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A new dinucleating bridging ligand 1,2-bis(2-(1*H*-imidazo[4,5-*f*]-[1,10]phenanthrolin-2-yl)phenoxy)ethane and its dinuclear ruthenium(II) complexes: Syntheses, characterization, luminescence, and electrochemical properties

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ABSTRACT

A new imidazo[4,5-*f*][1,10]phenanthroline-based dinucleating bridging ligand 1,2-bis(2-(1*H*-imidazo [4,5-*f*][1,10]phenanthrolin-2-yl)phenoxy)ethane (**L**) and its dinuclear Ru(II) complexes [(bpy)₂Ru(**L**)Ru (bpy)₂](ClO₄)₄ (**2**) and [(phen)₂Ru(**L**)Ru(phen)₂](ClO₄)₄ (**3**) (bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) and their characterization, photophysical, and electrochemical properties have been reported. The symmetric nature of the bridging ligand **L** enables the formation of dinuclear Ru(II) complexes **2** and **3** with equivalent metal centers. The compounds **2** and **3** exhibit the spin-allowed ¹MLCT (d_{π} - π^*) transition at 459 and 456 nm and Ru(II) metal centered emission at 616 and 600 nm, respectively, in fluid solution at room temperature. The emission profile and emission maxima are similar and independent of the excitation wavelength for each complex. The free bridging ligand is a blue emitter, while the complexes are red emitters in solution. The luminescence decay of the compounds **2** and **3** are mono-exponential and the luminescence lifetime is 174 and 141 ns, respectively. The photoluminescence quantum efficiency of the compound **2** is higher than that of [Ru(bpy)₃]²⁺. The compounds **2** and **3** undergo metal centered oxidation and the $E_{1/2}$ value for the Ru(II)/Ru(III) redox couple is 1.32 V versus Ag/Ag⁺. The study demonstrates the versatility of the imidazo[4,5-*f*][1,10]phenanthroline-based dinucleating bridging ligand in forming dinuclear Ru(II) complexes.

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1. Introduction

The design and construction of metallosupramolecular architectures have been the subject of considerable attention by many research groups over the past decade. In particular, much attention is devoted to 2,2'-bipyridine (bpy) because of its high complexing affinity with a variety of metal ions and interesting photophysical, photochemical, and electron transfer properties of its metal complexes [1]. Ru(II) complexes of polypyridine ligands [2], because of their unique combination of chemical stability, redox properties, luminescence intensity, and excited state lifetime, have been used extensively to construct supramolecular systems [3] to study photoinduced energy- and electron transfer processes and as photosensitizers in a variety of intermolecular electron transfer processes [4].

Since the luminescence and redox behavior of Ru(II) complexes are strongly ligand-dependent, considerable research interest has been dedicated to fine-tune these properties by changing the commonly employed polypyridyl ligands [3b-d,5]. Because of the convenient features of pyridine as a coordinating molecule, its higher oligomers have been used in the construction of bridging ligands and polynuclear supramolecular assemblies [3b,6]. The shape, size, and functions of polynuclear complexes depend to a large extent on the nature of the bridging ligands which connect the metal centers. The crucial role played by bridging ligands in determining the ground state metal-metal interaction is well recognized [7]. Polynuclear complexes employing imidazole [8] and pyrazine [9] containing bridging ligands are attracting considerable attention. In particular, the introduction of imidazolyl [8c,10] or triazolyl [11] rings in the backbone of bridging ligands has led to a number of polypyridine analogs in which the multidentate character of the *N*-heterocycles allowed the modulation of the spectroscopic and redox properties of the resulting polynuclear Ru(II) complexes [10a,b,12]. Incorporation of the imidazolyl moiety into a chelating ligand does not affect the coordinating ability of the latter and complexes of such ligands have been found to feature new optical properties [13]. So far only a few imidazo[4,5-f][1,10] phenanthroline-based dinucleating bridging ligands and their Ru(II) complexes have been reported. We have designed a new



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Chart 1. The compounds [(bpy)₂Ru(L)Ru(bpy)₂](ClO₄)₄ (2) and [(phen)₂Ru(L)Ru(phen)₂](ClO₄)₄ (3) containing dinuclear Ru(II) complexes.

imidazo[4,5-*f*][1,10]phenanthroline-based dinucleating bridging ligand by incorporating imidazolyl moieties in the ligand backbone (Chart 1) and we report herein the syntheses of 1,2-bis(2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxy)ethane (**L**) and its dinuclear Ru(II) complexes with 2,2'-bipyridine or 1,10-phenanthroline as ancillary ligands and their photophysical and electrochemical properties.

