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Preparation, Spectroscopic, and Electrochemical Properties of Two 4,5-Diazafluorene-Containing Ruthenium(II) Complexes: Bridging Ligands Composed of Two Kinds of Nonequivalent Coordinating Sites

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Preparation, Spectroscopic, and Electrochemical Properties of Two 4,5-Diazafluorene-Containing Ruthenium(II) Complexes: Bridging Ligands Composed of Two Kinds of Nonequivalent Coordinating Sites

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Two tetrapodal ligands L^1 and L^2 containing 4,5-diazafluorene fragments have been prepared and characterized. Both ligands are composed of two kinds of nonequivalent coordinating sites. Ligand L^1 consists of the 4-(4,5-diazafluoren-9-ylimino)phenoxy and 4,5-diazafluoren-9-ylimino)phenoxy moieties, ligand L^2 involves the 2-(4,5-diazafluoren-9-ylimino)phenoxy and 4,5-diazafluoren-9yliminoxy moieties. The Ru(II) complexes [(bpy)₈Ru₄(L^1)](PF₆)₈ and [(bpy)₈Ru₄(L^2)](PF₆)₈ (bpy = 2,2'-bipyridine) have been synthesized by refluxing Ru(bpy)₂Cl₂·2H₂O and each ligand in 2methoxyethanol. Both complexes exhibit metal-to-ligand charge transfer absorptions at around 443 nm, and emission at around 577 nm. Electrochemical studies of both complexes display one Ru(II)-centered oxidation at around 1.32 V and four ligandcentered reductions.

Keywords asymmetric tetrapodal ligand, electrochemistry, photophysics, Ru(II) complex

INTRODUCTION

Ru(II) polypyridyl complexes have attracted much interest as artificial photosynthesis, molecular recognition, DNA intercalation, pH switching and so on because of their unique combination of chemical stability, redox properties, reactivity, and emission.^[1–5] Oligometallic complexes incorporating Ru(II) polypyridyl fragment 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] Key components of oligonuclear Ru(II) polypyridyl complexes are the bridging ligands, since the interactions between the bridged units, and thereby the ground and excited state properties of polynuclear complexes, are strongly dependent on the size, shape, and electronic nature of the bridging ligands. Tuning the size, shape, and electronic properties of the bridging ligands can induce desirable changes in the electrochemical and spectroscopic properties of Ru(II) polypyridyl complexes.^[9-13] Thus, synthesizing appropriate bridging ligands is the most important step in realizing molecular devices based on oligonuclear Ru(II) complexes. A large number 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.^[14-16] Borgstrom et al.^[17] reported a novel bichromophoric system ([(bpy)2Ru(bpy-Phtpy)Ru(Metpy-PI)][PF₆]₃, where ligand bpy-Ph-tpy consists of a 2,2'-bipyridine unit and a 2,2':6',2"-terpyridine unit. Excitation of the (bpy)₂Ru(bpy-Ph-tpy) unit results in an initial energy transfer to the (bpy-Ph-tpy)Ru(Metpy-PI) unit. Subsequent electron transfer to the PI acceptor results in the formation of the charge separation state. Chao et al.^[18] reported a tetranuclear Ru(II) polypyridine complex based on the asymmetric bridging ligand pdtp. The bridging ligand directs center-to-periphery energy transfer occurring in the dendritic tetranuclear complex. Toward the aim of preparing novel oligonuclear Ru(II) complexes with interesting spectroscopic and electrochemical properties, herein, we describe the synthesis and characterization of two tetrapodal ligands incorporating two kinds of nonequivalent chelating sites. Ligand L¹ consists of the 4-(4,5-diazafluoren-9-ylimino)phenoxy and 4,5-diazafluoren-9-yliminoxy moieties, ligand L^2 involves the 2-(4,5-diazafluoren-9-ylimino)phenoxy and 4,5-diazafluoren-9-yliminoxy moieties. The electronic absorption, emission, and electrochemical properties of both complexes are also presented and discussed.

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EXPERIMENTAL

Materials and Physical Measurements

2,2'-Bipyridine, 1,10-phenanthroline, 4-aminophenol, 2aminophenol, p-toluenesulfonyl chloride, pentaerythritol, tetrabutylammonium perchlorate (TBAP), ethyl acetate, 2methoxyethanol, NH₂OH·HCl, RuCl₃·3H₂O, NH₄PF₆, K₂CO₃, CH₃CN, CH₂Cl₂, 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 CH₃CN, which was filtered over activated alumina and distilled from P₂O₅ immediately prior to use. 4,5-Diazafluoren-9one,^[19] 9-(4-hydroxy)phenylimino-4,5-diazafluorene,^[20] 9-(2hydroxy)phenylimino-4,5-diazafluorene,^[20] 4,5-diazaflu-oren-9-oxime,^[20] pentaerythrityl tetratosylate,^[21] and Ru(bpy)₂ Cl₂·2H₂O^[22] were prepared according to literature procedures.

