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ORIGINAL ARTICLE

Preparation of Different Substitued Polypyridine Ligands, Ruthenium(II)-Bridged Complexes and Spectoscopıc Studies

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Abstract Novel different substitued polypyridine ligands 4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde **(BA-PPY),** (E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine **(PR-PPY)**, (E)-N-(4-((4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine **(FN-PPY)**, 2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline **(BR-PPY)**, 2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline **(N3-PPY)** and triazole containing polypyridine ligand 3,4-bis[(4-(metoxy)-1,2,3-triazole)1-methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] benzaldehyde **(BA-DIPPY)** and Ruthenium(II) complexes were synthesized and characterized. Their photopysical properties were investigated. The complexes RuP(PR-PPY), RuB(PR-PPY, RuP(FN-PPY) and RuB(FN-PPY) exhibited a broad absorption bands at 485, 475, 476, and 453 nm, respectively, assignable to the spin-allowed MLCT (d_π–π^*) transition. The emission maxima of the pyrene-appended polypyridine ligand PR-PPY was observed at λems = 616 nm and the phenanthroline-appended polypyridine ligand FN-PPY was observed at λems = 668 nm. And the emission maxima of the complexes RuP(PR-PPY), RuB(PR-PPY), RuP(FN-PPY) and RuB(FN-PPY) were observed at λems = 646, 646, 685 and 685 nm, respectively. As seen in fluorescence spectra, the fluorescence intensities of the ligands are higher than their metal complexes. This is because of quenching effect of Ruthenium(II) metal on chromophore groups.

Keywords Polypyridine · Ruthenium(II) complex · Triazole · Different substitued ligands

Introduction

There is nowadays much interest in the design of photoinduced energy and electron transfer systems due to their potential applications in fields as artificial photosynthesis, photocatalysis, molecular informatics and so on [1–5]. Imidazo[4,5-f]-1,10-phenanthroline containing polypyridyl ligands and complexes have been extensively studied as a result of their remarkable photophysical properties and chemical stability. Tremendous interest has been attracted to mononuclear and dinuclear Ruthenium(II) polypyridine complexes with regard to the photochemical molecular devices, solar energy related research, molecular wires, DNA probes, sensors and switches [6–10]. Schiff base containing polypyridine ligands and complexes have also significant interest because of their excellent chemical, electrochemical and photochemical behavious as well as potential biological applications such as antitumor, antibacterial and antimicrobial activities [6, 11–13]. Fluorescent groups as phenanthroline or pyrene contribute additional photopysical properties to the Schiff base polypyridyl ligands. Among the existent fluorescent groups, phenanthroline and pyrene reveals to be one of the most commonly used fluorophores due to its peculiar fluorescence properties: intense fluorescence signals, long lifetime values [14, 15]. Because of these remarkable properties we have designed two of our novel ligands as fluorescent Schiff base molecules.

In this paper we have synthesized a series of molecules starting from organic ligands containing imidazo[4,5-f]-1,10-

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phenanthroline group. They are different substitued polypyridine ligands and they could be classifed as fluorescent Schiff base ligands, triazole containing ligand, aldeyde-ended ligand, bromine-ended ligand and azide-ended ligand. Triazole containing polypyridine ligand BA-DIPPY has been synthesized by copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Due to its high efficiency, functional group tolerance, simple purification procedure and compatibility with various solvents, the (CuAAC) has received remarkable attention. In addition to its role as a connector, the resulting 1,2,3-triazole has also recently been highlighted as a ligand for metal ions, in sensing, luminescence and magnetism [16, 17].

Experimental

Apparatus

All starting materials and reagents used were purchased from 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. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silicagel H, type60, Merck).

Method

1,10-Phenanthroline-5,6-dione [18], 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol [19], $[Ru(phen)_2Cl_2]\cdot 2H_2O$ [20], $[Ru(bpy)_2Cl_2].H_2O$ [21] and 3,4-bis(prop-2-ynyloxy)benzaldehyde [22] 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 % [18].

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 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 [19].

FT-IR (cm^{-1}): 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).

3,4-Bis(Prop-2-Ynyloxy)Benzaldehyde 3,4-Dihydroxybenzaldehyde (0.1 g, 0.72 mmol), 3-bromopropene (0.2 g, 1.8 mmol), NaI (0.01 g, 0.072 mmol) and K_2CO_3 were dissolved in 20 mL DMF. The solution was stirred for 3 h at room temperature. The resulting crude product was filtered, washed with water-brine and dried. It was purified with silica gel column (n-hexane: ethylacetate, 20:1) [22].