2. Experimental

2.1. Materials

Acetic acid, ammonium acetate, aqueous ammonia (25%), nitric acid, 1,10-phenanthroline monohydrate, potassium bromide, sodium hydrogencarbonate, sodium hydroxide, and sulfuric acid (Merck); 2,2'-bipyridyl, ruthenium(III) chloride trihydrate, and sodium perchlorate (Aldrich); 1,2-dibromoethane, lithium chloride, and salicylaldehyde (Fluka); and silica gel (TLC, 100-120 mesh, ACME) were used as received. Acetonitrile, dichloromethane, and diethyl ether were purified by the standard procedures [14]. 1,10-Phenanthroline-5,6-dione [15], [Ru(bpy)₂Cl₂]·2H₂O [16], and [Ru(phen)₂Cl₂]·2H₂O [16] were synthesized by the literature methods.

2.2. Physical measurements

CHN microanalyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Elemental Analyzer interfaced with a Perkin-Elmer AD 6 Autobalance. Helium was used as the carrier gas. Infrared spectra were recorded on a Perkin–Elmer Spectrum RX-I FT IR spectrometer in the range 4000–400 cm⁻¹ using KBr pellets. NMR spectra were recorded on a Bruker AVANCE III 500 MHz (AV 500) multinuclear NMR spectrometer working at 500 MHz at 25 °C. Standard 5 mm probe was used for the ¹H and ¹³C NMR measurements. The electrospray ionization mass spectra (ESI MS) were performed using a Micromass Quattro-II Triple Quadrupole mass spectrometer. 2,5-Dihydroxybenzoic acid or α -cyano-4-hydroxycinnamic acid, dissolved in chloroform and acetonitrile/methanol, was used as the matrix.

The electronic absorption spectra were recorded on a Shimadzu UV-2450 UV-Visible spectrophotometer controlled by the UV Probe version-2.33 software. The spectra were recorded in the region 190–900 nm in acetonitrile at 25 °C using a matched pair of Teflon stoppered guartz cell of path length 1 cm. Fluorescence spectra were recorded on a Fluorolog-3 FL3-221 spectrofluorometer. The excitation source was a 450 W CW Xenon lamp. The band pass for the excitation and double-grating emission monochromator was set at 2 nm. A matched pair of quartz cell of path length 10 mm was used. The emission spectra of the complexes were recorded in oxygen free acetonitrile at room temperature. Emission quantum yields ($\Phi_{\rm em}$) were calculated by comparing the wavelength-integrated fluorescence intensities of the samples to that of the standard fluorescent complex $[Ru(bpy)_3]^{2+}$, which has a quantum yield of 0.062 [17] in acetonitrile using Eq. (1) [18].

$$\Phi_{\text{sample}} = \{ \text{OD}_{\text{standard}} \times A_{\text{sample}} \times \eta_{\text{sample}}^2 \} / \{ \text{OD}_{\text{sample}} \times A_{\text{standard}} \\ \times \eta_{\text{standard}}^2 \} \times \Phi_{\text{standard}}$$
(1)

where, OD is optical density of the compound at the excitation wavelength (455 nm), *A* is the area under the emission spectral curve and η is the refractive index. The emission lifetimes were recorded on a Spectra-Physics LAB-150 laser flash photolysis spectrometer. The samples were irradiated using the third harmonic pulses of the Nd³⁺:YAG laser (Quanta-Ray) and 8 ns pulse width was used to excite the sample. The beam emerging through the sample was focused onto a Czerny-Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infiniium digital storage oscilloscope interfaced to a computer.

Cyclic voltammetry was performed on a EG&G PAR 273A Potentiostat/Galvanostat using RDE0018 Analytical Cell Kit consisting of a thermostated cell bottom, EG&G G0229 glassy carbon disk milli-electrode, platinum counter electrode, and EG&G K0265 Ag/ Ag⁺ reference electrode. The auxiliary electrode was connected to the test solution through the counter electrode bridge tube. The reference electrode was separated from the test solution through the bridge tube containing AgCI-KCI filling solution. The cyclic voltammograms were recorded using 10⁻³ M solution of the comoxygen free acetonitrile containing plexes in 01M tetraethylammonium perchlorate as the supporting electrolyte. Oxygen free argon, saturated with the solvent vapor, was flushed through each sample solution through the purge tube assembly for 30 min before voltammetry was performed and all measurements were carried out in an atmosphere of argon at 25 °C. All operations were performed through a computer using EG&G Model 270 Software and all electrochemical parameters were obtained using the EG&G PowerSuite software. The instrument was calibrated by recording the cyclic voltammograms of ferrocene (purum. Fluka) in oxygen free acetonitrile under the same experimental conditions.

