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ORIGINAL PAPER

Ruthenium (II) Complexes of Mono-, Di- and Tripodal Polypyridine Ligands: Synthesis, Characterization, and Spectroscopic Studies

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Abstract Mono-, di- and tripodal polypyridine ligands 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L1), 2-(4-(2-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzyloxy)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L2), 2-(4-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzyl oxy)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L3), 2-(4-(4,6-bis(4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)-1,3,5-triazine-2-yloxy)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L4), and their Ru (II) complexes have been synthesized and characterized. All the ligands (L1-L4) gave the emissions at three shoulder at 278 nm, 315 nm, and 328 nm and the complexes (C1-C4) exhibit Ru (II) metal centered emission at 265 nm, 288 nm and 328 nm in acetonitrile solution at room temperature. Maximum d-π* transition seen at 462 nm for all the complexes.

Keywords Dipodal ligand · Tripodal ligand · Ru(II) complex · Polypyridine

Introduction

1,10-Phenanthroline (phen) is a classic chelating bidentate ligand for transition metal ions with a rigid, planar, hydrophobic, and electron-poor π-conjugated system. Taking advantage of these structural features, metal complexes with phen-based ligands have been actively studied for their catalytic, redox, photochemical, and photophysical properties [1–5]. They have very important applications to molecule/ion recognition and sensing [6], DNA binding/cleavage, molecular self-assembling, etc. Polypyridine complexes are coordination complexes containing polypyridine ligands, such as 2,2′-bipyridine, 1,10-phenanthroline, or 2,2′;6′2″-terpyridine. They are multidentate ligands that give characteristic properties to the metal complexes that they form [7–9].

Herein we have reported the synthesis of imidazole containing mono-, di- and tripodal polypyridine ligands and their Ru (II) complexes. Imidazole-containing ligands are poor π-acceptors and good π-donors, and have the appreciable ability to control orbital energies by proton transfer compared with pyridine-containing ligands. Ru (II) polypyridine complexes have been the focus of considerable attention over the last few decades [10]. They have been widely used as DNA, cation, and anion sensors, because their outstanding photophysical and electrochemical properties are quite sensitive. Considering the spectroscopic properties of Ru (II) polypyridyl complexes are strongly dependent on the size, shape, and electronic nature of the bridging ligand [11].

There is nowadays much interest in the design of photoinduced energy and electron transfer systems due to their potential applications in fields as diverse as artificial photosynthesis, photocatalysis, molecular informatics and so on [12]. Ru(II) polypyridyl complexes are excellent building blocks for the construction of such devices because of their outstanding redox and spectroscopic properties [13]. In most cases, tuning the electronic properties of the bridging ligand can induce desirable changes in the redox and spectroscopic properties of Ru(II) polypyridyl complexes through ligand-field

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effects [14]. Thus, design of novel bridging ligand is one of the key factors in realizing molecular electronic devices.

In this paper, we have reported three polypyridine ligands derived from 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol L1 compound and their Ru(II) bridging complexes. These complexes can exhibit some changes due to the difference in the structure of ligands L1–L4. L1 ligand were prepared by the reaction of 1,10-phenanthroline-5,6-dione, ammonium acetate and 4-hydroxybenzaldehyde in hot glacial acetic acid medium. Then other L2, L3 and L4 ligands were prepared by the reaction of L1 imidazo-containing phenanthroline molecule and three different halogene-containing molecules. And the synthesis of mono-, di- and tripodal polypyridine ligands were completed. And their bridging Ru (II) complexes were synthesized by using $Ru(phen)_2Cl_2.2H_2O$ complex.

Experimental

Apparatus

All starting materials and reagents used were purchased from Alfa Aesar, Sigma Aldrich, Merck and used without further purification. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli Q Plus water purification system.^{1}H-NMR spectra were taken using a Varian 400-MHz Spectrometer. FT-IR spectra were recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Melting points were determined by Büchi Melting Point B-540 instrument. Elemental analyses were carried out using a LECO-CHNS- 932 elementel analyser. UV–vis spectra were recorded on Perkin Elmer Lambda 25 UV–Vis Spectrometer. The emission measurements were performed using a Perkin Elmer LS 55 Luminescence Spectrometer. Thinlayerchromatography (TLC) was performed using silica gel on glass TLC plates (silicagel H, type60,Merck).

Method

1,10-Phenanthroline-5,6-dione [15], 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol [16] and $[Ru(phen)_2Cl_2]\cdot 2H_2O$ [17] were synthesized by the literature methods. Other materials were commercially available and of reagent grade. All of them were used without purification.