4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl)Benzaldehyde, BA-PPY To the solution of 4-(bromomethyl)benzaldehyde in 30 mL DMF, 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (0.15 g, 0.5 mmol) and K_2CO_3 (0.13 g, 1 mmol) were added. The mixture was stirred for 36 h at 90 °C. Then cooled to room temperature and 50 mL water as added to the solution. The resulting crude product were filtered and washed with cold water.

MP: 305 °C, MW: 430 g/mol, FT-IR (cm^{-1}): 3049 (N-H), 1694 (C = O), 1208 (C-O-C), 804 (CH-pyridine). ^{1}H-NMR (DMSO-d6): δ (ppm) = 5.4 (s, 2H,O-CH_2), 7.3–8.95 (m, 12H, ArH), 9.2 (s, 2H, HC = N), 10.0 (s, 1H, HC = O), 13.75 (s, 1H, −NH).

$[Ru(Phen)_2(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl)Benzaldehyde)](ClO_4)_2$, RuP(BA-PPY) cis-$[Ru(phen)_2Cl_2]$ (0.069 g, 0.23 mmol) and **BA-PPY** (0.1 g, 0.23 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried. MP: > 399 °C, MW: 1090 g/ mol, FT-IR (cm^{-1}): 3068 (N-H), 1660 (C = N), 1049 (ClO_4), 804 (CH-pyridine), 540 (M-N). $C_{51}H_{34}Cl_2N_8O_{10}Ru$, Elemetal Analysis; Calculated (Found): C, 56.15 (55.7), H, 3.14 (3. 13), N, 10.27 (9.98).

[Ru(Bpy)$_2$(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl)Benzaldehyde)] (ClO_4)$_2$, RuB(BA-PPY) cis-[Ru(bpy)$_2$Cl$_2$] (0.063 g, 0.23 mmol) and **BA-PPY** (0.1 g, 0.23 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried. MP: > 399 °C, MW: 1042 g/ mol, FT-IR (cm^{-1}): 3073 (N-H), 1611 (C = N), 1073 (ClO_4), 802 (CH-piridin), 540 (M-N). $C_{47}H_{34}Cl_2N_8O_{10}Ru$, Elemetal Analysis; Calculated (Found): C, 54.13 (54.03), H, 3.29 (3.19), N, 10.75 (9.99).

(E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl)Benzylidene)-Pyrene-4-Amine, PR-PPY To a stirred solution of 1-pyrene(methylamine) hydrochloride (0.062 g, 0.23 mmol) i 25 mL methanol, 10 mL tirethylamine was added. After half and hour, the solution of **BA-PPY** (0.1 g, 0.23 mmol) in 5 mL methanol was added to this mixture and continued to stirring for 36 h at 70 °C. The resulting crude product were filtered and recrystallized from methanol.

MP: 306 °C, MW: 643 g/mol, FT-IR (cm^{-1}): 3044 (N-H), 1607 (C = N), 1250 (C-O-C), 813 (CH-pyridine). ^{1}H-NMR (DMSO-d6): δ (ppm) = 5.2 (s, 2H, O-CH_2), 5.4 (s, 2H, CH_2-N), 7.2–9.1 (m, 22H, ArH), 9.2 (s, 2H, HC = N), 13.8 (b, 1H, −NH).

[Ru(Phen)$_2$((E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl) Benzylidene) -Pyrene-4-Amine)] (ClO_4)$_2$, RuP(PR-PPY) cis-[Ru(phen)$_2$Cl$_2$] (0.082 g, 0.15 mmol) and **PR-PPY** (0.1 g, 0.15 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried.

MP:> 399 °C, MW: 1303 g/mol, FT-IR (cm^{-1}): 3131 (N-H), 1604 (C = N), 1060 (ClO_4), 711 (CH-pyridine), 580 (M-N). $C_{68}H_{45}Cl_2N_9O_9Ru$, Elemetal Analysis; Calculated (Found): C, 62.63 (61.90), H, 3.48 (3.20), N, 9.67 (8.99).

[Ru(Bpy)$_2$ ((E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl) Benzylidene)-Pyrene-4-Amine)] (ClO_4)$_2$, RuB(PR-PPY) cis-[Ru(bpy)$_2$Cl$_2$] (0.07 g,0.15 mmol) and **PR-PPY** (0.1 g, 0.15 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried.

MP:> 399 °C, MW: 1256 g/mol, FT-IR (cm^{-1}): 3027 (N-H), 1604 (C = N), 1060 (ClO_4), 721 (CH-pyridine), 580 (M-N). $C_{64}H_{45}Cl_2N_9O_9Ru$, Elemetal Analysis; Calculated (Found): C, 61.20 (60.85), H, 3.61 (3.26), N, 10.04 (9.93).