2.3. Synthesis of ligand

2.3.1. Stage-1: 1,4-Bis(2'-formylphenyl)-1,4-dioxabutane (1)

The dial 1 was synthesized by modifying the procedure reported by Armstrong et al. [19]. To a solution of salicylaldehyde (20.80 mL, 200 mmol) in ethanol (40 mL) was added a solution of sodium hydroxide (8 g, 200 mmol) in water (400 mL), warmed, and 1,2-dibromoethane (8.60 mL, 100 mmol) was added followed by ethanol (400 mL) to get a homogeneous solution. The solution was refluxed under nitrogen atmosphere for 100 h, cooled to 0 °C, and the colorless needles that separated out was filtered, washed with water, and recrystallized in ether-chloroform (1:1 v/v), (16.34 g, 61%). Anal. Calc. for C₁₆H₁₄O₄: C, 71.10; H, 5.22. Found: C, 71.02; H, 5.15%. IR (cm⁻¹, KBr): 3076 v_s(C-H), 1248 v_{as}(C-O-C), 753 δ(C-H) (aromatic), 2922 v_{as}(C-H), 2866 v_s(C-H) (aliphatic), 1652 v_s(C=O), 1597, 1484, and 1452 v_s(C=C) (aromatic), 944 ω (CH₂), 860 τ (CH₂), 834 ρ (CH₂) (methylene). $\delta_{\rm H}(500 \text{ MHz}; \text{ CDCl}_3; 298 \text{ K}) 4.54 \text{ (s, 4H, -O-CH}_2\text{-}), 7.07 \text{ (d, 2H, })$ I = 8.5 Hz, Ph-H), 7.09 (t, 2H, I = 8.5 Hz, Ph-H), 7.59 (t, 2H, *I* = 7.75 Hz, Ph-*H*), 7.86 (d, 2H, *I* = 7.5 Hz, Ph-*H*), 10.45 (s, 2H, -CHO). δ_C(125 MHz; CDCl₃; 298 K) 67.0, 112.8, 121.4, 125.2, 128.6, 135.9, 160.7, 189.3. FAB MS: m/z 271 $[M+H]^+$, 149 $[M-(C_7H_5O_2)]^+$, 136 $[M - (C_8 H_6 O_2)]^+$, 121 $[M - (C_{10} H_{10} O_2)]^+$.

2.3.2. Stage-2: 1,2-Bis(2-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenoxy)ethane (L)

To a solution of 1,10-phenanthroline-5,6-dione (0.42 g, 2 mmol) and ammonium acetate (3.08 g, 40 mmol) in hot glacial acetic acid (10 mL) was added a solution of 1,4-bis(2'-formylphenyl)-1,4dioxabutane (1) (0.27 g, 1 mmol) in glacial acetic acid (10 mL) dropwise over a period of 30 min with stirring in argon atmosphere, refluxed for 5 h, cooled to room temperature, and poured in water (200 mL). Aqueous ammonia (25%) was added dropwise with stirring whereupon a pale yellow precipitate separated out. The product was filtered, washed with large portions of water, and dried in vacuo (0.37 g, 57%). Anal. Calc. for $C_{40}H_{26}N_8O_2$: C, 73.83; H, 4.03; N, 17.22. Found: C, 73.79; H, 3.92; N, 17.14%. IR (cm⁻¹, KBr): 3394 v(N-H), 2936 v_{as}(C-H), 1598 v(C=N), 1454 v_s(C=C), 1237 v_{as}(C-O-C), 1062 v_s(C-O-C), 804 v_s(C-H) (pyridine), 743 (β-ring) (pyridine), 663 v(C-C). δ_H(500 MHz; DMSO-d₆; 298 K) 4.68 (s, 4H, $-O-CH_2-$), 6.77 (t, 2H, J = 7.5 Hz, H_f), 7.14 (d, 2H, $I = 7.75 \text{ Hz}, H_h$, 7.22–7.27 (m, 2H, H_g), 7.44 (d, 4H, $I = 8.5 \text{ Hz}, H_h$), 7.60 (t, 2H, J = 7.5 Hz, H_e), 8.19 (d, 4H, J = 7.5 Hz, H_c), 9.12 (s, 4H, H_a , 14.03 (s, 2H, -NH). ESI MS: m/z 689 [M+K]⁺, 651 [M]⁺.

