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Preparation, photophysical, and electrochemical properties of two tetranuclear ruthenium(II) polypyridyl complexes containing 4,5-diazafluorene

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Abstract Two tetrapodal ligands L^1 and L^2 containing 4,5-diazafluorene units have been synthesized and characterized. Both ligands are composed of two kinds of nonequivalent coordinating sites: one involves the 4-(4,5-diazafluoren-9-ylimino)phenoxy moiety, and the other one involves the 2-(4,5-diazafluoren-9-ylimino)phenoxy moiety. The Ru(II) complexes $[(bpy)_8Ru_4(L^1)](PF_6)_8$ and $[(bpy)_8Ru_4(L^2)](PF_6)_8$ (bpy = 2,2′-bipyridine) have been obtained by refluxing $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and each ligand in 2-methoxyethanol. Both complexes exhibit metal-to-ligand charge transfer (MLCT) absorptions at around 443 nm and emission at around 574 nm. Electrochemical studies of both complexes display one Ru(II)-centered oxidation at around 1.33 V and three ligand-centered reductions.

Introduction

There is at present a great interest in the chemistry of polypyridyl complexes of ruthenium because of their outstanding photophysical and electrochemical properties and their extensive use in luminescence sensing, solar energy conversion, DNA intercalation, pH switching, etc. [1–3]. Polynuclear Ru(II) polypyridyl complexes have received special attention in recent years in connection with the development of artificial multicomponent systems for photoinduced electron or energy transfer and other related photonic devices [4–7]. In the design of such Ru(II) systems, the bridging ligands that are used to link two or more metal polypyridine subunits are crucial because the interactions between the bridged units, and thereby the ground and excited state properties of the polynuclear complex, are strongly dependent on the size, shape, and electronic nature of the bridging ligands [8, 9]. Thus, the synthesis of appropriate bridging ligands is the most important factor in realizing molecular devices based on polynuclear Ru(II) complexes. A wide range of bridging ligands have been prepared in order to assemble Ru(II) polypyridine building blocks over the past decade. However, the vast majority of such studies have focused on systems containing symmetric bridging ligands. The study of polynuclear Ru(II) complexes, bridged with ligands containing two kinds of nonequivalent coordinating sites, has attracted less attention [10–13]. Toward the aim of synthesizing new polynuclear Ru(II) complexes with interesting photophysical and electrochemical properties, herein, we describe the synthesis and characterization of two tetrapodal ligands incorporating two kinds of nonequivalent chelating sites: one involving the 4-(4,5-diazafluoren-9-ylimino)phenoxy moiety, and the other involving the 2-(4,5-diazafluoren-9-ylimino)phenoxymethyl moiety. The absorption and emission spectra, and electrochemical properties of both complexes are also presented and discussed.

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Experimental

2,2′-Bipyridine, 1,10-phenanthroline, 4-aminophenol, 2-aminophenol, p-toluenesulfonyl chloride, pentaerythritol, tetrabutylammonium perchlorate (TBAP), ethyl acetate, $RuCl_3{\cdot}3H_2O$, NH_4PF_6, K_2CO_3, CH_3CN, CH_2Cl_2, EtOH, and DMF were

purchased from the Tianjin Chemical Reagent Factory. Solvents and raw materials were of analytical grade and used as received, apart from CH_3CN, which was filtered over activated alumina and distilled from P_2O_5 immediately prior to use. 4,5-Diazafluoren-9-one [14], 9-(4-hydroxy)phenylimino-4,5-diazafluorene [15], 9-(2-hydroxy)phenylimino-4,5-diazafluorene [15], pentaerythrityl tetratosylate [16], and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ [17] were prepared according to literature procedures.