Synthesis

1,10-Phenantroline-5,6-dione

Phenanthroline (0.54 g, 3 mmol) was added into a solution of 60 % sulfuric acid (7 mL). After the solid compound was dissolved, potassium bromate (0.55 g, 3.3 mmol) was added in batches over a period of half an hour. The mixture was stirred at room temperature for 20 h. Then, the mixture was poured over ice and was carefully neutralized to pH:7 using a saturated solution of sodium hydroxide. The solution was then filtered, extracted with dichloromethane and evaporated to dryness. The crude product was recrystallized from methanol to provide the desired product in 85–90 % [15]. FT-IR: 1683 (C=O), 1573, 1557, 1455, 1412, 1290, 1202, 1112, 922, 813, 736. ^{1}H NMR ($CDCl_3$): δ=7.62 (d, 2H), 8.53 (dd, 2H), 7.40 (dd,2H), 9.15 (dd,2H).

4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol, L1

1,10-Phenanthroline-5,6-dione (0.1 g, 0.46 mmol) and ammonium acetate (0.58 g, 13.3 mmol) were dissolved in 10 mL of hot glacial acetic acid. While the mixture was stirred, a solution of 4-hydroxybenzaldehyde (0.056 g, 0.46 mmol) in 10 mL of glacial acetic acid was added dropwise to the mixture. The mixture was heated at 90 °C for 3 h and was then poured in 200 mL of water. The solution was neutralized with ammonia to pH:7 and was then cooled to room temperature. The precipitate was filtered off and washed with large portions of water. The product was dried for 48 h in vacuo at 50 °C [16]. FT-IR: 3392 (O-H), 3165 (N-H), 2998 (CH_2), 1659 (C=N), 1230 (C-O-C), 736 (CH, pyridine). ^{1}H NMR ($CDCl_3$): δ= 6.95-7.13 (d, 2H), 7.77-7.88 (m, 2H), 8.08-8.15 (d, 2H), 8.86-8.93 (dd, 2H), 8.97-9.03 (dd, 2H), 10 (OH), 13.5 (s, 1H).

2-(4-(2-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl) phenoxy)methyl)benzyloxy)phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline, L2

To a solution of 1,2-Bis(bromomethyl)benzol (0.042 g, 0.16 mmol) in dry DMF (30 mL) was added potassium carbonate (0.08 g, 0.57 mmol) and 4-(1H-imidazo[4,5-f][1, 10]phenanthroline-2-yl)phenol (L1) (0.1 g, 0.32 mmol). The mixture was stirred at 80 °C for 24 h, then cooled to room temperature. 50 ml distilled water was added and the resulting crude product were filtered and washed with water. Solid product was recrystallized in hot methanol. FT-IR: 3055 (N-H), 2919 (CH_2), 1607 (C=N), 1241 (C-O-C), 740 (CH, pyridine). ^{1}H NMR (DMSO-d6): δ=5.4 (s, 2H), 7.40 (m, 4H), 7.55 (d, 4H), 7.85 (m, 4H), 8.15 (d, 4H), 8.18 (d, 4H), 8.89 (dd, 2H), 8.92 (dd, 2H), 8.99 (dd, 2H), 9.02 (dd, 2H). Elemental Analysis: C: 76.05, H: 4.08, N: 15,60.

2-(4-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl) phenoxy)methyl)benzyloxy) phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline, L3

To a solution of 1,4-Bis(bromomethyl)benzol (0.042 g, 0.16 mmol) in dry DMF (30 mL) was added potassium carbonate (0.08 g, 0.57 mmol) and 4-(1H-imidazo[4,5-f][1,

10]phenanthroline-2-yl)phenol (L1) (0.1 g, 0.32 mmol). The mixture was stirred at 80 °C for 24 h, then cooled to room temperature. 50 ml distilled water was added and the resulting crude product were filtered and washed with water. Solid product was recrystallized in hot methanol. FT-IR: 3340 (N-H), 2850 (CH_2), 1678 (C=N), 1246 (C-O-C), 720 (CH, pyridine). ^{1}H NMR (DMSO-d6): δ=5.25 (s, 2H), 7.25 (m, 4H), 7.5 (d, 4H), 7.8 (m, 4H), 8.20 (d, 4H), 8.25 (d, 4H), 8.85 (dd, 2H), 8.92 (dd, 2H), 9.00 (dd, 2H), 9.02 (dd, 2H). Elemental Analysis: C: 76.09, H: 4.10, N: 15,40.

2-(4-(4,6-bis(4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)-1,3,5-triazine-2-yloxy)phenyl) -1H-imidazo[4,5-f][1,10]phenanthroline, L4

To a solution of cyanuric chloride (0.0196 g., 0.10 mmol), in benzene (5 mL) was added sodium carbonate (1 g) and 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L1) (0.1 g, 0.32 mmol). The mixture was refluxed for 20 h, then cooled to room temperature. Resulting compound were filtered and washed with ethylacetate and %10 Na_2CO_3 solution. FT-IR: 3064 (N-H), 1608 (C=N), 1180 (C-O-C), 737 (CH, pyridine).