2.4. Synthesis of heteroleptic ruthenium(II) complexes

Caution: Perchlorate salts are potentially explosive and, therefore, should be handled in small quantities with care!

2.4.1. $[(bpy)_2Ru(L)Ru(bpy)_2](ClO_4)_4$ (2)

A solution of [Ru(bpy)₂Cl₂]·2H₂O (1.09 g, 2.10 mmol) and 1,2bis(2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxy)ethane (L) (0.68 g, 1.05 mmol) in ethylene glycol (20 mL) was refluxed for 6 h under argon atmosphere. The solution was cooled to room temperature, water (40 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate dropwise with stirring whereupon a reddish orange solid separated out. The product was filtered, dried in air, and recrystallized in hot acetonitrilewater (1:1 v/v), (1.56 g, 79%). Anal. Calc. for C₈₀H₅₈Cl₄N₁₆O₁₈Ru₂: C, 51.24; H, 3.12; N, 11.95. Found: C, 51.20; H, 3.11; N, 11.92%. IR (cm⁻¹, KBr): 3394 v(N–H), 1601 v(C=N), 1446 v(C–N) (pyridine), 1243 v_{as}(C-O-C), 1087 v(ClO₄), 766 v_s(C-H) (pyridine), 625 v(C-C). δ_H(500 MHz; DMSO-d₆; 298 K) 4.51 (s, 4H, -CH₂-), 7.09-7.13 $(m, 4H, H_h, H_f)$, 7.36 $(t, 4H, I = 6.75 \text{ Hz}, H'_2)$, 7.43 $(t, 2H, I = 7.5 \text{ Hz}, H'_2)$ $H_{\rm g}$), 7.61 (t, 4H, I = 6.5 Hz, H_2) 7.64 (d, 4H, I = 5.5 Hz, H_1), 7.87 (d, 4H, I = 5.5 Hz, H_1), 7.94 (t, 4H, I = 6.5 Hz, H_b), 8.10–8.13 (m, 6H, H_e , H'_3), 8.20–8.24 (m, 8H, H_a , H_3), 8.84 (d, 4H, J = 8 Hz, H'_4), 8.88 (d, 4H, J = 8 Hz, H_4), 9.14 (d, 4H, J = 7 Hz, H_c). ESI MS: m/z 838 $[M-2ClO_4]^{2+}$, 788 $[M-3ClO_4]^{2+}$, 738 $[M-4ClO_4]^{2+}$, 493 $[M-4ClO_4]^{3+}$, 459 $[(M-C_{59}H_{40}Cl_4N_{12}O_{16}Ru)]^+$, 370 $[M-4ClO_4]^{4+}$, $362 [(M-C_{41}H_{31}Cl_4N_8O_{17}Ru)]^{2+}, 237 [(M-C_{67}H_{49}Cl_4N_{12}O_{17}Ru_2)]^{+}.$

2.4.2. $[(phen)_2 Ru(L) Ru(phen)_2](ClO_4)_4$ (3)