^{1}H NMR spectra were obtained on a Mercury Plus 300 spectrometer and a Mercury Plus 400 spectrometer using TMS as internal standard. ESI-HRMS spectra were obtained on a Bruker Daltonics APEXII47e mass spectrometer and ESI–MS spectra with a Bruker Daltonics Esquire 6000 mass spectrometer. Elemental analyses were obtained using a Perkin-Elmer 240C analytical instrument. Absorption spectra were obtained on a Varian Cary-100 UV–Visible spectrophotometer and emission spectra with a Hitachi F-4600 spectrophotometer. Emission quantum yields were calculated relative to $Ru(bpy)_3^{2+}$ ($\Phi_{std} = 0.376$) in EtOH:MeOH (4:1) glassy matrix [18]. Electrochemical measurements were carried out at room temperature using a CHI 660B electrochemical workstation. Cyclic voltammetry and differential pulse voltammetry were performed in CH_3CN and DMF solutions using a micro cell equipped with a platinum disk working electrode, a platinum auxiliary electrode, and a saturated potassium chloride calomel reference electrode with 0.1 mol/L TBAP as supporting electrolyte. All samples were purged with nitrogen prior to measurement.

Synthesis of 1,1′-di[4-(4,5-diazafluoren-9-ylimino)-phenoxymethyl]-1″,1‴-di(p-tosyloxymethyl)-methane (compound 1)

A mixture of pentaerythrityl tetratosylate (652 mg, 0.87 mmol), 9-(4-hydroxy)phenylimino-4,5-diazafluorene (486 mg, 1.78 mmol), and K_2CO_3 (273 mg, 1.98 mmol) in DMF (20 mL) was heated to 80 °C for 24 h under nitrogen atmosphere. The solution was poured into 200 mL of water after cooling down to room temperature, and a red precipitate which formed was collected by filtration. The crude product was chromatographed on silica, being eluted first with CH_2Cl_2-ethyl acetate (2:1, v/v) to remove impurities, then with CH_2Cl_2-EtOH (25:1, v/v) to afford the desired product as a red solid. Yield: 233 mg (28.2 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.44$ (s, 6H), 4.09 (s, 4H), 4.31 (s, 4H), 6.84 (d, $J = 8.7$ Hz, 4H), 6.97 (d, $J = 9.0$ Hz, 4H), 7.06 (d, $J = 3.0$ Hz, 4H), 7.31 (d, $J = 8.1$ Hz, 4H), 7.41 (dd, $J = 7.5$, 4.8 Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 4H), 8.25 (d, $J = 7.5$ Hz, 2H), 8.67 (d, $J = 3.6$ Hz, 2H), 8.81 (d, $J = 4.8$ Hz, 2H). ESI–MS: m/z 955.4 $(M + H)^+$. Found: C, 66.5; H, 4.3; N, 8.6. Calcd for $C_{53}H_{42}N_6O_8S_2$: C, 66.7; H, 4.4; N, 8.8.

Synthesis of 1,1′,1″-tris[4-(4,5-diazafluoren-9-ylimino)-phenoxymethyl]-1‴-(p-tosyloxymethyl)-methane (compound 2)

A mixture of pentaerythrityl tetratosylate (815 mg, 1.08 mmol), 9-(4-hydroxy)phenylimino-4,5-diazafluorene (1,162 mg, 4.26 mmol), and K_2CO_3 (623 mg, 4.51 mmol) in DMF (20 mL) was heated to 80 °C for 24 h under nitrogen atmosphere. The solution was poured into 200 mL of water after cooling down to room temperature, and a red precipitate which formed was collected by filtration. The crude product was chromatographed on silica, being eluted first with CH_2Cl_2-ethyl acetate (2:1, v/v) to remove impurities, then with CH_2Cl_2-EtOH (20:1, v/v) to afford the desired product as a red solid. Yield: 193 mg (16.9 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (s, 3H), 4.38 (s, 6H), 4.55 (s, 2H), 6.94–7.12 (m, 18H), 7.29 (d, $J = 7.5$ Hz, 2H), 7.39 (dd, $J = 8.1$, 5.4 Hz, 3H), 7.80 (d, $J = 8.1$ Hz, 2H), 8.24 (dd, $J = 7.8$, 1.2 Hz, 3H), 8.66 (dd, $J = 4.8$, 1.2 Hz, 3H), 8.80 (dd, $J = 6.3$, 1.5 Hz, 3H). ESI-HRMS: m/z 1,056.3291 $(M + H)^+$, 1,078.3136 $(M + Na)^+$. Found: C, 71.3; H, 4.1; N, 11.7. Calcd for $C_{63}H_{45}N_9O_6S$: C, 71.6; H, 4.3; N, 11.9.