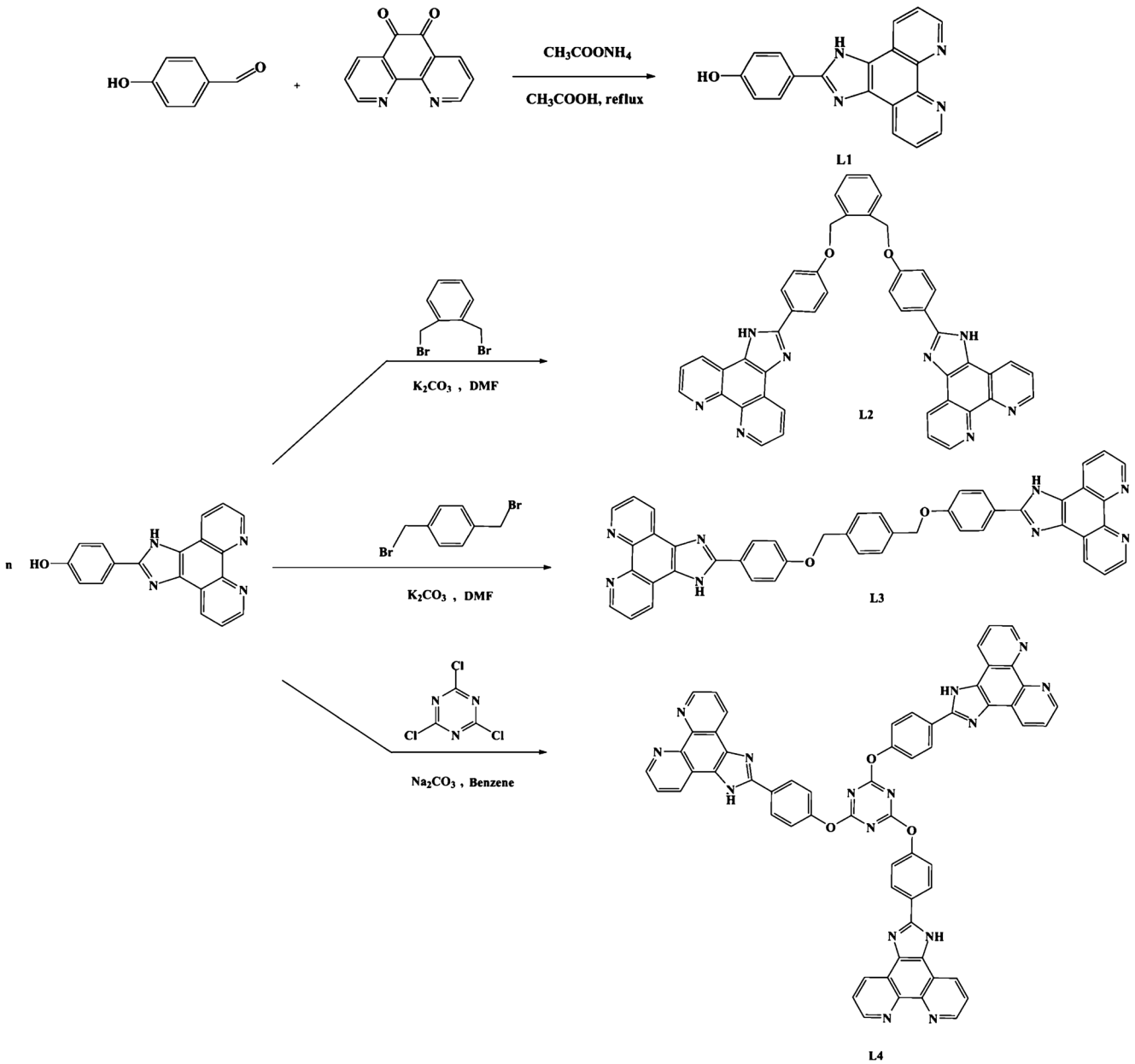

Fig. 1 Synthesis scheme for mono-, di-, tripodal ligands, L1, L2, L3, L4

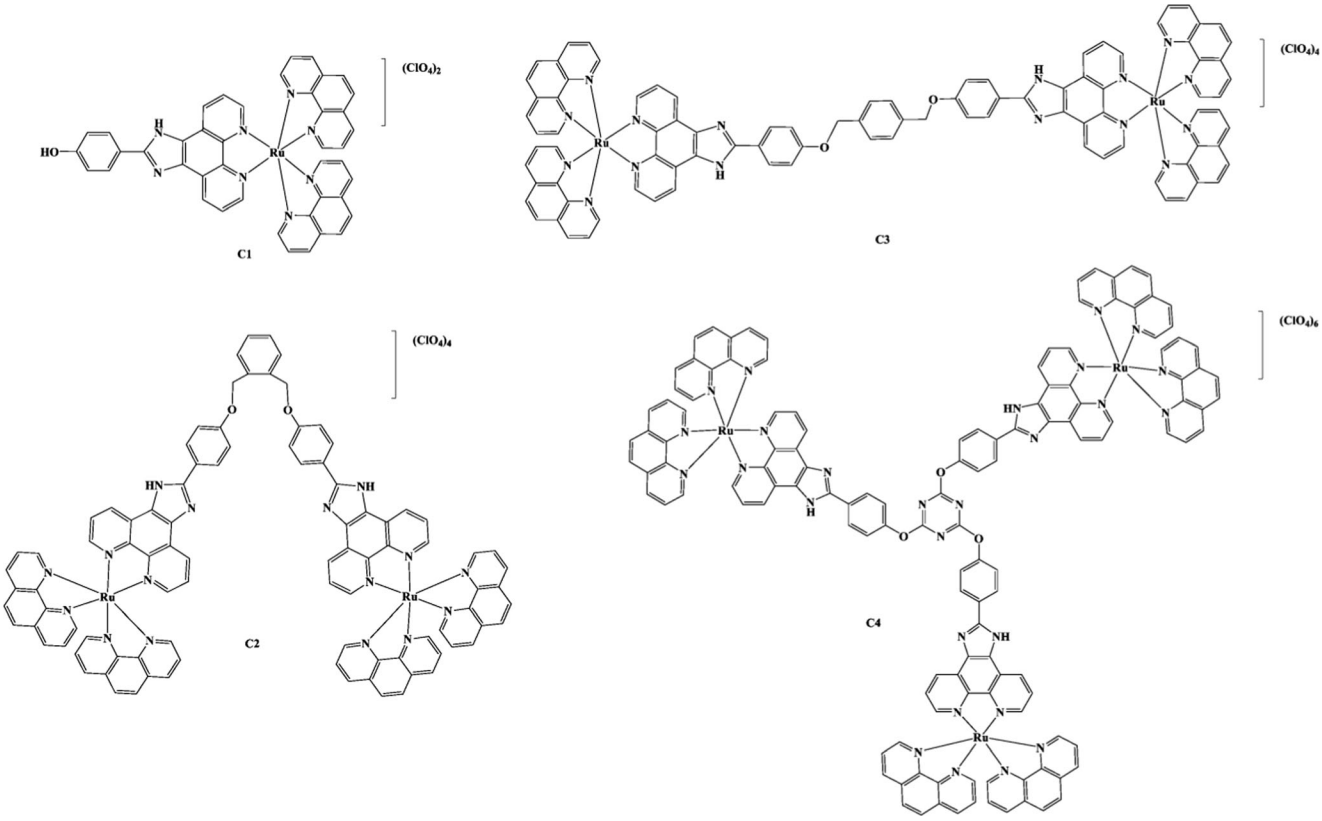

Fig. 2 Ru(II) polypyridine complexes of mono-, di-, tripodal ligands

^{1}H NMR (DMSO-d6): δ=5.35 (s, 3H), 6.8 (d, 6H), 7.7 (m, 6H), 8.2 (m, 6H), 8.75 (m, 12H). Elemental Analysis: C: 71.15, H: 3.30, N: 20,60.

$Ru(phen)_2Cl_2.2H_2O$

$RuCl_3.3H_2O$ (3.2 g, 12.5 mmol), 1,10-phenanthroline (3.55 g, 20 mmol) and LiCl (4.4 g, 105 mmol) were refluxed in degassed DMF (50 ml) for 8 h under stirring. The reaction mixture was cooled to r.t. and poured into 250 ml of 10 % of LiCl aqueous solution, stirred for 30 min and filtered to obtain a brown–black solid. The solid was washed three times with 25-ml portions of water and ether. The crude product was recrystallized by suspending it in 300 ml of 1:1 water–ethanol and refluxing the mixture until all solids had dissolved to form a deep brown–red solution. This solution was filtered while hot and evaporated down in the presence of lithium chloride (20 g) to remove all the alcohol. After 4 h at room temperature, the $Ru(phen)_2Cl_2$ complex recrystallized leaving a yellow–green mother liquor. The crystals were collected and washed with water (20 ml), ethanol (20 ml), and finally ether. The compound was dried under vacuum. A green–black product was obtained in 69 % yield [17].