A solution of [Ru(phen)₂Cl₂]·2H₂O (1.19 g, 2.10 mmol) and 1,2bis(2-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenoxy)ethane (L) (0.68 g, 1.05 mmol) in ethylene glycol (20 mL) was refluxed for 6 h under argon atmosphere. The solution was cooled to room temperature, water (40 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate dropwise with stirring whereupon a reddish orange solid separated out. The product was filtered, dried in air, and recrystallized in hot acetonitrilewater (1:1 v/v), (1.55 g, 75%). Anal. Calc. for C₈₈H₅₈Cl₄N₁₆O₁₈Ru₂: C, 53.61; H, 2.97; N, 11.37. Found: C, 53.50; H, 2.89; N, 11.28%. IR (cm⁻¹, KBr): 3431 v(N–H), 1627 v(C=N), 1423 v_s(C–H) (pyridine), 1246 v_{as}(C-O-C) 1086 v(ClO₄), 722 (β-ring) (pyridine), 626 v(C-C). $\delta_{\rm H}(500 \text{ MHz}; \text{ DMSO-}d_6; 298 \text{ K}) 4.55 \text{ (s, 4H, -CH}_2\text{-}), 7.13 \text{ (d, })$ 4H, J = 5 Hz, H_h , H_f), 7.45 (t, 2H, J = 8 Hz, H_g), 7.73–7.76 (m, 8H, H_2 , H_7), 7.79–7.81 (m, 4H, H_b), 8.02 (d, 4H, J = 5 Hz, H_1), 8.06 (d, 4H, J = 5 Hz, H_8), 8.12 (d, 2H, J = 5 Hz, H_e), 8.21 (d, 4H, J = 8 Hz, H_a), 8.36 (s, 8H, H_4 , H_5), 8.74 (d, 8H, J = 7.5 Hz, H_3 , H_6), 9.13 (d, 4H, J = 5 Hz, H_c). ESI MS: m/z 1872 $[M-ClO_4]^+$, 886 $[M-2ClO_4]^{2+}$, 836 [M-3ClO₄]²⁺, 558 [M-3ClO₄]³⁺, 525 [M-4ClO₄]³⁺, 484 $[M - (C_{62}H_{43}Cl_4N_{12}O_{18}Ru)]^+$, 394 $[M - 4ClO_4 + H]^{4+}$.

3. Results and discussion

3.1. Synthesis of the bridging ligand

The dial derivative **1** is synthesized by modifying the procedure reported by Armstrong et al. [19] by the O-alkylation of salicylalde-hyde (2 equiv) with 1,2-dibromoethane (1 equiv) (Williamson's synthesis) in the presence of sodium hydroxide (2 equiv) in water–ethanol as colorless needles. The bridging ligand 1,2-bis(2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxy)ethane (**L**) is synthesized on the basis of the imidazole ring preparation established by Steck et al. [20] by a two-step reaction involving the formation of a quinone–diimine intermediate by the reaction of 1,10-phenanthroline-5,6-dione with ammonium acetate followed by an aldol-type condensation of the intermediate with **1** in acetic acid.



Scheme 1. Synthetic routes for the preparation of the bridging ligand (L).

The reaction involving the synthesis of the dinucleating ligand **L** is depicted in Scheme 1. The ligand **L** is a polyaromatic bridging ligand containing two equivalent chelating sites of phenanthroline ring. In the ligand **L**, the two imidazo[4,5-*f*][1,10]phenanthroline moieties are bridged by a flexible ethoxyphenyl spacer moiety. It is characterized by IR, ESI MS, ¹H NMR and elemental analysis and is hardly soluble in common organic solvents, but partly soluble in DMF and DMSO.

3.2. Synthesis of complexes

The heteroleptic dinuclear compounds $[(bpy)_2Ru(L)Ru(bpy)_2](-ClO_4)_4$ (**2**) and $[(phen)_2Ru(L)Ru(phen)_2](ClO_4)_4$ (**3**) are prepared by the reaction of the preformed dinucleating imidazo[4,5f][1,10]phenanthroline-based bridging ligand **L** with [Ru(b $py)_2Cl_2]\cdot 2H_2O$ and $[Ru(phen)_2Cl_2]\cdot 2H_2O$ in ethylene glycol. The compounds are isolated as perchlorate salts and stable in air and in solution. In the ESI-MS of the compound **2**, the peaks at m/z838, 788, and 370 are due to the species $[M-2ClO_4]^{2+}$, $[M-3ClO_4]^{2+}$, and $[M-4ClO_4]^{4+}$ formed by the loss of two-, three-, and four perchlorate ions, respectively, from the molecular ion. In the ESI-MS of the compound **3**, the peaks at m/z 1872, 886, 558, and 525 are due to the species $[M-ClO_4]^+$, $[M-2ClO_4]^{2+}$, $[M-3ClO_4]^{3+}$, and $[M-4ClO_4]^{3+}$ formed by the loss of one-, two-, three-, and four perchlorate ions, respectively, from the molecular ion.

3.3. NMR spectra of the ligand and complexes

The ¹H NMR spectral data of the ligand and complexes are presented in Table 1. In the ¹H NMR spectrum of **L**, the resonances at 9.12, 8.19, and 7.44 ppm are assigned to the H_a, H_c, and H_b protons, respectively, of the phenanthroline ring. The resonances at 7.60, 7.24, 7.14, and 6.77 ppm are assigned to the H_e, H_g, H_h, and H_f protons, respectively, of the phenyl spacer. The H_i (methylene) protons of the linker moiety resonate at 4.68 ppm.

