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Synthesis, Spectroscopic, and Electrochemical Properties of Three Tetranuclear Ruthenium(II) Polypyridyl Complexes Based on 4,5-Diazafluorene

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Abstract. Three tetrapodal ligands 1,2,4,5-tetrakis[4-(4,5-diazafluoren-9-ylimino)phenoxymethyl]benzene (L^1), 1,2,4,5-tetrakis[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]benzene (L^2), and 1,2,4,5-tetrakis[(4,5-diazafluoren-9-ylimino)methyl]benzene (L^3), and their corresponding Ru^{II} polypyridyl complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^{1-3})](PF_6)_8$ (bpy = 2,2′-bipyridine) were synthesized and characterized. The spectroscopic behavior of the three complexes was investigated by UV/Vis absorption and emission spectroscopy. They display metal-to-ligand charge transfer (MLCT) absorptions at around 443 nm in CH_3CN solution at room temperature, and emission at around 575 nm in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K. Electrochemical studies of the three complexes show one Ru^{II}-based oxidation at around 1.35 V and three ligand-based reductions.

Introduction

Ruthenium(II) polypyridyl complexes are currently under investigation because of their outstanding photophysical and electrochemical properties and their extensive use in molecular recognition, solar energy conversion, DNA intercalation, pH switching, etc.[1–5] Polynuclear complexes incorporating Ru^{II} polypyridyl unit 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.[6–8] *Cooke* et al. have shown a new series of supramolecular complexes, Ru^{II} polypyridyl species have been assembled about 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 CH_3CN solution.[9] *Yamamoto* et al. have reported a novel type of light-harvesting complexes, which was synthesized with a linear-shaped Re^{I} oligomer as a photon absorber and a Ru^{II} polypyridyl complex as an energy acceptor.[10] 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 complexes, are strongly dependent on the size, shape, and electronic nature of the bridging ligands.[11–15] Thus, the judicious choice of an appropriate bridging ligand is the most important factor in the design of such Ru^{II} polypyridyl complex systems. A wide range of bridging ligands have been reported in recent years and many of them contain 2,2′-bipyridine or 1,10-phenanthroline (phen) units.[16–18] 4,5-Diazafluoren-9-one (dafo) is structurally similar to bpy 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. The electronic property of the ligand dafo is different from those of bpy and phen, as a consequence, Ru^{II} complexes containing 4,5-diazafluorene group have different photophysical and electrochemical properties compared to $Ru(bpy)_3{}^{2+}$ and $Ru(phen)_3{}^{2+}$ based complexes.[19,20]

This paper aims on the synthesis of new polynuclear Ru^{II} complexes with interesting photophysical and electrochemical properties. Herein the synthesis of three tetrapodal ligands and their corresponding tetranuclear Ru^{II} complexes containing 4,5-diazafluorene co-ligands is described. The molecular structures of the three tetrapodal ligands are slightly different because, in most cases, small changes in electronic properties of the bridging ligands can cause large changes in the spectroscopic and electrochemical properties of the complexes. The spectroscopic and electrochemical properties of the three Ru^{II} complexes are also presented and discussed.

Experimental Section

Materials: 2,2’-Bipyridine, 1,10-phenanthroline, 4-aminophenol, 2-aminophenol, tetrabutylammonium perchlorate (TBAP), ethyl acetate, 1,2,4,5-tetrakis(bromomethyl)benzene, $NH_2OH\cdot HCl$, $RuCl_3\cdot 3H_2O$, NH_4PF_6, K_2CO_3, CH_3CN, CH_2Cl_2, EtOH, MeOH, 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 through activated alumina and distilled

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from P_2O_5 immediately prior to use. 4,5-Diazafluoren-9-one,[21] 9-(4-hydroxy)phenylimino-4,5-diazafluorene,[22] 9-(2-hydroxy)phenylimino-4,5-diazafluorene,[22] 4,5-diazafluoren-9-oxime,[22] and $Ru(bpy)_2Cl_2{\cdot}2H_2O$[23] were prepared according to literature procedures.