¹H NMR spectra were obtained on a Mercury Plus 300 spectrometer and a Mercury Plus 400 spectrometer using TMS as internal standard. ESI-MS spectra were obtained on 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 $Ru(bpy)_3^{2+}$ $(\Phi_{\text{std}} = 0.376)$ in EtOH-MeOH (4:1, v/v) glassy matrix.^[23] Electrochemical measurements were carried out at room temperature using a CHI 660D electrochemical workstation. Cyclic voltammetry and differential pulse voltammetry were performed in CH₃CN 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

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, 9-(4-hydroxy)phenylimino-4,5-diazafluorene 0.87 mmol), (486 mg, 1.78 mmol), and K₂CO₃ (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 that formed was collected by filtration. The crude product was chromatographed on silica, being eluted first with CH₂Cl₂-ethyl acetate (2:1, v/v) to remove impurities, then with CH2Cl2-EtOH (25:1, v/v) to afford the desired product as a red solid. Yield: 233 mg (28.2%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.44$ (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. Anal. Calcd. for $C_{53}H_{42}N_6O_8S_2$: C, 66.7; H, 4.4; N, 8.8.

1,1'-Di[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1",1"' -di(p-tosyloxymethyl)-methane (compound 2)

Compound **2** was prepared by the same procedure as that described for compound **1**, except 9-(2-hydroxy)phenylimino-4,5-diazafluorene (533 mg, 1.95 mmol) was used instead of 9-(4-hydroxy)phenylimino-4,5-diazafluorene to react with pentaerythrityl tetratosylate (712 mg, 0.95 mmol). Yield: 192 mg (21.3%) of a red solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.35$ (s, 6H), 3.63 (s, 4H), 3.73 (s, 4H), 6.50 (d, J = 7.6 Hz, 2H), 6.85 (dd, J = 7.6, 1.6 Hz, 2H), 6.89–6.94 (m, 4H), 7.02 (td, J = 8.4 Hz, 4H), 7.36–7.40 (m, 6H), 8.16 (dd, J = 7.6, 1.2 Hz, 2H), 8.59 (dd, J = 4.4, 2.0 Hz, 2H), 8.81 (dd, J = 4.4, 2.0 Hz, 2H), ESI-MS: m/z 955.5 (M + H)⁺. Found: C, 66.9; H, 4.5; N, 8.6. Anal. Calcd. for C₅₃H₄₂N₆O₈S₂: C, 66.7; H, 4.4; N, 8.8.

1,1'-Di[4-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1'',1'''-di[(4,5-diazafluoren-9-yliminoxy)methyl]-methane (L^1)

A mixture of compound 1 (507 mg, 0.53 mmol), 4,5diazafluoren-9-oxime (429 mg, 2.18 mmol), and K₂CO₃ (416 mg, 3.01 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 that formed was collected by filtration. The crude product was purified twice by column chromatography on silica, being eluted with CH₂Cl₂-EtOH (10:1, v/v) to afford the desired product as a red solid. Yield: 117 mg (21.9%). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3): \delta = 4.48 \text{ (s, 4H)}, 5.05 \text{ (s, 4H)}, 6.93 \text{ (dd, } J =$ 7.6, 4.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 4H), 7.07–7.13 (m, 6H), 7.20 (dd, J = 7.6, 4.8 Hz, 2H), 7.25-7.27 (m, 2H), 7.41 (dd, J =7.6, 4.8 Hz, 2H), 7.91 (dd, J = 7.6, 1.6 Hz, 2H), 8.26 (dd, J =7.6, 2.0 Hz, 2H), 8.46 (dd, J = 8.0, 1.6 Hz, 2H), 8.65 (dd, J =4.8, 1.2 Hz, 2H), 8.72 (d, J = 4.4 Hz, 4H), 8.82 (dd, J = 4.8, 1.2 Hz, 2H). ESI-MS: m/z 1005.3 (M + H)⁺. Found: C, 72.6; H, 3.9; N, 16.5. Anal. Calcd. for C₆₁H₄₀N₁₂O₄: C, 72.9; H, 4.0; N, 16.7.