(E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl)Benzylidene)-1,10-Phenanthroline-5amine, FN-PPY To a stirred solution of 1,10-phenanthroline-5amine (0.02 g, 0.11 mmol) 25 mL methanol, the solution of **BA-PPY** (0.05 g, 0.11 mmol) in 5 mL methanol was added to this mixture and continued to stirring for 36 h at 70 °C. The resulting crude product were filtered and recrystallized from methanol.

MP: 225 °C, MW: 607 g/mol, FT-IR (cm^{-1}): 3024 (N-H), 1608 (C = N), 1242(C-O-C), 802 (CH-pyridine). ^{1}H NMR (DMSO-d6): δ (ppm) = 5.15 (s, 2H, O-CH_2), 7.2–9.0 (m, 21H, ArH), 8.9 (s, 1H, HC = N), 13.6 (b, 1H, −NH).

[(Ru(Phen)$_2$)$_2$((E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl) Benzylidene)-1,10-Phenanthroline-5amine)] (ClO_4)$_4$, RuP(FN-PPY) cis-[Ru(phen)$_2$Cl$_2$] (0.17 g, 0.32 mmol) and **FN-PPY** (0.1 g, 0.16 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried.

MP:> 399 °C, MW: 1927 g/mol, FT-IR (cm^{-1}): 3402 (N-H), 1650 (C = N), 1033 (ClO_4), 750 (CH-pyridine), 580 (M-N). $C_{87}H_{57}Cl_4N_{15}O_{17}Ru_2$, Elemetal Analysis; Calculated (Found): C, 54.19 (54.01), H, 2.98 (2.10), N, 10.89 (9.94).

[(Ru(Bpy)$_2$)$_2$((E)-N-(4-((4-(1H-Imidazo[4,5-f][1,10]Phenanthroline-2-yl)Phenoxy)Methyl) Benzylidene) -1,10-Phenanthroline-5amine)] (ClO_4)$_4$, RuB(FN-PPY) cis-[Ru(bpy)$_2$Cl$_2$] (0.16 g, 0.32 mmol) and **FN-PPY** (0.1 g, 0.16 mmol) were added to 20 ml methanol. 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 filtered and washed with water and dried.

MP:> 399 °C, MW: 1831 g/mol, FT-IR (cm^{-1}): 3310 (N-H), 1606 (C = N), 1069 (ClO_4), 722 (CH-pyridine), 580 (M-N). $C_{79}H_{57}Cl_4N_{15}O_{17}Ru_2$, Elemetal Analysis; Calculated (Found): C, 51.78 (51.60), H, 3.14 (3.09), N, 11.47 (11.09).

2-(4-(Bromomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline, BR-PPY A mixture of 1,10-phenanthroline-5,6-dione (0.25 g, 1.2 mmol), ammonium acetate (2.6 g, 1.2 mmol), 4-(bromomethyl) benzaldehyde (0.25 g, 0.46 mmol) and30 mL glacial acetic acid were refluxed for 48 h and then poured in 200 mL of water. The solution was neutralized with ammonia to pH:7 and cooled to room temperature. The precipitate was collected and washed with water. The crude yellow product was dried under vacuo.

MP: 193 °C, MW: 388 g/mol, FT-IR (cm^{-1}): 3081 (N-H), 1744 (C = N), 689 (C-Br), ^{1}H-NMR (DMSO-d6): δ (ppm) = 5.15 (s, 2H, Br-CH_2), 7.15–9.0 (m, 8H, ArH), 9.1 (s,2H, HC = N), 13.75 (b, −NH).

[Ru(Phen)$_2$ (2-(4-(Bromomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline)] (ClO_4)$_2$, RuP(BR-PPY) cis-[Ru(phen)$_2$Cl$_2$] (0.076 g, 0.25 mmol) and **BR-PPY** (0.1 g, 0.25 mmol) were added to 20 ml methanol. The mixture was refluxed for 12 h under an nitrogen atmosphere. The cooled reaction mixture was diluted with water (30 ml) and filtered to remove solid impurities. The complex was then separated from soluble impurities by precipitation with sodium perchlorate. The precipitated complex was filtered and washed with water and dried.

MP:> 399 °C, MW: 1047 g/mol, FT-IR (cm^{-1}): 3480 (N-H), 1633 (C = N), 1085 (ClO_4), 715 (CH-pyridine), 530 (M-N). $C_{44}H_{29}BrCl_2N_8O_8Ru$, Elemetal Analysis; Calculated (Found): C, 50.35 (51.23), H, 2.78 (2.40), N, 10.68 (10.30).