Physical Measurements: ^{1}H NMR spectra were obtained with a Mercury Plus 400 spectrometer using TMS as internal standard. ESI-MS spectra were obtained with a Bruker Daltonics Esquire 6000 mass spectrometer. Elemental analyses were obtained with a Perkin-Elmer 240C analytical instrument. Absorption spectra were obtained with a Varian Cary-100 UV/Vis 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, v/v) glassy matrix.[24] Electrochemical measurements were carried out at room temperature using a CHI 660D 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 $mol{\cdot}L^{-1}$ TBAP as supporting electrolyte. All samples were purged with nitrogen prior to measurement.

Preparation of 1,2,4,5-Tetrakis[4-(4,5-diazafluoren-9-ylimino)phenoxymethyl]benzene (L^1): A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (232 mg, 0.52 mmol), 9-(4-hydroxy)phenylimino-4,5-diazafluorene (717 mg, 2.63 mmol), and K_2CO_3 (381 mg, 2.76 mmol) in DMF (20 mL) was heated to 85 °C for 48 h in a nitrogen atmosphere. The solution was poured into water (200 mL) 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 (30:1, v/v) to afford the desired product as a red solid. Yield: 328 mg (51.7 %). **^{1}H NMR** (400 MHz, $CDCl_3$): $\delta = 5.36$ (s, 8 H), 6.99–7.02 (m, 12 H), 7.08–7.13 (m, 12 H), 7.39 (dd, $J = 8.0$, 4.8 Hz, 4 H), 7.87 (s, 2 H), 8.22 (dd, $J = 8.0$, 1.6 Hz, 4 H), 8.65 (dd, $J = 4.8$, 1.6 Hz, 4 H), 8.81 (dd, $J = 4.8$, 1.6 Hz, 4 H) ppm. **ESI-MS**: $m/z = 1219.4$ $[M + H]^+$. $C_{78}H_{50}N_{12}O_4$: calcd. C 76.83; H 4.13; N 13.78 %; found: C 76.62; H 4.01; N 13.57 %.

1,2,4,5-Tetrakis[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]benzene (L^2): L^2 was prepared by the same procedure as that described for L^1, except 9-(2-hydroxy)phenylimino-4,5-diazafluorene (618 mg, 2.26 mmol) was used instead of 9-(4-hydroxy)phenylimino-4,5-diazafluorene to react with 1,2,4,5-tetrakis(bromomethyl)benzene (193 mg, 0.43 mmol). Yield: 249 mg (47.2 %) of a red solid. **^{1}H NMR** (400 MHz, $CDCl_3$): $\delta = 4.61$ (s, 8 H), 6.71–6.74 (m, 4 H), 6.79–6.87 (m, 12 H), 6.98–7.07 (m, 10 H), 7.17 (dd, $J = 7.6$, 4.8 Hz, 4 H), 8.12 (dd, $J = 7.6$, 1.6 Hz, 4 H), 8.51 (dd, $J = 4.8$, 1.6 Hz, 4 H), 8.68 (dd, $J = 4.8$, 1.6 Hz, 4 H) ppm. **ESI-MS**: $m/z = 1219.4$ $[M + H]^+$. $C_{78}H_{50}N_{12}O_4$: calcd. C 76.83; H 4.13; N 13.78 %; found: C 76.54; H 3.93; N 13.55 %.

1,2,4,5-Tetrakis[(4,5-diazafluoren-9-ylimino)methyl]benzene (L^3): A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (203 mg, 0.46 mmol), 4,5-diazafluoren-9-oxime (511 mg, 2.59 mmol), and K_2CO_3 (389 mg, 2.81 mmol) in DMF (20 mL) was heated to 85 °C for 48 h in a nitrogen atmosphere. The solution was poured into water (200 mL) after cooling down to room temperature, and a white precipitate which formed was collected by filtration. The precipitate was washed successively with H_2O, CH_2Cl_2, hot ethanol, hot DMF, and ethyl ether, affording the desired product as a white solid. Yield: 278 mg (66.8 %). The ^{1}H NMR spectrum of it was not obtained due to its poor solubility in common NMR solvents. **ESI-MS**: $m/z = 915.4$ $[M + H]^+$. $C_{54}H_{34}N_{12}O_4$: calcd. C 70.89; H 3.75; N 18.37 %; found: C 71.12; H 3.90; N 18.22 %.