1,1'-Di[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-1",1"" -di[(4,5-diazafluoren-9-yliminoxy)methyl]-methane (L²)

L² was prepared by the same procedure as that described for L¹, except compound **2** (602 mg, 0.63 mmol) was used instead of compound **1** to react with 4,5-diazafluoren-9-oxime (510 mg, 2.59 mmol). Yield: 122 mg (19.3%) of a red solid. ¹H NMR (400 MHz, CDCl₃): δ = 3.91 (s, 4H), 4.18 (s, 4H), 6.68 (dd, J = 8.0, 1.2 Hz, 2H), 6.72 (dd, J = 8.0, 4.8 Hz, 2H), 6.94 (dd, J = 7.6, 1.6 Hz, 2H), 6.98 (dd, J = 7.6, 1.6 Hz, 2H), 7.08–7.14 (m, 8H), 7.25–7.31 (m, 2H), 7.74 (dd, J = 7.6, 1.6 Hz, 2H), 8.08 (dd, J = 7.6, 1.6 Hz, 2H), 8.14 (dd, J = 7.6, 1.6 Hz, 2H), 8.42 (dd, J = 4.8, 1.2 Hz, 2H), 8.66 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 4.8, 1.6 Hz, 2H), 8.75 (dd, J = 5.2, 1.6 Hz, 2H), 8.69 (dd, J = 5.2, 1.6 Hz, 2H), 8.69

2H). ESI-MS: m/z 1005.5 (M + H)⁺ $_{\circ}$ Found: C, 72.7; H, 3.9; N, 16.5. Anal. Calcd. for C₆₁H₄₀N₁₂O₄: C, 72.9; H, 4.0; N, 16.7.

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

A mixture of ligand L^1 (67 mg, 0.07 mmol) and Ru(bpy)₂Cl₂·2H₂O (179 mg, 0.34 mmol) in 2-methoxyethanol (50 mL) was heated to 120°C for 12 h under nitrogen to give a clear deep red solution, then the solvent was evaporated under reduced pressure. The residue was purified twice by column chromatography on alumina, being eluted first with CH₃CN-EtOH (8:1, v/v) to remove impurities, then with MeOH 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 NH₄PF₆ until no more precipitate formed. The precipitate was recrystallized from CH₃CN-Et₂O mixture (vapor diffusion method) to afford a red solid. Yield: 105 mg (41.2%). ¹H NMR (400 MHz, DMSO-d₆): $\delta = 4.51$ (s, 4H), 5.05 (s, 4H), 7.18–7.21 (m, 6H), 7.31 (d, J = 5.2 Hz, 4H), 7.52–7.57 (m, 16H), 7.56 (d, J = 5.6 Hz, 4H), 7.63–7.67 (m, 6H), 7.76 (d, J = 5.6 Hz, 2H), 7.83–7.87 (m, 8H), 8.05–8.08 (m, 6H), 8.15-8.24 (m, 22H), 8.36 (d, J = 7.6 Hz, 4H), 8.49(d, J = 7.6 Hz, 2H), 8.80-8.86 (m, 16H). ESI-MS: m/z 1763.7 $(M - 2PF_6)^{2+}$, 1127.4 $(M - 3PF_6)^{3+}$, 810.0 $(M - 4PF_6)^{4+}$, 618.5 (M – 5PF₆)⁵⁺. Found: C, 44.7; H, 2.9; N, 10.5. Anal. Calcd. for C₁₄₁H₁₀₄F₄₈N₂₈O₄P₈Ru₄: C, 44.4; H, 2.8; N, 10.3.

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

[(bpy)₈Ru₄(L²)](PF₆)₈ was prepared by the same procedure as that described for [(bpy)₈Ru₄(L¹)](PF₆)₈, except L² (73 mg, 0.07 mmol) was used instead of L¹ to react with Ru(bpy)₂Cl₂·2H₂O (193 mg, 0.37 mmol). Yield: 107 mg (38.5%) of a red solid. ¹H NMR (400 MHz, DMSO-d₆): δ = 3.96 (s, 4H), 4.14 (s, 4H), 7.42 (d, J = 5.6 Hz, 4H), 7.50–7.56 (m, 16H), 7.59–7.64 (m, 8H), 7.69 (d, J = 4.8 Hz, 2H), 7.76 (d, J = 5.6 Hz, 4H), 8.50(td, J = 7.6, 1.2 Hz, 4H), 8.72–8.76 (m, 6H), 8.81 (dd, J = 5.2, 1.2 Hz, 2H), 8.83–8.88 (m, 16H). ESI-MS: m/z 1127.6 (M – 3PF₆)³⁺, 810.7 (M – 4PF₆)⁴⁺, 619.8 (M – 5PF₆)⁵⁺. Found: C, 44.6; H, 2.9; N, 10.5. Anal. Calcd. for C₁₄₁H₁₀₄F₄₈N₂₈O₄P₈Ru₄: C, 44.4; H, 2.8; N, 10.3.