Table 1 Table of the FT-IR spectra bands data for the ligands and their Ru(II) complexes

Sample	ν (C=N)	ν (N-H)	ν (ClO_4^-)	ν (M-N)
L1	1659	3165	–	–
L2	1607	3055	–	–
L3	1678	3340	–	–
L4	1608	3064	–	–
C1	1660	3068	1049	560
C2	1609	3068	1082	564
C3	1730	3063	1082	572
C4	1640	3230	1085	575

$[Ru(phen)_2$ (4-(1H-imidazo[4,5-f][1,10]fenantrolin-2-il) fenol)], C1

cis-$[Ru(phen)_2Cl_2]$ (0.17 g, 0.32 mmol) and 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L1) (0.1 g, 0.32 mmol) were added to 10 ml ethylene glycol. The mixture was refluxed for 12 h under an nitrogen atmosphere. The cooled reaction mixture was diluted with water (20 ml) and filtered to remove solid impurities. The complex was then separated from soluble impurities by precipitation with sodium perchlorate. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography over alümina oxide using acetonitrile–toluene (2:1, v/v) as an eluent [18]. FT-IR: FT-IR: 3068 (N-H), 2985 (CH_2), 1660 (C=

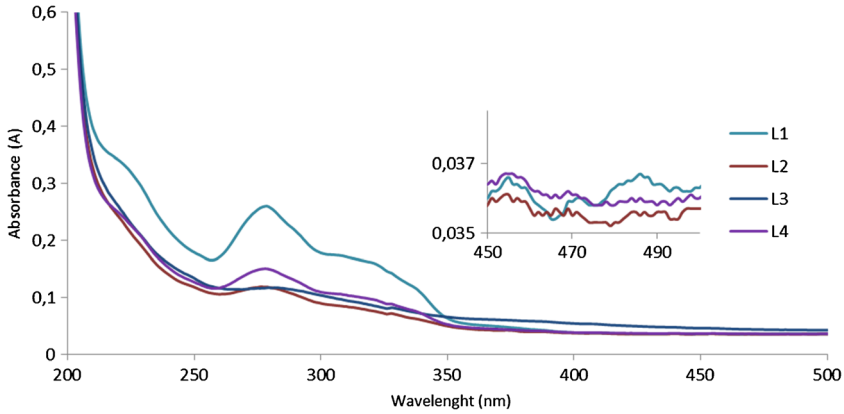

Fig. 3 Absorbance spectra of the mono-, di- and tripodal polypyridine ligands at 1×10^{-4} M in acetonitrile medium

N), 1049 (ClO_4), 718 (b-ring pyridine), 629 (C-C) (ring), 560 (M-N). ^{1}H NMR (DMSO-d6, d ppm): 7.04 (2H, d), 7.8 (6H, m) 8.00 (2H, d) 8.13 (2H, d) 8.15 (2H, d) 8.16 (2H, d) 8.39 (4H, s) 8.8 (4H, d) 9.06 (2H, d) 11.00 (1H, s).

[Ru(phen)$_2$(2-(4-(2-((4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)methyl) benzyloxy)phenyl) -1H-imidazo[4,5-f][1,10]phenanthroline)], C2

To a solution of $[Ru(phen)_2Cl_2]\cdot2H_2O$ (0.1 g, 0.18 mmol) in ethylene glycol (20 mL) under reflux was added 2-(4-(2-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl) benzyloxy)phenyl)-1H-imidazo[4,5-f][1, 10]phenanthroline (L2) (0.068 g, 0.093 mmol) as solid under an nitrogen atmosphere and the resulting mixture was refluxed for 24 h. The solution was cooled to room temperature, water (60 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate dropwise with stirring whereupon a red solid separated out. The product was filtered, dried in air, and recrystallized in hot methanol. FT-IR: 3068 (N-H), 2923 (CH_2), 1609 (C=N), 1089 (ClO_4), 718 (b-ring pyridine), 629 (C-C) (ring), 565 (M-N). ^{1}H NMR (DMSO-d6): 5.45 (s, 2H), 7.85 - 7.5 (m, 4H), 8.00 (d, 8H), 8.15 (m, 12H), 8.2 (m, 8H), 8.35 (m, 4H), 8.5 (d, 4H), 8.8 (d, 8H), 9.1 (d, 12H).

[Ru(phen)$_2$(2-(4-(4-((4-(1H-imidazo[4,5 f][1,10] phenanthroline-2-yl)phenoxy)methyl) benzyloxy)phenyl) -1H-imidazo[4,5-f][1,10]phenanthroline)], C3

To a solution of $[Ru(phen)_2Cl_2]\cdot2H_2O$ (0.1 g, 0.18 mmol) in ethylene glycol (20 mL) under reflux was added 2-(4-(4-((4-(1H-imidazo[4,5f][1,10]phenanthroline-2-yl)phenoxy)methyl) benzyloxy)phenyl)-1H-imidazo[4,5-f][1, 10]phenanthroline (L3) (0.068 g, 0.093 mmol) as solid under an nitrogen atmosphere and the resulting mixture was refluxed for 24 h. The solution was cooled to room temperature, water (60 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate dropwise with stirring whereupon a red solid separated out. The product was filtered, dried in air, and recrystallized in hot methanol. FT-IR: 3063 (N-H), 2922 (CH_2), 1730 (C=N), 1082 (ClO_4), 717 (b-ring pyridine), 628 (C-C) (ring), 570 (M-N). ^{1}H NMR (DMSO-d6): 5.23 (s, 2H), 7.73 – 7.79 (m, 4H), 8.08 (d, 8H), 8.38 (m, 12H), 8.50 (m, 8H), 8.6 (m, 4H), 8.65 (d, 4H), 8.75 (d, 8H), 8.79 (d, 12H).