On coordination to the metal ion, the chemical shift of the ligand protons in the compounds **2** and **3** are shifted when compared to that of the free ligand. The H_a protons of the imidazo[4,5-*f*][1,10]phenanthroline moiety in the compounds **2** and **3** encounter upfield shift, while the H_b and H_c protons experience downfield shift. The dramatic upfield shift of the H_a proton

Table 1							
The ¹ H NMF	spectral	data	of the	ligand	and	complex	es

may be due to the effect of the ring current of the bpy and phen ancillary ligands. The H_e, H_f, and H_g protons of the phenyl spacer encounter downfield shift, while the H_h protons do not show significant shift. The NH proton resonance of the ligand is not observed in the complexes because of the fast exchange between the nitrogens of the imidazole ring, characteristic of an active proton. In the compound **2**, the two pyridine rings of each bpy are not chemically and magnetically equivalent due to the shielding influence of the adjacent coordinated bpy and the imidazo[4,5*f*][1,10]phenanthroline moiety of the bridging ligand leading to eight signals for the bpy protons: four signals $(H'_1 - H'_4)$ for the pyridine ring adjacent to the imidazo[4,5-*f*][1,10]phenanthroline and the other four signals (H_1-H_4) for the pyridine ring adjacent to the coordinated bpy. The protons of the pyridine rings of the coordinated bpy ligands are highly deshielded compared to that of the pyridine rings of the ligand framework and hence the chemical shifts for the former proton is higher than that of the latter. Such a behavior has been reported for the Ru(II) polypyridine complexes containing imidazo[4,5-*f*][1,10]phenanthroline [21]. The ¹H NMR spectra of the compounds 2 and 3 are presented in Fig. 1.

3.4. Electronic absorption spectra

The electronic absorption spectral data of the dinuclear Ru(II) complexes are presented in Table 2. The compounds 2 and 3 exhibit intense absorption bands at 200-300 nm assignable to the spinallowed ligand centered (¹LC) $\pi - \pi^*$ transition of the ligand framework and a broad band at 459 ($\varepsilon/dm^3 mol^{-1} cm^{-1}$ 20,322) and 456 nm (25,443), respectively, assignable to the spin-allowed ¹MLCT ($d_{\pi}-\pi^*$) transition [22]. The MLCT band of the compound 2 with bpy as ancillary ligands and that of the compound 3 with phen as ancillary ligands are bathochromically shifted with respect to that of $[Ru(bpy)_3]^{2+}$ ($\lambda_{max} = 451 \text{ nm}$) and $[Ru(phen)_3]^{2+}$ $(\lambda_{\text{max}} = 446 \text{ nm})$ which can be attributed to the extended structural framework of the bridging ligand [23]. However, the MLCT band of the complexes are not significantly shifted compared to that of the mononuclear counterpart $[Ru(bpy)_2(PIP)]^{2+}$ (PIP = 2-phenyl-imidazo[4,5-f][1,10]phenanthroline) [24]. The Ru(II) complexes are bright red in solution and in the solid state due to the strong ¹MLCT absorption band at 456-459 nm. The electronic absorption spectra of the compounds 2 and 3 are presented in Fig. 2.

Compound entry no.	Chemical shift (ppm)								
	H _a	H _b	H _c	H _d	He	H_f	H_g	H_h	H _i
L	9.12	7.44	8.19	14.03	7.60	6.77	7.24	7.14	4.68
2	8.22	7.94	9.14	-	8.12	7.11	7.43	7.11	4.51
3	8.21	7.80	9.13	-	8.12	7.13	7.45	7.13	4.55

^a Data obtained from 500 MHz ¹H NMR spectra recorded in DMSO-d₆ at 298 K.



Fig. 1. 500 MHz ¹H NMR spectra of [(bpy)₂Ru(L)Ru(bpy)₂](ClO₄)₄ (2) (a) and [(phen)₂Ru(L)Ru(phen)₂](ClO₄)₄ (3) (b) in DMSO-d₆ at 298 K (resonances in the aromatic region only are shown).