$[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$: A mixture of ligand L^1 (71 mg, 0.06 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (157 mg, 0.30 mmol) in 2-methoxyethanol (100 mL) was heated to 120 °C for 12 h in a nitrogen atmosphere to give a clear deep red solution. Afterwards, the solvent was evaporated under reduced pressure. The residue was purified twice by column chromatography on alumina, being eluted first with CH_3CN/EtOH (6:1, v/v) to remove impurities, finally with EtOH to afford the complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]Cl_8$. The 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: 101 mg (43.0 %). **^{1}H NMR** (400 MHz, $[D_6]$DMSO): $\delta = 5.38$ (s, 8 H), 7.21–7.23 (m, 16H), 7.32–7.35 (m, 8H), 7.51–7.56 (m, 24H), 7.76 (d, $J = 5.2$ Hz, 4 H), 7.83–7.86 (m, 10 H), 8.09 (d, $J = 5.2$ Hz, 4 H), 8.16–8.22 (m, 20 H), 8.41 (d, $J = 7.8$ Hz, 4H), 8.81–8.87 (m, 16 H) ppm. **ESI-MS**: $m/z = 1199.7$ $(M - 3PF_6)^{3+}$, 863.0 $(M - 4PF_6)^{4+}$, 661.7 $(M - 5PF_6)^{5+}$. $C_{158}H_{114}F_{48}N_{28}O_4P_8Ru_4$: calcd. C 47.06; H 2.85; N 9.73 %; found: C 46.87; H 2.76; N 9.83 %.

