (92)
Ru-L^4	1.33 (62)	−0.85	−1.40 (102)	−1.67 (89)

Oxidation potentials are recorded in 0.1 mol L^{-1} TBAP/CH$_3$CN, reduction potentials are recorded in 0.1 mol L^{-1} TBAP/DMF and potentials are given *vs.* SCE; scan rate = 200 mVs^{-1}; $E_{1/2}$ refers to $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$.

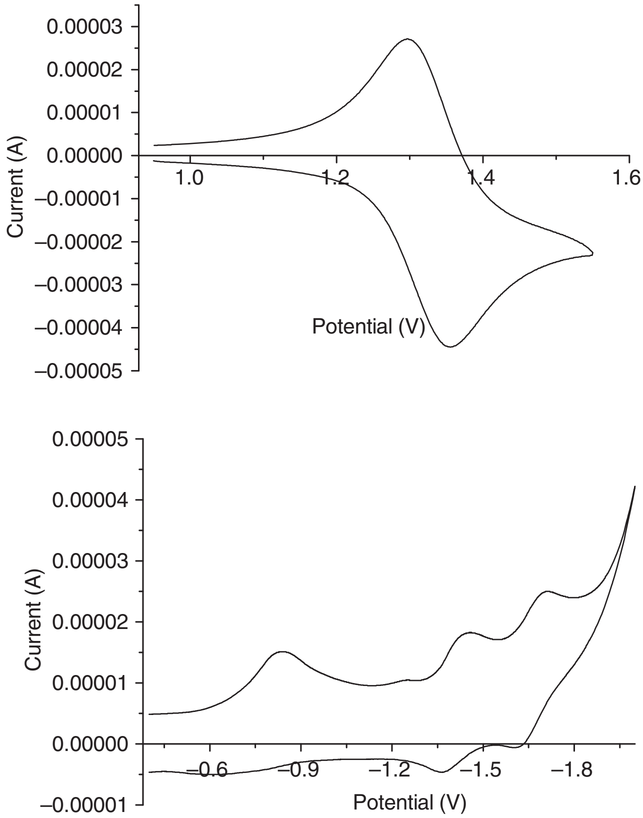


Figure 4. Cyclic voltammetry of Ru-L^1; oxidation potential was recorded in 0.1 mol L^{-1} TBAP/CH$_3$CN, reduction potentials were recorded in 0.1 mol L^{-1} TBAP/DMF.

pulse voltammetry. A three-electron process for each oxidation wave of the complexes was confirmed by coulometry. So, the oxidation wave can be ascribed to a three-electron reversible process.

In the reduction processes of the complexes, the first reduction process is irreversible due to adsorption of reduced species onto the surface of the platinum electrode.

Table 3. Predicted UV-Vis absorption maxima from electrochemistry data.

	$E_{1/2}$ (V)							
		1st reduction						
Complex	1st oxidation	L	bpy	$\Delta E_{1/2}(1)$ (V)[a]	$\lambda_{1\max}$ (nm)[b]	$\Delta E_{1/2}(2)$ (V)[c]	$\lambda_{2\max}$ (nm)[d]	Exptl $\lambda_{\max}$ (nm)
Ru-L^1	1.33	−0.84	−1.41	2.17	573	2.74	453	443
Ru-L^2	1.33	−0.84	−1.41	2.17	573	2.74	453	443
Ru-L^3	1.34	−0.86	−1.42	2.20	565	2.76	450	443
Ru-L^4	1.33	−0.85	−1.40	2.18	570	2.73	455	442
Ru(bpy)_3^{2+}	1.28		−1.32			2.60	478	450

[a] $\Delta E_{1/2}(1) = E_{1/2}$ (1st oxidation) − $E_{1/2}$ (1st L reduction).
[b] $\lambda_{1\max}$ was calculated on the basis of $\Delta E_{1/2}(1)$ data.
[c] $E_{1/2}(2) = E_{1/2}$ (1st oxidation) − $E_{1/2}$ (1st bipy reduction).
[d] $\lambda_{2\max}$ was calculated on the basis of $\Delta E_{1/2}(2)$ data.

Diazafluorene derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series [25] and promoted electrons should be associated with the phenylimino-4,5-diazafluorene of L^1, so the first reduction process of Ru-L^1 at −0.84 V is consistent with the addition of electrons to the LUMO localized on L^1, giving $[(\text{bipy})_2\text{Ru}^{\text{II}}\text{L}^{3-}\text{Ru}^{\text{II}}(\text{bipy})_2\text{Ru}^{\text{II}}(\text{bipy})_2]^{3+}$. The second quasi-reversible reduction process at −1.41 V is located on one of the two 2,2′-bipyridine ligands on each metal terminal, adding electrons to the 2,2′-bipyridine localized LUMO + 1 orbitals yielding $[(\text{bipy})(\text{bipy}^{\bullet-})\text{Ru}^{\text{II}}\text{L}^{3-}\text{Ru}^{\text{II}}(\text{bipy}^{\bullet-})(\text{bipy})\text{Ru}^{\text{II}}(\text{bipy}^{\bullet-})(\text{bipy})]$. Similar to the oxidation process, the reductions of the remote 2,2′-bipyridine appear at the same potential, indicating little interaction between the three sites. The third reduction at −1.67 V is quasi-reversible and affords $[(\text{bipy}^{\bullet-})(\text{bipy}^{\bullet-})\text{Ru}^{\text{II}}\text{L}^{3-}\text{Ru}^{\text{II}}(\text{bipy}^{\bullet-})(\text{bipy}^{\bullet-})\text{Ru}^{\text{II}}(\text{bipy}^{\bullet-})(\text{bipy}^{\bullet-})]^{3-}$. It is well-established that the lowest energy MLCT transitions ($\lambda_{\max}$) are, for a related class of ligands, linearly related to the difference between the potential of the first reduction (LUMO) and the first oxidation (HOMO) ($\Delta E_{1/2}$) [29]. In all the complexes reported here, the oxidation is localized on Ru(II) and the first reduction is localized on the tripodal ligand. Electrochemical data are used to calculate the expected energy transitions for the MLCT bands and are listed in table 3. As a result, the lowest energy MLCT transition of Ru-L^1 is expected to be $d\pi(\text{Ru}) \rightarrow \pi^*(\text{L})$ at 573 nm, but experimentally no absorption in this region is observed. The MLCT band more closely matches the $d\pi(\text{Ru}) \rightarrow \pi^*(\text{bipy})$ transition of Ru(bipy)_3^{2+}, which suggests the $d\pi(\text{Ru}) \rightarrow \pi^*(\text{L})$ transitions are forbidden. The electrochemical behaviors of Ru-$L^{2\text{–}4}$ are similar to that of Ru-L^1.

4. Conclusion

Four trinuclear Ru(II) complexes derived from 9-(2-hydroxy)phenylimino-4,5-diazafluorene have been synthesized and characterized. These complexes show rich photophysical and redox properties. Replacement of bipy in Ru(bipy)_3^{2+} based complexes for a 4,5-diazafluorene based ligand leads to dramatic change of the photophysical and redox behavior. Electrochemical properties show little interaction between the four Ru(II) polypyridine complexes. It is well-documented that an interaction of a few reciprocal centimeters (which cannot be noticed in spectroscopic and electrochemical experiments) is sufficient to cause fast intercomponent electron or energy transfer processes [30], so the complexes have potential applications in photoinduced electron or energy transfer.

Supplementary material

^{1}H NMR and MS of the ligands and Ru(II) complexes are included.

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