7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 PRM

8.0. 7.9

Table 2

Photophysical and electrochemical data of the complexes.^a

9.2 9.1 9.0 8.9

Complex	Absorption λ_{max} (nm) ($\epsilon \times 10^4$, Lmol ⁻¹ cm ⁻¹)	Excitation λ _{ex} (nm)	Emission λ _{em} (nm)	${\Phi_{ m em}}^{ m b}$	τ ^c (ns)	$k_r^{d} 10^4$ (s ⁻¹)	$k_{nr}^{e} 10^{5}$ (s ⁻¹)	$E_{1/2}^{f}(V)$	
								Metal centered oxidation	Ligand centered reductions
$[(bpy)_2Ru(L)Ru(bpy)_2](ClO_4)_4$ (2)	243 (4.0)	272	616	0.0845	174	49	53	1.32	-0.55, -1.37,
	254 (3.7)	299							-1.58
	285 (10.3)	460							
	459 (2.0)								
$[(phen)_2Ru(L)Ru(phen)_2](ClO_4)_4 (3)$	200 (12.0)	279	600	0.0612	141	43	67	1.32	-0.56, -1.41,
	222 (11.4)	457							-1.72
	264 (13.4)								
	456 (2.5)								
[Ru(bpy) ₂ (PIP)](ClO ₄) ₂ ^g	244 (3.6)		615					1.28	-0.85, -1.43,
	253 (3.5)								-1.63
	283 (10.0)								
	458 (1.8)								

Absorption and emission spectra were recorded using 1.5×10^{-5} M solution of the complexes in acetonitrile at 298 K. а

8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1

b Relative quantum yield calculated by the method given under experimental section using $[Ru(bpy)_3]^{2+}$ as the standard.

с The emission decays were calculated as single exponential (λ_{exc} = 355 nm).

^d $k_r = \Phi_{\rm em}/\tau$. ^e $k_{nr} = 1/\tau - k_r$.

 $^{\rm f}$ The data are computed from the cyclic voltammograms recorded on a glassy carbon millielectrode in acetonitrile (10⁻³ M) using tetraethylammonium perchlorate as the supporting electrolyte (0.1 M) at 298 K at the scan rate of 50 mVs⁻¹. Potentials are reported in volts versus Ag/Ag⁺.

^g From Ref. [24].



Fig. 2. Electronic absorption spectra of $[(bpy)_2Ru(L)Ru(bpy)_2](ClO_4)_4$ (2) (a) and $[(phen)_2Ru(L)Ru(phen)_2](ClO_4)_4$ (3) (b) in acetonitrile at room temperature.

3.5. Luminescence spectra

The emission spectral data (wavelength of excitation and emission), luminescence quantum yield, emission lifetime, and radiative and nonradiative decay rates are presented in Table 2. All measurements are made with solutions deoxygenated by purging argon. The excitation spectra of the compounds are monitored at the emission maxima of each compound at room temperature. The excitation spectrum of the free ligand **L** contains bands at 286, 302, and 343 nm. The free ligand emits at 426 nm upon excitation onto the excitation maxima. This fluorescence band of the ligand is no longer observed in its metal complexes. The excitation spectrum of $[(bpy)_2Ru(L)Ru(bpy)_2](CIO_4)_4$ (2) contains two intense bands at 272 and 299 nm and a weak band at 460 nm, while the excitation spectrum of $[(phen)_2Ru(L)Ru(phen)_2](CIO_4)_4$ (3) contains an intense band at 279 nm and a weak band at 457 nm. The compounds 2 and 3 upon excitation onto their excitation maxima

exhibit an emission band at 616 and 600 nm, respectively. The emission profile and emission maxima are similar and independent of the excitation wavelength. The free bridging ligand is a blue emitter, while the complexes are red emitters in solution. The emission maxima of the compound **2** ($\lambda_{em} = 616$ nm) containing bpy ancillary ligands is not significantly shifted compared to that of [Ru(bpy)₂(PIP)]²⁺ ($\lambda_{em} = 615$ nm).