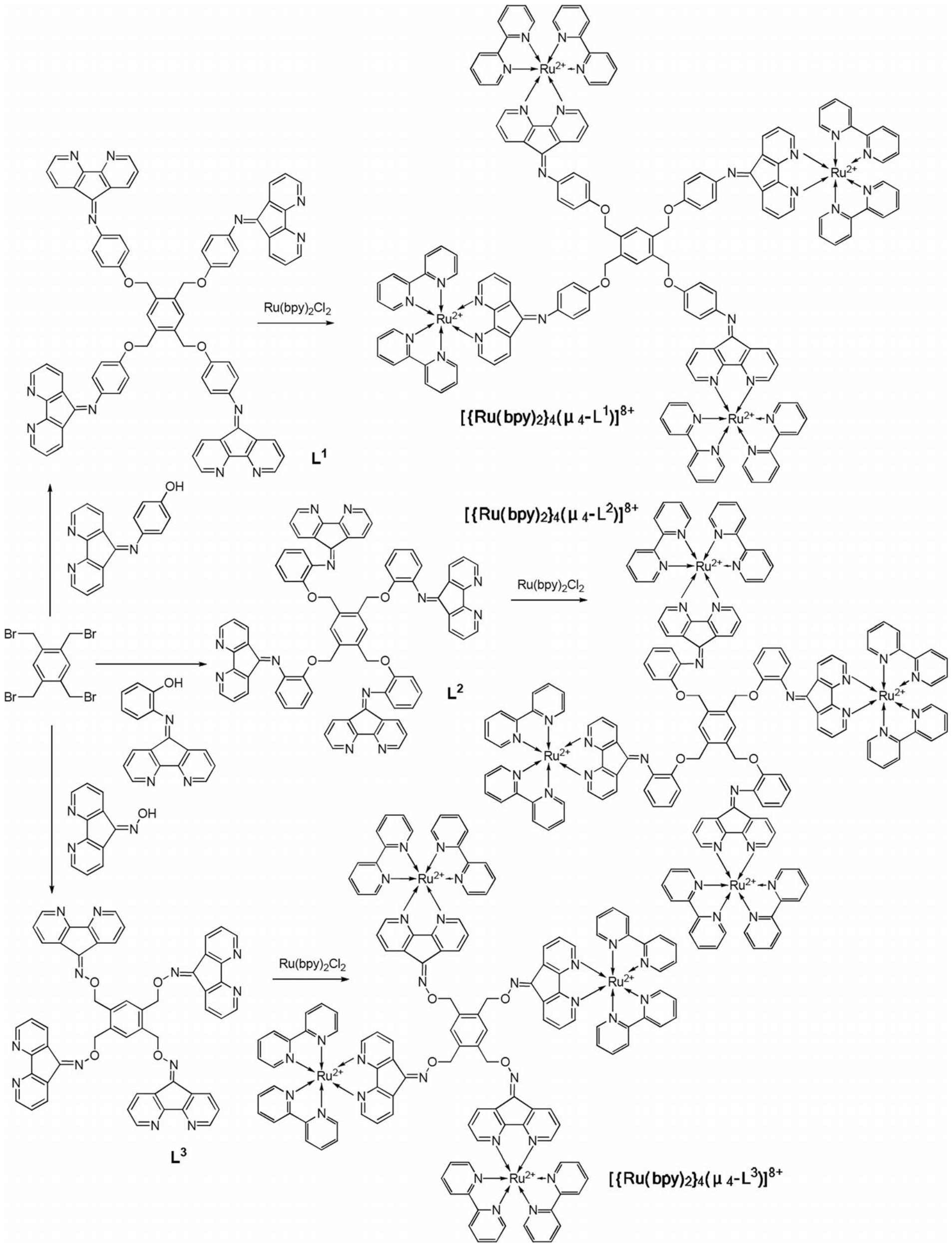
$[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)](PF_6)_8$: $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)](PF_6)_8$ was prepared by the same procedure as that described for $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$, except L^2 (77 mg, 0.06 mmol) was used instead of L^1 to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (181 mg, 0.35 mmol). Yield: 98 mg (38.4 %) of a red solid. **^{1}H NMR** (400 MHz, $[D_6]$DMSO): $\delta = 5.15$ (s, 8H), 7.01–7.05 (m, 20H), 7.28–7.32 (m, 8H), 7.54–7.56 (m, 18H), 7.58–7.62 (m, 4H), 7.75 (d, $J = 5.6$ Hz, 4H), 7.80–7.83 (m, 8H), 8.15–8.18 (m, 24H), 8.28 (d, $J = 6.4$ Hz, 4H), 8.84 (s, 8H), 8.86 (s, 8H) ppm. **ESI-MS**: $m/z = 863.0$ $(M - 4PF_6)^{4+}$, 661.6 $(M - 5PF_6)^{5+}$. Calcd for $C_{158}H_{114}F_{48}N_{28}O_4P_8Ru_4$: calcd. C 47.06; H 2.85; N 9.73 %; found: C 47.29; H 2.78; N 9.57 %.

$[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)](PF_6)_8$: $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)](PF_6)_8$ was prepared by the same procedure as that described for $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$, except L^3 (68 mg, 0.07 mmol) was used instead of L^1 to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (206 mg, 0.39 mmol). Yield: 153 mg (55.2 %) of a red solid. **^{1}H NMR** (400 MHz, $[D_6]$DMSO): $\delta = 5.84$ (s, 8H), 7.43–7.54 (m, 20H), 7.63–7.66 (m, 8H), 7.81–7.84 (m, 8H), 7.91 (s, 2H), 8.04–8.07 (m, 8H), 8.12–8.19 (m, 24H), 8.42 (d, $J = 7.8$ Hz, 4H), 8.81 (s, 8H), 8.84 (s, 8H). **ESI-MS**: $m/z = 1097.4$ $(M - 3PF_6)^{3+}$, 786.4 $(M - 4PF_6)^{4+}$. $C_{134}H_{98}F_{48}N_{28}O_4P_8Ru_4$: calcd. C 43.17; H 2.65; N 10.52 %, found: C 42.88; H 2.52; N 10.70 %.