Synthesis of 1,1′-di[4-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1″,1‴-di[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-methane (L^1)

A mixture of compound 1 (641 mg, 0.67 mmol), 9-(2-hydroxy)phenylimino-4,5-diazafluorene (613 mg, 2.25 mmol), and K_2CO_3 (330 mg, 2.39 mmol) in DMF (50 mL) was heated to 90 °C for 72 h under nitrogen atmosphere. The solution was poured into 500 mL of water after cooling down to room temperature, and a red precipitate which formed was collected by filtration. The crude product was purified twice by column chromatography on silica, being eluted with CH_2Cl_2-EtOH (20:1, v/v) to afford the desired product as a red solid. Yield: 202 mg (26.0 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.66$ (s, 4H), 3.99 (s, 4H), 6.52 (d, $J = 8.4$ Hz, 4H), 6.75 (d, $J = 7.6$ Hz, 2H), 6.81–6.85 (m, 6H), 6.98–7.02 (m, 10H), 7.04–7.08 (m, 2H), 7.33 (dd, $J = 7.6$, 5.2 Hz, 2H), 7.41 (dd, $J = 7.6$, 5.2 Hz, 2H), 8.16 (dd, $J = 7.6$, 1.2 Hz, 2H), 8.26 (dd, $J = 7.6$, 1.2 Hz, 2H), 8.51 (dd, $J = 7.6$, 1.2 Hz, 2H), 8.67 (dd, $J = 4.0$, 2.4 Hz, 2H), 8.75 (dd, $J = 4.8$, 1.6 Hz, 2H), 8.81 (dd, $J = 4.8$, 1.6 Hz, 2H). ESI–MS: m/z 1,157.4 $(M + H)^+$. Found: C, 75.6; H, 4.1; N, 14.3. Calcd for $C_{73}H_{48}N_{12}O_4$: C, 75.8; H, 4.2; N, 14.5.

Synthesis of 1,1′,1″-tris[4-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1‴-[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-methane (L^2)

L^2 was prepared by the same procedure as that described for L^1, except compound 2 (672 mg, 0.58 mmol) was used instead of compound 1 to react with 9-(2-hydroxy)phenylimino-4,5-diazafluorene (293 mg, 1.08 mmol). Yield: 281 mg (38.2 %) of a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 6H), 4.47 (s, 2H), 6.81–6.84 (m, 6H), 6.88–6.93 (m, 7H), 7.02–7.05 (m, 4H), 7.06–7.11 (m, 5H), 7.22–7.24 (m, 1H), 7.29–7.32 (m, 2H), 7.40 (dd, J = 7.6, 4.8 Hz, 3H), 8.22 (dd, J = 7.6, 1.6 Hz, 1H), 8.25 (dd, J = 7.6, 1.6 Hz, 3H), 8.55 (dd, J = 5.2, 1.6 Hz, 1H), 8.66 (dd, J = 4.8, 1.3 Hz, 3H), 8.72 (dd, J = 5.2, 1.6 Hz, 1H), 8.81 (dd, J = 5.2, 1.6 Hz, 3H). ESI–MS: m/z 1,157.4 $(M + H)^+$. Found: C, 75.5; H, 4.0; N, 14.3. Calcd for $C_{73}H_{48}N_{12}O_4$: C, 75.8; H, 4.2; N, 14.5.