The luminescence bands of the compounds **2** and **3** are quite similar in shape to the luminescence bands of their mononuclear counterpart [Ru(bpy)₂(PIP)]²⁺. Thus, the photophysical properties of the heteroleptic compounds **2** and **3** with bpy and phen as ancillary ligands are not significantly different from that of the mononuclear complex [Ru(bpy)₂(PIP)]²⁺. The emission of the Ru(II) centers in the complexes is, therefore, assigned to the ³MLCT state involving the bridging ligand as the acceptor site and the emitting MLCT state of the acceptor ligand does not extend over to the flexible spacer of the bridging ligand [25], but it may involve only the phenyl group directly connected to the imidazo[4,5-f][1,10]phenanthroline moiety. The photoluminescence quantum efficiency of the compound **2** is higher than that of $[Ru(bpy)_3]^{2+}$ which can be attributed to the higher energy of the emission maxima of the former as expected from the energy gap law [4b]. The luminescence decay of the compounds 2 and 3 are monoexponential and the luminescence lifetime is 174 and 141 ns. respectively. The emission and the excitation spectra of the compounds 2 and 3 are depicted in Fig. 3.

3.6. Electrochemistry of complexes

The redox behavior of the complexes has been investigated in acetonitrile solution to complement the spectroscopic data. The investigation of electrochemical behavior is very useful to determine the extent of electronic interaction between the metal centers. The cyclic voltammetric data of the complexes are presented in Table 2. In the present study only one oxidation process is observed for the compounds **2** and **3** and the $E_{1/2}$ values for the Ru(II)/Ru(III) redox couple is 1.32 V versus Ag/Ag⁺ which is anodically shifted with respect to that of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ ($E_{1/2} = 1.27$ V versus Ag/Ag⁺) [23]. From the separation between the anodic and cathodic peak potential of *ca*. 63 mV, it is apparent that the oxidation process



Fig. 3. Emission spectra of [(bpy)₂Ru(L)Ru(bpy)₂](ClO₄)₄ (2) (a) and [(phen)₂Ru(L)Ru(phen)₂](ClO₄)₄ (3) (b) in acetonitrile at room temperature, inset: excitation spectra of 2 (a) and 3 (b).

involves two electrons for each one of the dinuclear complexes, which are attributed to two simultaneous independent one-electron metal-centered processes. This indicates that the electrostatic interaction between the metal centers is negligible due to the large distance of separation of the Ru(II) centers. The occurrence of a single oxidation wave for these complexes confirms that each metal-centered subunit is electronically "isolated" from the electrochemical viewpoint. Oxidation of these complexes stabilizes the metal d_{π} orbital directly and the ligand π^* -orbital indirectly through charge interactions. Subsequent d_{π} - π^* back bonding further stabilizes the metal d_{π} -orbital but destabilizes the ligand π^* -orbital [26] and hence the oxidation response of the dinuclear complexes shifts positively by *ca*. 40 mV compared to that of the mononuclear complex [Ru(bpy)₂(PIP)]²⁺. On reduction, several ill-behaved processes take place and adsorption of the compounds on the electrode surface also occurs. However, the first reduction potential is still safely measured which is assigned to the reduction of the bridging ligand although more precise assignment could not be made. The first reduction, usually expected to involve the ligand having the most stable lowest unoccupied molecular orbital (LUMO) [26,27], obviously L here, appears irreversible and the other two successive reductions are characteristic of the bpy/phen ligands [4b,27b-f,28]. It is concluded that reduction of the complexes occur first on the bridging ligand and then on the bpy/phen ligands.

4. Conclusions

A new imidazo[4,5-f][1,10]phenanthroline-based dinucleating bridging ligand 1,2-bis(2-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenoxy)ethane and its dinuclear Ru(II) polypyridine complexes have been synthesized and characterized by NMR techniques. The bridging ligand readily form dinuclear Ru(II) complexes and its symmetric nature ensures the formation of dinuclear complexes with equivalent metal centers. The methodology developed in the present work can be exploited to synthesize similar dinuclear heteroleptic polypyridine complexes with a variety of ancillary ligands. Absorption spectra and luminescent properties have been studied and these properties of the Ru(II) species are dominated by MLCT transitions and excited states. The results also show that each metal-based subunit retains its own spectroscopic properties in the dinuclear arrays. The synthetic strategy reported in the present work could be exploited to develop new bridging ligands with multiple imidazo[4,5-f][1,10]phenanthroline coordinating moieties by the reaction of polvaldehyde functionalized molecules with 1,10-phenanthroline-5,6-dione. Such ligands would enable the synthesis of polynuclear complexes of higher nuclearity and supramolecular assemblies. The heteroleptic dinuclear Ru(II) complexes could be used to construct polynuclear complexes by using the modular synthetic approach in coordination compounds by exploiting the coordinating ability of the imidazole nitrogen donors of imidazo[4,5-*f*][1,10]phenanthroline.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.014.

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