Table 2 Table of the absorptions for the ligands and the complexes

Sample	278 nm (λ_{max})	315 nm (λ_{max})	328 nm (λ_{max})	462 nm (λ_{max})
L1	0.2601	0.1662	0.1361	–
L2	0.1184	0.0810	0.0698	–
L3	0.1166	0.0913	0.0805	–
L4	0.1506	0.1010	0.0854	–
Sample	265 nm (λ_{max})	288 nm (λ_{max})	328 nm (λ_{max})	462 nm (λ_{max})
C1	0.3736	0.4102	0.1611	0.1092
C2	0.1001	0.0913	0.0575	0.0416
C3	0.1056	0.0843	0.0491	0.0399
C4	0.1193	0.0923	0.0547	0.0429

The data is for spin-allowed ligand centered π-π* transitions of the ligand frameworks peaks and imidazoline-phenanthroline group peak and d-π* transitions peak

[Ru(phen)$_2$(2-(4-(4,6-bis(4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)-1,3,5-triazine-2-yloxy)phenyl) -1H-imidazo[4,5-f][1,10]phenanthroline)], C4

To a solution of [Ru(phen)$_2$Cl$_2$]·2H$_2$O (0.1 g, 0.18 mmol) in ethylene glycol (20 mL) under reflux was added 2-(4-(4,6-bis(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)-1,3,5-triazine-2-yloxy)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L4) (0.063 g, 0.062 mmol) as solid under an nitrogen atmosphere and the resulting mixture was refluxed for 24 h. The solution was cooled to room temperature, water (60 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate dropwise with stirring whereupon a red solid separated out. The product was filtered, dried in air, and recrystallized in hot methanol (1.70 g, 79 %). FT-IR: 3230 (N-H), 1640 (C=N), 1085 (ClO_4), 718 (b-ring pyridine), 629 (C-C) (ring), 575 (M-N). ^{1}H NMR (DMSO-d6): 5.4 (s, 3H), 7.10 (m, 6H), 7.85 (d, 18H), 8.2 (d, 18H), 8.4 (d, 18H), 8.9 (d, 18H).

Result and Discussion

Synthesis and Characterization

An outline of the synthesis of the mono-, di- and tripodal polypyridine ligands 4-(1H imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L1), 2-(4-(2-((4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)methyl)benzyloxy)phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline (L2), 2-(4-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy) methyl)benzyloxy)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L3), 2-(4-(4,6-bis(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)-1,3,5-triazine-2-yloxy)phenyl)-1H-imidazo [4,5-f][1,10]phenanthroline (L4) is presented in Fig. 1. The ligand L1 is a starting material. It was prepared by the condensation reaction between one equivalent of 1,10-phenanthroline-5,6-dione and one equivalent of 4-hydroxybenzaldehyde in the presence of an excess of ammonium acetate in refluxing acetic acid. Other ligands L2, L3, L4 were prepared by the reaction of L1 and 1,2-bis(bromomethyl)benzol, 1,4-bis(bromomethyl)benzol, cyanuric chloride, respectively. The heteroleptic mono-, di- and trinuclear complexes [Ru(phen)$_2$(L1)](ClO$_4$)$_2$, [Ru(phen)$_2$(L2)](ClO$_4$)$_4$, [Ru(phen)$_2$(L3)](ClO$_4$)$_4$, [Ru(phen)$_2$(L4)](ClO$_4$)$_6$ were prepared by the reaction of the performed mono-, di-, tripodal imidazo [4,5-f][1,10]-phenanthroline-cored ligands and [Ru(phen)$_2$Cl$_2$]. 2H$_2$O in ethylene glycol. The complexes were isolated as perchlorate salts and stable in air and in solution (Fig. 2). The L2, L3, L4 ligands and C2, C3, C4 complexes were syntehsized originally. L1 and C1 were synthesized according to the literature methods [16, 18].

All the ligands and complexes were characterized by ^{1}H-NMR spectroscopy, FT-IR spectroscopy, elemental analysis. Their aborsption and emission studies were performed in acetonitrile medium. The ^{1}H-NMR data and important FT-IR frequencies were given in experimental part. In general the spectroscopic values were similar with each other for all the compounds. The ^{1}H-NMR spectrum of the monopodal ligand L1 shows the resonances at 8.97, 8.86 and 8.08 ppm are assigned to the protons of the phenanthroline ring. The resonances at 7.77 and 7.00 ppm are assigned to the protons of the phenyl spacer. In the ^{1}H-NMR spectrum of the dipodal ligand L2, the resonances at 9.02, 8.92 and 8.18 ppm are assigned to the protons of the phenanthroline ring. The resonances at 7.85 and 7.55 ppm are assigned to the protons of the phenyl spacer. And the ^{1}H-NMR spectrum of the other dipodal ligand L3 shows nearly same the chemical shifts because L3 is the para-position and the L2 is the orto-position of the same molecule. So, the protons at 9.02, 8.92 and 8.25 ppm are for the phenanthroline ring and at 7.8 and 7.5 ppm are for the phenyl spacer. In the ^{1}H-NMR spectrum of the dipodal ligand L4, the resonances at 8.8, 8.75 and 8.2 ppm are assigned to the