Results and Discussion

Synthesis

The outline of the synthesis of the three tetrapodal ligands and their Ru^{II} polypyridyl complexes is presented in Scheme 1. Starting compounds 9-(4-hydroxy)phenylimino-4,5-diazafluorene, 9-(2-hydroxy)phenylimino-4,5-diazafluorene, and 4,5-diazafluoren-9-oxime were prepared from 4,5-diazafluoren-9-one according to the literature procedure.[22] L^1, L^2, and L^3 were prepared in moderate yields by the reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with 9-(4-hydroxy)phenylimino-4,5-diazafluorene, 9-(2-hydroxy)phenylimino-4,5-diazafluorene, and 4,5-diazafluoren-9-oxime, respectively, in DMF solution in a nitrogen atmosphere. The Ru^{II} complexes were prepared by heating $Ru(bpy)_2Cl_2{\cdot}2H_2O$ with the appropriate



Scheme 1. Synthesis of tetrapodal ligands L^{1-3} and their Ru^{II} complexes.

ligand in 2-methoxyethanol solution to reflux, and were isolated as their PF_6^- salts. These compounds were characterized by ^1H NMR spectroscopy, ESI-MS, and elemental analysis.

Absorption Spectroscopy

The absorption spectra of the ligands were studied in $CHCl_3$ solution, and their Ru^{II} complexes studied in CH_3CN solution. The concentrations of the ligands and complexes are 10^{-5} and 5×10^{-6} mol·L^{-1}, respectively. The energy maxima and absorption coefficients are summarized in Table 1, and the spectra are shown in Figure 1. Absorption bands of the ligands can be assigned to ligand-centered intraligand π→π* or n→π* transitions. Assignments of the absorption bands of the complexes were made on the basis of the well-documented optical transitions of analogous Ru^{II} polypyridyl complexes.[25,26] The absorption spectra of the complexes show three well-resolved bands. Those at ca. 286 and 238 nm can be assigned to intraligand π→π* transitions centered on the 2,2′-bipyridine. The lowest energy band at around 443 nm is attributed to MLCT, dπ→π* transition, which consists of overlapping dπ(Ru)→π*(bpy) and dπ(Ru)→π*(L) transitions. The three complexes contain two different kinds of ligands with different accepting properties, which results in the appearance of a nonsymmetrical MLCT band. The MLCT absorption maxima of the complexes are blue-shifted by about 8 nm compared with that of $Ru(bpy)_3^{2+}$,[27] which shows the donor properties of tetrapodal ligands are weaker than that of 2,2′-bipyridine.

Table 1. Photophysical and electrochemical data of ligands and Ru^{II} polypyridyl complexes.

Compound	Absorption λ_{max} /nm ($10^4\varepsilon$ /$M^{-1}\cdot cm^{-1}$)	Emission a) λ_{max} /nm	Φ	$E_{1/2}$ /V (ΔE_p /mV) b) Oxidation	Reduction
L^1	427 (0.83) 301 (3.47)				–0.84 (126)
L^2	426 (0.62 301 (4.06)				–0.82 (132)
$[(bpy)_8Ru_4(L^1)]^{8+}$	444 (5.40) 286 (19.23) 238 (17.64)	573	0.161	1.37 (131)	–0.80 (82) –1.40 (96) –1.65 (91)
$[(bpy)_8Ru_4(L^2)]^{8+}$	443 (5.78) 286 (23.52) 236 (19.69)	573	0.157	1.36 (118)	–0.79 (88) –1.41 (92) –1.63 (99)
$[(bpy)_8Ru_4(L^3)]^{8+}$	441 (4.88) 286 (27.61) 240 (11.62)	578	0.357	1.33 (54)	–0.95 (102) –1.41 (106) –1.67 (103)

a) The emission quantum yields are calculated relative to $Ru(bpy)_3^{2+}$ (Φ_{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^{-1} TBAP/CH_3CN, reduction potentials are recorded in 0.1 mol·L^{-1} TBAP/DMF and potentials are given vs. SCE, scan rate = 200 mV·s^{-1} and ΔE_p is the difference between the anodic and cathodic waves.