RESULTS AND DISCUSSION

Synthesis

The outline of the preparation of ligands L^1 and L^2 and the corresponding Ru(II) complexes $[(bpy)_8Ru_4L^1](PF_6)_8$ and $[(bpy)_8Ru_4L^2](PF_6)_8$ is presented in Scheme 1. The starting compounds 9-(4-hydroxy)phenylimino-4,5-diazafluorene, 9-(2hydroxy)phenylimino-4,5-diazafluorene, and 4,5-diazafluoren-9-oxime were prepared from 4,5-diazafluoren-9-one according to the literature procedure.^[20] Tetrapodal ligands L^1 and L^2 have been prepared by two steps, 9-(4-hydroxy)phenylimino-4,5diazafluorene and 9-(2-hydroxy)phenylimino-4,5-diazafluorene react with pentaerythrityl tetratosylate in DMF for 24 h affording compounds **1** and **2**, respectively. Compounds **1** and **2** react with 4,5-diazafluoren-9-oxime in DMF for 72 h yielding ligands L^1 and L^2 , respectively. The Ru(II) complexes were prepared by refluxing Ru(bpy)₂Cl₂·2H₂O with the appropriate ligand in 2methoxyethanol solution, and isolated as their PF₆⁻ salts. These compounds were characterized by elemental analyses, ESI-MS, and ¹H NMR spectroscopy.

Absorption Spectra

The UV-Vis absorption spectra of both complexes have been studied in CH₃CN solution, at a working concentration of 5 \times 10^{-6} mol/L. The energy maxima and absorption coefficients are summarized in Table 1, and the spectra are shown in Figure 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.^[24,25] The absorption spectra of the complexes both show three well-resolved bands. Those at *ca*. 286 and 238 nm can be assigned to intraligand π $\rightarrow \pi^*$ transitions centered on the 2,2'-bipyridine. The lowest energy band at around 443 nm is attributed to 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 two complexes contain two different kinds of ligands with different accepting properties (2,2'-bipyridine and 4,5-diazafluorene), which results in the appearance of a non-symmetrical MLCT band. The MLCT absorption maxima of both complexes are blue-shifted by about 7 nm compared with that of $Ru(bpy)_3^{2+,[26]}$ suggesting that the donor properties of ligands L^1 and L^2 are weaker than that of 2,2'-bipyridine.

Emission Spectra

Both Ru(II) complexes are non-emissive in CH₃CN solution at room temperature upon excitation into the MLCT band. The emission properties of Ru(II) polypyridyl complexes generally follow the energy gap law.^[27,28] The ³MLCT state is reasonably long-lived and is thought to be deactivated by three processes: radiative decay, kr, radiationless decay, knr, and thermal population of a higher lying excited state, $k_0 exp(-\delta E/RT)$. 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 Figure 2 originally proposed by Crosby, Meyer, and others.^[29-33] The values of δE for the Ru(II) difficult complexes containing 4,5diazafluorene are substantially lower than the corresponding value for $Ru(bpy)_3^{2+}$. These results are consistent with ligand field theory, because 4,5-diazafluorene derivatives are known to be lower than 2,2'-bipyridine in the spectrochemical series,^[34–36] 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 and they are essentially nonemissive at room temperature. However, the energy transfer is inhibited



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

	Absorption	Emission ^a		$E_{1/2}, V (\delta E_p, mV)^b$	
Complex	λ_{max} , nm (10 ⁴ ε , M ⁻¹ cm ⁻¹)	λ_{max} , nm	Φ	Oxidation	Reduction
$[(bpy)_8Ru_4(L^1)]^{8+}$	443 (7.57) 286 (32.92) 238 (19.98)	577	0.273	1.32 (63)	$-0.82(55) -0.98^{\text{irr}} -1.39(91) -1.64(106)$
$[(bpy)_8Ru_4(L^2)]^{8+}$	444 (7.21) 286 (33.71) 237 (17.50)	576	0.258	1.33 (82)	$-0.81(52) - 1.01^{\text{irr}} - 1.40(86) - 1.65(112)$