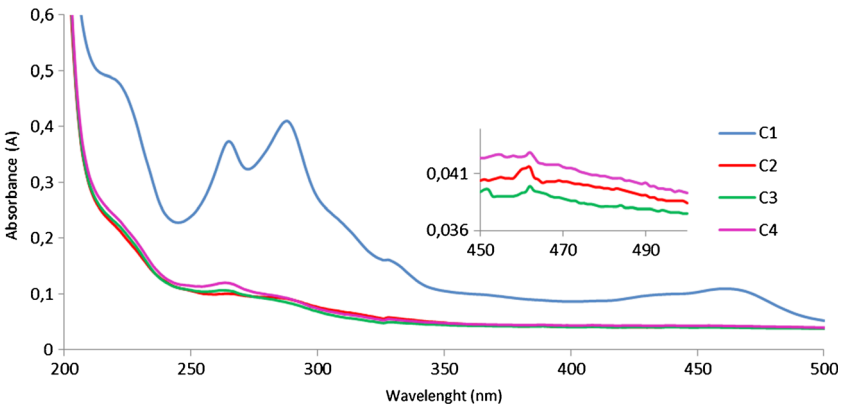

Fig. 4 Absorbance spectra of Ru(II) complexes of the mono-, di- and tripodal polypyridine ligands at 1×10^{-4} M in acetonitrile medium