Synthesis of $[(bpy)_8Ru_4(L^1)](PF_6)_8$

A mixture of ligand L^1 (79 mg, 0.07 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (187 mg, 0.36 mmol) in 2-methoxyethanol (50 mL) was heated to 120 °C for 12 h under nitrogen to give a clear deep red solution, and then the solvent was evaporated under reduced pressure. The residue was purified twice by column chromatography on alumina, being eluted first with CH_3CN-EtOH (5:1, v/v) to remove impurities, then with EtOH to afford the complex $[(bpy)_8Ru_4(L^1)]Cl_8$. This complex was dissolved in the minimum amount of water followed by dropwise addition of saturated aqueous NH_4PF_6 until no more precipitate formed. The precipitate was recrystallized from CH_3CN-Et_2O mixture (vapor diffusion method) to afford a red solid. Yield: 96 mg (35.4 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.09 (s, 8H), 6.99–7.04 (m, 16H), 7.07–7.12 (m, 4H), 7.54–7.65 (m, 24H), 7.77 (d, J = 4.8 Hz, 4H), 7.83–7.86 (m, 8H), 8.03–8.08 (m, 4H), 8.16–8.20 (m, 24H), 8.34–8.41 (m, 4H), 8.83 (s, 8H), 8.85 (s, 8H). ESI–MS: m/z 848.2 $(M—4PF_6)^{4+}$, 649.3 $(M—5PF_6)^{5+}$. Found: C, 46.2; H, 2.7; N, 9.7. Calcd for $C_{153}H_{112}F_{48}N_{28}O_4P_8Ru_4$: C, 46.3; H, 2.8; N, 9.9.

Synthesis of $[(bpy)_8Ru_4(L^2)](PF_6)_8$

$[(bpy)_8Ru_4(L^2)](PF_6)_8$ was prepared by the same procedure as that described for $[(bpy)_8Ru_4(L^1)](PF_6)_8$, except L^2 (85 mg, 0.07 mmol) was used instead of L^1 to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (191 mg, 0.37 mmol). Yield: 127 mg (43.5 %) of a red solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.08 (s, 8H), 7.04–7.22 (m, 12H), 7.32–7.44 (m, 8H), 7.55–7.62 (m, 20H), 7.76 (d, J = 4.8 Hz, 6H), 7.85 (d, J = 5.6 Hz, 6H), 7.88 (d, J = 5.6 Hz, 6H), 8.17 (d, J = 4.8 Hz, 3H), 8.19–8.35 (m, 18H), 8.29 (d, J = 7.6 Hz, 3H), 8.38–8.45 (m, 6H), 8.82–8.86 (m, 16H). ESI–MS: m/z 1,179.0 $(M—3PF_6)^{3+}$, 847.8 $(M—4PF_6)^{4+}$. Found: C, 46.1; H, 2.6; N, 9.7. Calcd for $C_{153}H_{112}F_{48}N_{28}O_4P_8Ru_4$: C, 46.3; H, 2.8; N, 9.9.