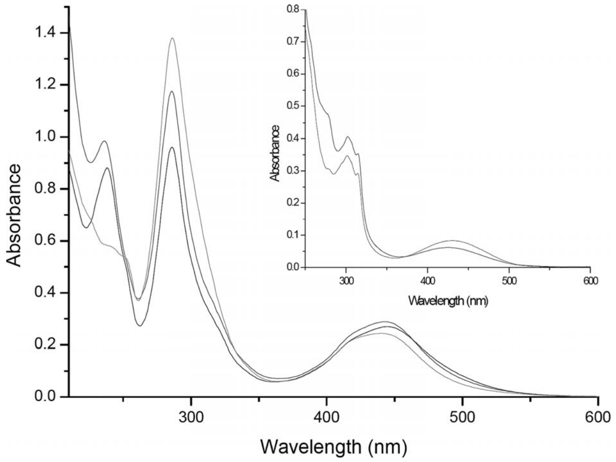


Figure 1. Absorption spectra of complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$ (black), $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)](PF_6)_8$ (dark grey), and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)](PF_6)_8$ (light grey) in CH_3CN solution; absorption spectra of ligands L^1 (grey) and L^2 (black) in $CHCl_3$ solution.

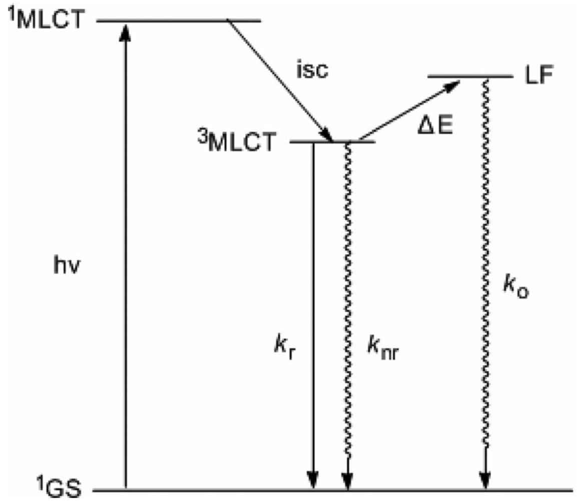


Figure 2. Energy state diagram based on the Crosby-Meyer model.

Emission Spectroscopy

The three complexes display no emission at all in CH_3CN solution at room temperature upon excitation into the MLCT band. The emission properties of Ru^{II} polypyridyl complexes generally follow the energy gap law.[28,29] 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 this presumed ligand field state should depend on the ligand field strength. The emission intensities follow the model shown in Figure 2 originally proposed by *Crosby*, *Meyer*, and others.[30–34] The values of ΔE for the Ru^{II} polypyridyl complexes containing 4,5-diazafluorene are substantially lower than the corresponding value for $Ru(bpy)_3^{2+}$, these results are consistent with ligand field theory. 4,5-Diazafluorene derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series,[35–37] hence the ligand field excited state energy will be lowered if 2,2′-bipyridine ligands are replaced by 4,5-diazafluorene derivatives. Consequently, population of the ligand field state is very efficient for these complexes at room temperature and they are essentially non-emissive at room temperature. However, the energy transfer is inhibited at 77 K, so they show vibrational components similar to that of $Ru(bpy)_3^{2+}$ in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K (Figure 3).[35–37] The three complexes (10^{-5} mol·L^{-1}) exhibit characteristic emission at around 575 nm in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K with an excitation wavelength at 436 nm (Table 1). The emission intensities of complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)]^{8+}$ are weaker than that of complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$. This may involve rapid radiationless decay. It has been well documented that the energy of the metal-centered excited state depends on the ligand field strength, which in turn depends on the σ donor and π acceptor properties of ligands,[38] the larger π framework of ligands L^1 and L^2 decreases the σ donor and increases the π acceptor properties slightly, resulting in weakening of the ligand field strength around the central metal atom and in turn lowering the metal σ* orbitals slightly. This makes radiationless decay via low-lying MC states more efficient than in complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$.