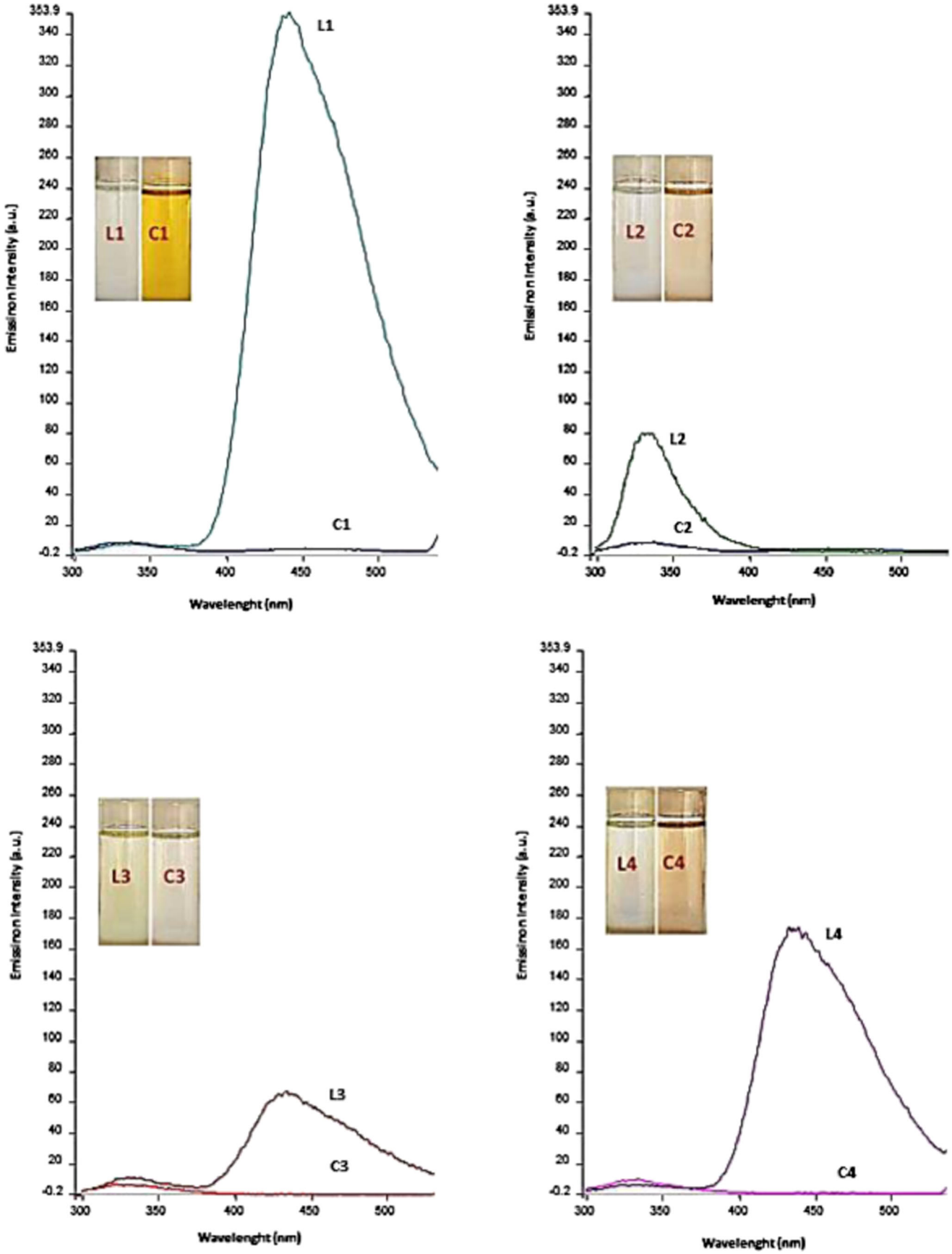

Fig. 5 The emission spectra of mono-, di- and tripodal polypyridine ligands and their Ru(II) complexes

protons of the phenanthroline ring. The resonances at 7.7 and 6.8 ppm are assigned to the protons of the phenyl spacer. The ^{1}H-NMR spectra of the complexes shows the expected peaks in the aromatic and aliphatic regions as well. Upon Ru(II) coordination, the chemical shifts of the ligands shifted obviously. This is because of the coordination of phenanthroline nitrogen atoms to Ru(II) leads to the electron deficiency of the phenanthroline group.

The FT-IR spectra of the ligands L1, L2, L3 and L4 show the C=N bands at 1659, 1607, 1678 and 1608 cm^{-1}, respectively. The N-H bands at 3165, 3055, 3340, 3064 cm^{-1}. All the bands were shifted to the lower frequencies for their Ru(II) complex forms. In addition, for the complexes a new band was observed at 560, 564, 572 and 575 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1049, 1082, 1082 and 1085 cm^{-1} could be assigned to the counter anion ClO_4^- (Table 1).

UV–Vis Absorbance and Emission Studies

Absorption and emission studies of the mono-, di- and tripodal polypyridine ligands and their Ru(II) complexes were investigated by UV–vis spectroscopy and fluorescence spectroscopy with the concentration of $1x10^{-4}$ M in acetonitrile. The absorption spactra were measured using a 1 cm absorption cell. Emission spectra of the same solutions were measured with a 1 cm quartz cell (Exc: 275 nm). Emission spectra were recorded in the range 200 – 800 nm with a slit width of 1.0 nm. In acetonitrile solution the L1, L2, L4, C3 were colorless under daylight and L3, C1, C2, C4 were yellow color.

The UV–vis absorption spectra of ligands and complexes in acetonitrile solution at room temperature are displayed in Fig. 3, respectively. All the ligands show three intense bands at 278, 315, 328 nm, which could be assigned to intraligand charge transfer (ILCT). The double shoulders at 278 and 315 nm show π-π* transitions of the ligand framework and a little shoulder at 328 nm is for imidazole-phenanthroline group. All the complexes show the ILCT bands at 265 nm, 288, 328 nm and additionally low-energy absorptions were observed at 462 nm for the Ru(II) complexes corresponding to the metal-ligand charge transfer (MLTC) (Table 2). These values and assignments are consistent with literature values [19, 20].

The emission spectra of the ligands and complexes in acetonitrile solution are shown in Fig. 4. When excitated at 275 nm, the maximum emission intensities were seen at 433 nm for the ligands and 330 nm for their complexes. The high fluorescence intensities were seen for the ligands and after complexation with Ru(II) the fluorescence were quenced. As seen in Fig. 5, emission spectrum for the ligands L1, L2, L3, L4, the intensities were L1: 345-fold, L2: 80-fold, L3: 70-fold, and L4: 180-fold when they were compared with each other at 433 nm. And after complexation with Ru(II) they were all quenced.

Conclusion

In summary, the mono-, di-, tripodal polypyridine ligands and their $[Ru(phen)_2Ln](ClO_4)_X$ complexes were synthesized and characterized (n=1, 2, 3, 4 and x=2, 4, 6). The ligand L1 was synthesized first and It was prepared by the condensation reaction between one equivalent of 1,10-phenanthroline-5,6-dione and one equivalent of 4-hydroxybenzaldehyde in the presence of an excess of ammonium acetate in refluxing acetic acid. Other ligands L2, L3, L4 were prepared by the reaction of L1 and 1,2-bis (bromomethyl)benzol, 1,4-bis (bromomethyl)benzol, cyanuric chloride, respectively.

The compounds were characterized by ^{1}H-NMR spectroscopy, FT-IR spectroscopy, Elemental Analysis. The absorption and emission spectra were recorded. UV–vis spectra of the complexes shows the new Metal-N band at 462 nm for the complexes. Emission spectra shows Ru(II) quench the fluorescence intensities of the ligands.

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