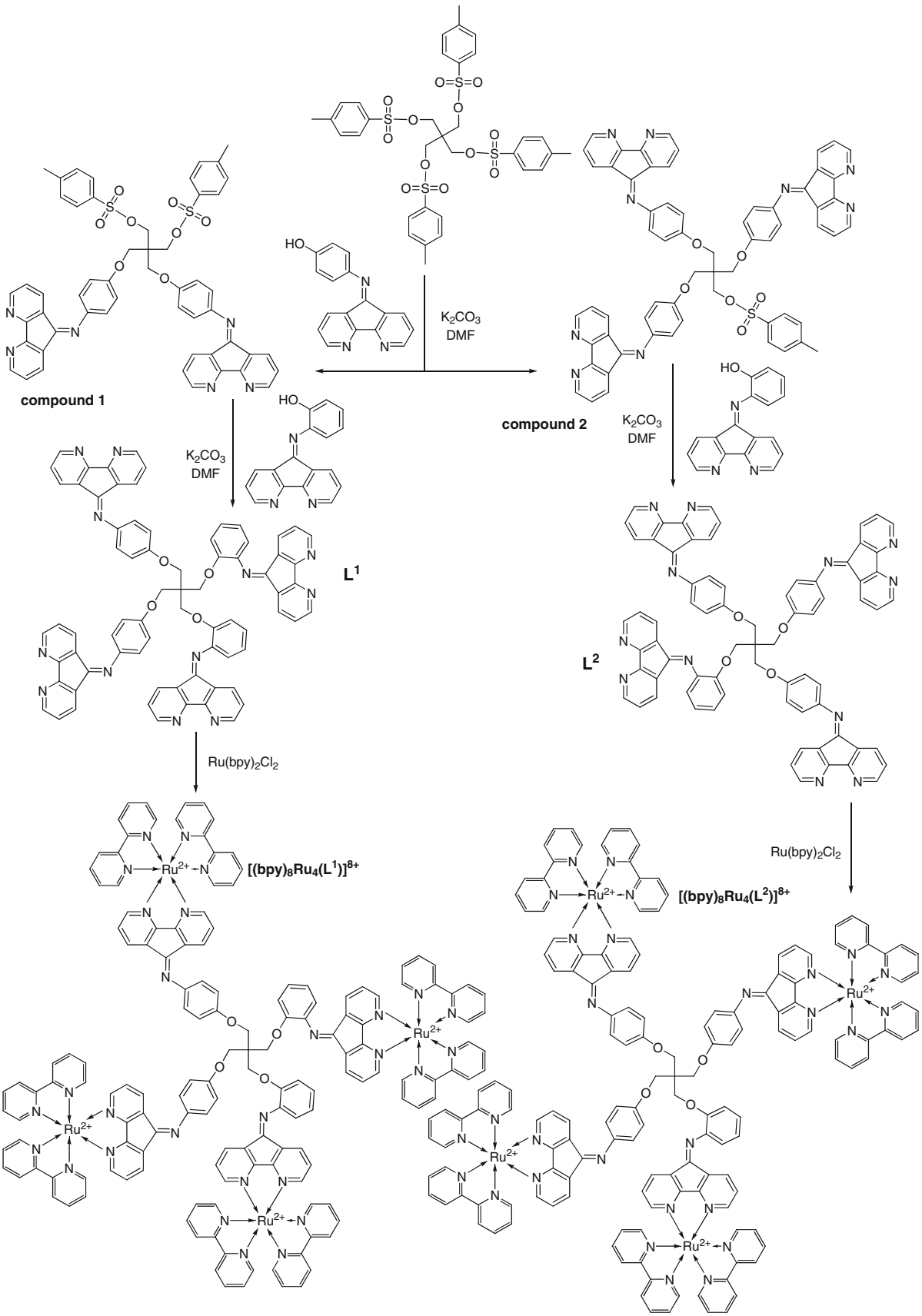
Results and discussion

Synthesis

The procedure of the synthesis of the two tetrapodal ligands and their Ru(II) complexes is presented in Scheme 1. Starting compounds 9-(4-hydroxy)phenylimino-4,5-diazafluorene and 9-(2-hydroxy)phenylimino-4,5-diazafluorene were prepared from 4,5-diazafluoren-9-one according to the literature procedure [15]. Tetrapodal ligands L^1 and L^2 have been prepared by two steps, 9-(4-hydroxy)phenylimino-4,5-diazafluorene reacted with pentaerythrityl tetratosylate for 24 h at different molar ratio affording compounds 1 and 2, respectively. Compounds 1 and 2 reacted with 9-(2-hydroxy)phenylimino-4,5-diazafluorene in DMF for 72 h yielding ligands L^1 and L^2, respectively. Both Ru(II) complexes were obtained by refluxing $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and the ligand in 2-methoxyethanol solution and isolated as their PF_6^- salts in good yields. Both complexes were characterized by elemental analyses, ESI–MS, and ^{1}H NMR spectroscopy.

Absorption spectra

The UV–Vis absorption spectra of both complexes were recorded in CH_3CN solution, at a working concentration of 5×10^{-6} mol/L. The energy maxima and absorption coefficients are summarized in Table 1, and the spectra are shown in Fig. 1. Assignments of the absorption bands of the complexes have been made on the basis of the well-documented optical transitions of analogous Ru(II) polypyridyl complexes [19–21]. The absorption spectra of both complexes show three well-resolved bands. Those at ca. 286 and 238 nm can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions centered on the 2,2′-bipyridine. The lowest energy band at around 443 nm is attributed to an MLCT, $d\pi \rightarrow \pi^*$ transition, which consists of overlapping $d\pi(Ru) \rightarrow \pi^*(bpy)$ and $d\pi(Ru) \rightarrow \pi^*(L)$ components. The lowered symmetry removes the degeneracy of the π^* levels, which results in the appearance of a nonsymmetric MLCT band. The MLCT absorption maxima of the complexes are blue-shifted by about 7 nm compared with that of $Ru(bpy)_3^{2+}$ [22], suggesting that the donor properties of ligands L^1 and L^2 are weaker than those of 2,2′-bipyridine.