 TABLE 1

 Photophysical and electrochemical data of Ru(II) polypyridyl complexes

^aThe emission quantum yields are calculated relative to $\text{Ru}(\text{bpy})_3^{2+}$ ($\Phi_{\text{std}} = 0.376$) in EtOH-MeOH (4:1, v/v) glassy matrix at 77 K, the uncertainty in quantum yields is 15%. ^bOxidation potentials are recorded in 0.1 mol/L TBAP/CH₃CN, reduction potentials are recorded in 0.1 mol/L TBAP/DMF, and potentials are given *vs* SCE, where scan rate = 200 mV/s and δE_p is the difference between the anodic and cathodic waves.

at 77 K, so both complexes show similar emission spectra to that of $\text{Ru}(\text{bpy})_3^{2+}$ in EtOH-MeOH (4:1, v/v) glassy matrix at 77 K (Figure 3).^[34-36] The complexes (10⁻⁵ mol/L) show characteristic emission at around 577 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 both complexes have been studied in DMF and CH₃CN solutions with 0.1 mol/L TBAP as supporting electrolyte. The reduction waves of the complexes are not well behaved in CH₃CN 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 the solvent. Therefore, the oxidation potentials were recorded in CH₃CN solution, and the reduction potentials were recorded in DMF solution (Table 1).

The complex $[(bpy)_8Ru_4(L^1)]^{8+}$ exhibits a Ru(II)-centered reversible oxidation wave at 1.32 V (Figure 4). This potential is slightly more negative (by about 70 mV) than that of the parent complex $[(bpy)_2Ru(dafo)]^{2+}$ (dafo = 4,5-diazafluoren-



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 CH₃CN solution at room temperature.



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



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.



FIG. 4. Cyclic voltammetry and differential pulse voltammetry of complex $[(bpy)_8Ru_4(L^1)](PF_6)_8$ (5 × 10⁻⁴ mol/L, scan rate = 200 mV/s): (a) oxidation potential is recorded in 0.1 mol/L TBAP CH₃CN solution, (b) reduction potentials are recorded in 0.1 mol/L TBAP DMF solution.

9-one),^[34] but slightly more positive (by about 40 mV) than that of Ru(bpy)₃²⁺ (+1.28 V vs. SCE),^[37] which indicates that the ligand L¹ is a stronger π -acceptor than 2,2'-bipyridine but a weaker π -acceptor than dafo. Complex [(bpy)₈Ru₄(L¹)]⁸⁺ has four Ru(II) centers; two of one type of coordination environment, while the other two are different. The complex shows a single wave in cyclic voltammetry and a single peak without broadening in differential pulse voltammetry (Figure 4), which indicates that the small redox potential difference caused by these different coordination environments is not resolved by the electrochemical means.

Electrochemical studies of both complexes display four ligand-centered reductions. The first reversible reduction wave of complex $[(bpy)_8Ru_4(L^1)]^{8+}$ is consistent with the

addition of two electrons to the LUMO localized on 4,5diazafluoren-9-oxime fragment of ligand L¹, giving the species $[(bpy)_2Ru(bpy)_2Ru(bpy)_2Ru(bpy)_2Ru(bpy)_2]^{6+}$.^[38,39] The second irreversible reduction at around -0.98 V adds the 9-(4-hydroxy)phenylimino-4,5electrons to two diazafluorene fragment of ligand L^1 , giving complex $[(bpy)_2$ $Ru(bpy)_2RuL^{4-}Ru(bpy)_2Ru(bpy)_2]^{4+}$. The third reduction with a peak at -1.43 V and a return wave at -1.34 V is quasireversible. This reduction is located on one of the two 2,2'-bipyridine ligands on each metallic terminal, adding electrons to the 2,2'-bipyridine to give the species [(bpy^{.-})(bpy) $Ru(bpy)(bpy^{-})RuL^{4-}Ru(bpy^{-})(bpy)Ru(bpy^{-})(bpy)].$ 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 fourth reduction at -1.64 V is quasi-reversible and affords the species [(bpy⁻)(bpy⁻) $Ru(bpy^{\cdot-})(bpy^{\cdot-})RuL^{4-}Ru(bpy^{\cdot-})(bpy^{\cdot-})Ru(bpy^{\cdot-})(bpy^{\cdot-})]^{4-}$ 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-containing tetranuclear Ru(II) polypyridyl complexes incorporating two kinds of nonequivalent chelating sites have been prepared. The UV-Vis absorption and emission properties of both complexes are dominated by MLCT transitions and excited states. The emission properties of both Ru(II) complexes follow the ligand field theory, they exhibit intense emission at around 577 nm originating from the lowest energy MLCT excited state in EtOH-MeOH (4:1, v/v) glassy matrix at 77 K. Cyclic voltammetry and differential pulse voltammetry 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 . Both complexes have potential applications in the research area of electron or energy transfer.

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