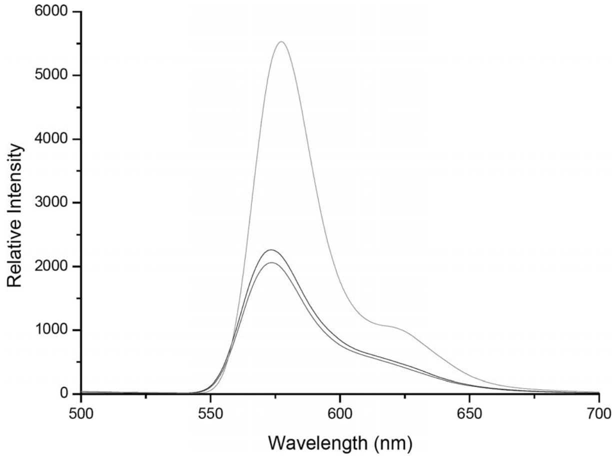


Figure 3. Emission spectra of complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$ (black), $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)](PF_6)_8$ (dark grey), and $[\{Ru(bpy)_2\}_4\text{-}(\mu_4\text{-}L^3)](PF_6)_8$ (light grey) in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K.

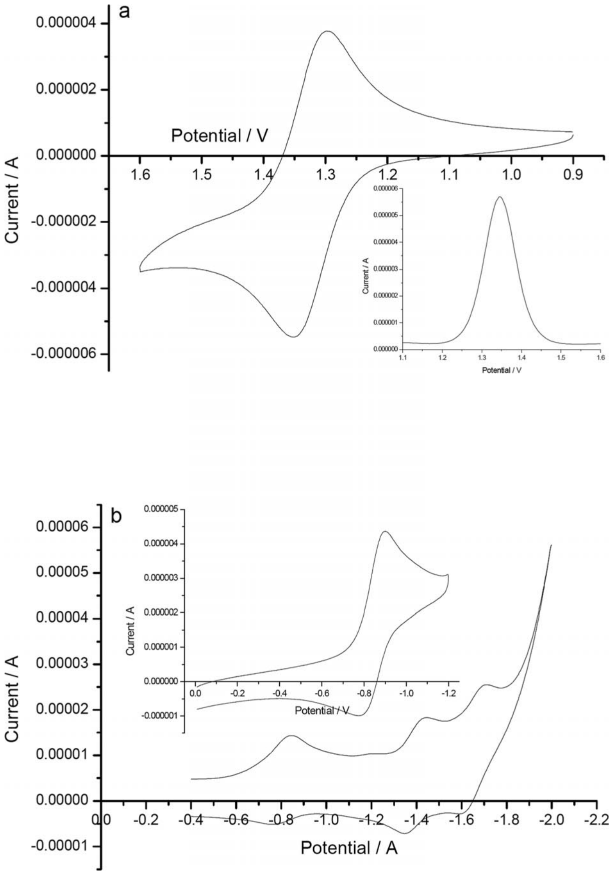


Figure 4. Cyclic voltammetry of complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)](PF_6)_8$ (5×10^{-4} mol·L^{-1}, scan rate = 200 mV·s^{-1}), (a) oxidation potential is recorded in 0.1 mol·L^{-1} TBAP CH_3CN solution, (b) reduction potentials are recorded in 0.1 mol·L^{-1} TBAP DMF solution; cyclic voltammetry of ligand L^1 (5×10^{-4} mol·L^{-1}, scan rate = 200 mV·s^{-1}) is recorded in 0.1 mol·L^{-1} TBAP DMF solution.

Electrochemical Properties

The electrochemical behaviors of the three complexes have been studied in CH_3CN and DMF solutions with 0.1 mol·L^{-1} TBAP as supporting electrolyte. The reduction waves of 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 three complexes display clear reduction processes, but do not exhibit the oxidative waves due to the insufficient anodic window of the solvent. Therefore, the oxidation potentials were recorded in CH_3CN solution, and the reduction potentials were recorded in DMF solution (Table 1).

The complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ exhibits a Ru^{II}-centered reversible oxidation wave at 1.37 V (Figure 4a). This potential is slightly more negative (by about 20 mV) than that of the parent complex $[(bpy)_2Ru(dafo)]^{2+}$[35] but slightly more positive (by about 100 mV) than that of complex $Ru(bpy)_3{}^{2+}$, which indicates that the ligand L^1 is a stronger π acceptor than 2,2′-bipyridine but a weaker π acceptor than dafo. Complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$ is easier to oxidize than complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)]^{8+}$ due to the extended π delocalization of ligands L^1 and L^2. In the current study, the three tetranuclear complexes show a single, unperturbed wave in cyclic voltammetry and a single peak without broadening in differential pulse voltammetry (Figure 4a), a four-electron process for each couple of the three complexes was confirmed by coulometry. On the basis of the above results, the oxidation can be ascribed to a four-electron reversible process.

Electrochemical studies of the three complexes exhibit three ligand-centered reductions. The free L^1 ligand shows one reduction wave at –0.84 V. Upon coordination to ruthenium, the first reduction wave at –0.80 V were observed. This reduction is consistent with the addition of electrons to the LUMO localized on L^1, giving the species $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^{4-})]^{4+}$ (Figure 4b). It appears that the tetrapodal ligand L^1 is more easily reduced than 2,2′-bipyridine based on the reduction data, so complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ should possess an excited state lower in energy than the $Ru^{II} \rightarrow$ bpy charge transfer states. 4,5-Diazafluorene derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series,[35–37] and the absorption spectrum of complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ does not show any particular band significantly lower in energy than $Ru(bpy)_3{}^{2+}$, so such an easy reduction should involve an orbital, which does not receive significant contribution from the chelating nitrogen atoms of the tetrapodal ligand. The promoted electron should be associated with the C=N moiety of the tetrapodal ligand L^1. This first reduction wave of complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$ shows that this complex is a weaker electron acceptor than $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)]^{8+}$ by about 0.15 V. The second quasi-reversible reduction at –1.40 V is located on one of the two 2,2′-bipyridine ligands on each metallic terminal, adding electrons to the 2,2′-bipyridine localized LUMO+1 yielding the species $[\{Ru(bpy^{\bullet-})(bpy)\}_4(\mu_4\text{-}L^{4-})]$. Similar to the oxidation process, the reductions of the remote 2,2′-bipyridine appear at the same potential, indicating no interaction between the four sites. The third reduction appearing at –1.65 V is quasi-reversible and yields the species $[\{Ru(bpy^{\bullet-})_2\}_4(\mu_4\text{-}L^{4-})]^{4-}$. Electrochemistry behaviors of complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)]^{8+}$ and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$ are similar to that of complex $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$.

Conclusions

Three tetrapodal ligands derived from 4,5-diazafluorene-9-one, and their corresponding tetranuclear Ru^{II} complexes were synthesized and characterized. The UV/Vis absorption and emission properties of the three complexes are dominated by MLCT transitions and excited states. The three complexes exhibit intense emission at around 575 nm originating from the lowest energy MLCT excited state in EtOH/MeOH (4:1, v/v) glassy matrix at 77 K. Electrochemical studies of the complexes exhibit one single Ru^{II}-based oxidation wave. The spectroscopic and electrochemical properties of the three complexes are somewhat different to those of $Ru(bpy)_3^{2+}$ due to the different electronic nature of the tetrapodal ligands. These properties of complexes $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^1)]^{8+}$ and $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^2)]^{8+}$ are also somewhat different to those of $[\{Ru(bpy)_2\}_4(\mu_4\text{-}L^3)]^{8+}$ due to the slightly variation of the three bridging ligands. Electrochemical properties show little interaction between the three Ru^{II} polypyridyl complexes. It is well-documented that an interaction of a few reciprocal centimeters (which can not be noticed in spectroscopic and electrochemical experiments) is sufficient to cause fast intercomponent electron or energy transfer processes,[39–43] so the three complexes have potential applications in the area of photoinduced electron or energy transfer.

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