Scheme 1 Synthesis of tetrapodal ligands L^{1-2} and their Ru(II) complexes

Table 1 Photophysical and electrochemical data of Ru(II) polypyridyl complexes

Complex	Absorption	Emission[a]		$E_{1/2}$, V (ΔE_p, mV)[b]	
	λ_{max} (nm) ($10^4\varepsilon$, M^{-1} cm^{-1})	λ_{max} (nm)	Φ	Oxidation	Reduction
$[(bpy)_8Ru_4(L^1)]^{8+}$	444 (7.04)	574	0.158	1.33 (59)	-0.86^{irr}
	286 (26.19)				−1.42 (96)
	238 (21.46)				−1.68 (92)
$[(bpy)_8Ru_4(L^2)]^{8+}$	443 (6.70)	574	0.152	1.34 (65)	-0.85^{irr}
	286 (25.21)				−1.41 (98)
	238 (21.93)				−1.69 (95)

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

[b] Oxidation potentials are recorded in 0.1 mol/L TBAP/CH_3CN, reduction potentials are recorded in 0.1 mol/L TBAP/DMF and potentials are given versus SCE, scan rate = 200 mV/s and ΔE_p is the difference between the anodic and cathodic waves

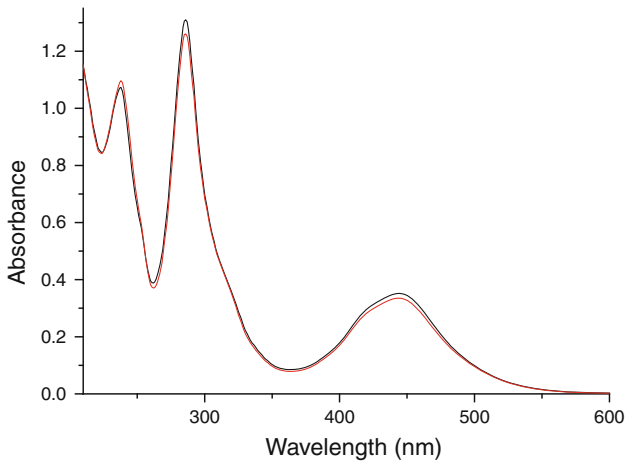


Fig. 1 Absorption spectra of complexes $[(bpy)_8Ru_4(L^1)](PF_6)_8$ (*black*) and $[(bpy)_8Ru_4(L^2)](PF_6)_8$ (*red*) in CH_3CN solution at room temperature. (Color figure online)

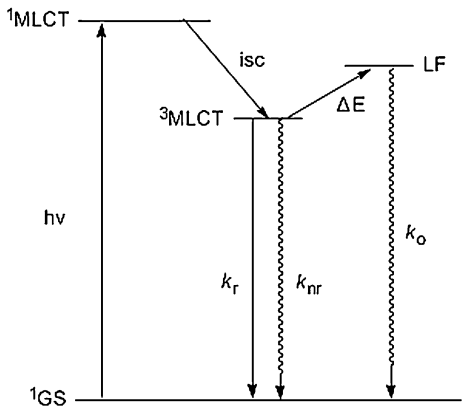


Fig. 2 Energy state diagram based on the Crosby–Meyer model

Emission spectra

Upon excitation into the MLCT band, both Ru(II) complexes are nonemissive in CH_3CN solution at room temperature. The emission properties of Ru(II) polypyridyl complexes generally follow the energy gap law [23–25]. The ^{3}MLCT state is reasonably long-lived and is thought to be deactivated by three processes: 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 excited state. The energy of the ligand field state should depend on the ligand field strength. The emission intensities follow the model shown in Fig. 2 originally proposed by Crosby, Meyer, and others [26–30]. The values of ΔE for the Ru(II) diimine complexes containing diazafluorene are substantially lower than the corresponding value for $Ru(bpy)_3^{2+}$. These results are consistent with ligand field theory, since diazafluorenone derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series [31], hence the ligand field excited state energy will be lowered if 2,2′-bipyridine ligands are replaced by diazafluorenone derivatives. Consequently, population of the ligand field state is very efficient for these complexes, and they are essentially nonemissive at room temperature. However, the energy transfer is inhibited at 77 K, so both complexes show vibrational components similar to that of $Ru(bpy)_3^{2+}$ in EtOH:MeOH (4:1, v/v) glassy matrix at 77 K (Fig. 3) [32, 33]. The complexes (10^{-5} mol/L) show characteristic emission at around 574 nm and a shoulder at around 620 nm in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K when excited at 436 nm (Table 1).

Electrochemistry

The electrochemical behaviors of the complexes have been studied in DMF and CH_3CN solutions with 0.1 mol/L TBAP as supporting electrolyte. The reduction waves of

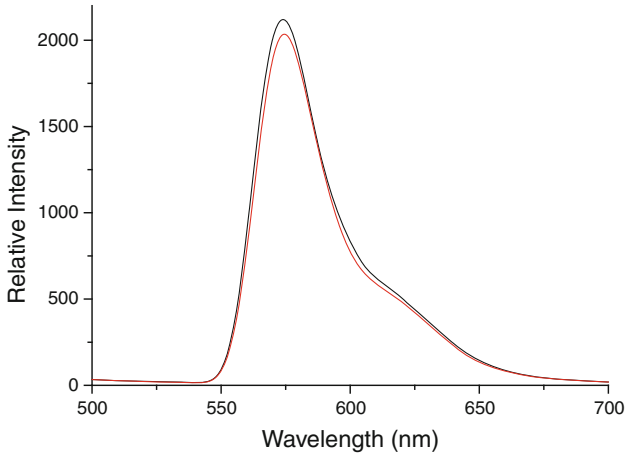


Fig. 3 Emission spectra of complexes $[(bpy)_8Ru_4(L^1)](PF_6)_8$ (*black*) and $[(bpy)_8Ru_4(L^2)](PF_6)_8$ (*red*) in EtOH:MeOH (4:1, v/v) glassy matrix at 77 K. (Color figure online)

the complexes are not well behaved in CH_3CN 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 the oxidative waves due to the insufficient anodic window of this solvent. Therefore, the oxidation potentials were recorded in CH_3CN solution, and the reduction potentials were recorded in DMF solution (Table 1).

The complex $[(bpy)_8Ru_4(L^1)]^{8+}$ displays a Ru(II)-centered reversible oxidation couple at 1.33 V (Fig. 4a). This potential is slightly more positive (by about 50 mV) than that of $Ru(bpy)_3^{2+}$ (+1.28 V vs. SCE) [34], but slightly more negative (by about 60 mV) than that of the parent complex $[(bpy)_2Ru(dafone)]^{2+}$ (dafo = 4,5-diazafluoren-9-one) [31], which indicates that the ligand L^1 is a stronger π-acceptor than 2,2′-bipyridine but a weaker π-acceptor than dafone. Complex $[(bpy)_8Ru_4(L^1)]^{8+}$ has four Ru(II) centers; two of one type of coordination environment, whilst the other two are different. The complex shows a single wave in cyclic voltammetry and a single peak without broadening in differential pulse voltammetry (Fig. 4a), which indicates that the small redox potential difference caused by these different coordination environments is not resolved by the electrochemical technique.

Electrochemical studies of both complexes reveal three ligand-centered reductions. A four-electron process for each couple of both complexes has been confirmed by coulometry. The first irreversible reduction wave of complex $[(bpy)_8Ru_4(L^1)]^{8+}$ at −0.86 V shows that this complex is a better electron acceptor than $[Ru(bpy)_3]^{2+}$ by about 0.7 V (Fig. 4b), which is consistent with the addition of four electrons to the LUMO localized on the ligand L^1 to give the species $[(bpy)_2Ru(bpy)_2RuL^{4-}Ru(bpy)_2Ru(bpy)_2]^{4+}$. The second reduction at −1.42 V is located on one of the two 2,2′-bipyridine ligands of each Ru(II) center, thus adding four

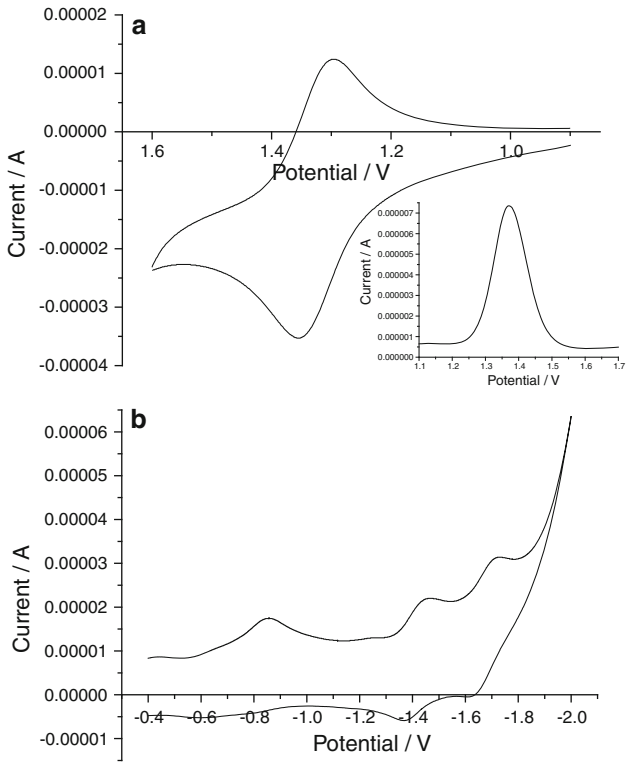


Fig. 4 Cyclic voltammetry of complex $[(bpy)_8Ru_4(L^1)](PF_6)_8$ (5×10^{-4} mol/L), **a** oxidation potential is recorded in 0.1 mol/L TBAP CH_3CN solution, **b** reduction potentials are recorded in 0.1 mol/L TBAP DMF solution

electrons to the LUMO + 1 orbital localized on the 2,2′-bipyridine ligand to give the species $[(bpy^{\cdot-})(bpy)Ru(bpy)(bpy^{\cdot-})RuL^{4-}Ru(bpy^{\cdot-})(bpy)Ru(bpy^{\cdot-})(bpy)]$. The third reduction at −1.68 V affords the species $[(bpy^{\cdot-})(bpy^{\cdot-})Ru(bpy^{\cdot-})(bpy^{\cdot-})RuL^{4-}Ru(bpy^{\cdot-})(bpy^{\cdot-})Ru(bpy^{\cdot-})(bpy^{\cdot-})]^{4-}$. The electrochemical behavior of complex $[(bpy)_8Ru_4(L^2)]^{8+}$ is similar to that of $[(bpy)_8Ru_4(L^1)]^{8+}$.

Conclusion

In summary, two 4,5-diazafluorene-based tetranuclear Ru(II) polypyridyl complexes incorporating two kinds of nonequivalent chelating sites have been synthesized. Both complexes exhibit intense emission at around 574 nm originating from the lowest energy MLCT excited state in EtOH:MeOH (4:1, v/v) glassy matrix at 77 K. Electrochemical studies of both complexes show one single Ru(II)-centered oxidation wave without broadening. The photophysical and electrochemical properties of both complexes are somewhat different to those of $Ru(bpy)_3^{2+}$ due to the different electronic nature of the tetrapodal ligands L^1 and L^2. Taking into account the tetranuclear structure of both Ru(II) complexes, they have potential

applications in the research area of electron or energy transfer.

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