[Ru(Bpy)$_2$(2-(4-(Bromomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline)](ClO_4)$_2$, RuB(BR-PPY) cis-[Ru(bpy)$_2$Cl$_2$] (0.07 g, 0.25 mmol) and **BR-PPY** (0.1 g, 0.25 mmol) were added to 20 ml methanol. The mixture was refluxed for 12 h under an nitrogen atmosphere. The cooled reaction mixture was diluted with water (30 ml) and filtered to remove solid impurities. The complex was then separated from soluble impurities by precipitation with sodium perchlorate. The precipitated complex was filtered and washed with water and dried.

MP:> 399 °C, MW: 999 g/mol, FT-IR (cm^{-1}): 3402 (N-H), 1610 (C = N), 1090 (ClO_4), 716 (CH-pyridine), 530 (M-N). $C_{40}H_{29}BrCl_2N_8O_8Ru$, Elemetal Analysis; Calculated (Found): C, 47.97 (46.70), H, 2.92 (2.89), N, 11.19 (11.23).

2-(4-(Azidomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline, N3-PPY To the solution of **BR-PPY** (0.1 g, 0.25 mmol) in 20 mL DMF sodium azide (0.021 g, 0.32 mmol) was added. The mixture was stirred for 36 h at 90 °C. Then cooled to room temperature and 200 mL water was added to the solution, extracted with DCM. Then organic phase was collected and dried with Na_2SO_4. Solvent was removed by evaporation and resulting crude yellow product were collected.

MP: 277 °C, MW: 351 g/ mol, FT-IR (cm^{-1}): 3081 (N-H), 2150 (N = N = N), 1735 (C = N). ^{1}H-NMR (DMSO-d6): δ (ppm) = 2.6 (s, 2H, N_3-CH_2), 7.5–9.0 (m, 8H, ArH), 8.98 (s,2H, HC = N), 13.75 (b, 1H, −NH).

[Ru(Phen)$_2$(2-(4-(Azidomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline)] (ClO_4)$_2$, RuP(N3-PPY) cis-[Ru(phen)$_2$Cl$_2$] (0.08 g, 0.28 mmol) and **N3-PPY** (0.1 g, 0.28 mmol) were added to 20 ml methanol. The mixture was refluxed for 12 h under an nitrogen atmosphere. The cooled reaction mixture was diluted with water (30 ml) and filtered to remove solid impurities. The complex was then separated from soluble impurities by precipitation with sodium perchlorate. The precipitated complex was filtered and washed with water and dried.

MP:> 399 °C, MW: 1011 g/ mol, FT-IR (cm^{-1}): 3350 (N-H), 1601 (C = N), 1038 (ClO_4), 723 (CH-pyridine), 502 (M-N). $C_{44}H_{29}Cl_2N_{11}O_8Ru$, Elemetal Analysis; Calculated (Found): C, 52.23 (52.24), H, 2.89 (2.84), N, 15.23 (14.99).

[Ru(Bpy)$_2$(2-(4-(Azidomethyl)Phenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline)] (ClO_4)$_2$, RuB(N3-PPY) cis-[Ru(bpy)$_2$Cl$_2$] (0.07 g, 0.28 mmol) and **N3-PPY** (0.1 g, 0.28 mmol) were added to 20 ml methanol. The mixture was refluxed for 12 h under an nitrogen atmosphere. The cooled reaction mixture was diluted with water (30 ml) and filtered to remove solid impurities. The complex was then separated from soluble impurities by precipitation with sodium perchlorate. The precipitated complex was filtered and washed with water and dried.

MP:> 399 °C, MW: 963 g/ mol, FT-IR (cm^{-1}): 3501 (N-H), 1602 (C = N), 1084 (ClO_4), 726 (CH-pyridine), 502 (M-N). $C_{40}H_{29}Cl_2N_{11}O_8Ru$, Elemetal Analysis; Calculated (Found): C, 49.85 (50.02), H, 3.03 (3.01), N, 15.99 (14.89).

3,4-Bis[(4-(Methoxy)-1,2,3-Triazole)-1-Methylphenyl)-1H-Imidazo[4,5-f][1,10]Phenanthroline)] Benzaldehyde, BA-DIPPY To a mixture of $CHCl_3$:MeOH:H_2O (10:1:1), 3,4-bis(prop-2-ynyloxy)benzaldehyde (0.026 g, 0.074 mmol) and **N3-PPY** (0.035 g, 0.16 mmol) were added. Then sodium ascorbate (0.0045 g, 0.022 mmol) was added to this mixture

and stirred for 15 min., followed by the addition of $CuSO_4$ (0.0018 g, 0.011 mmol). The heterogenous mixture was stirred vigorously for 120 h at room temperature. After the reaction completed, the solvents were evaporated and the residue was extracted with $CHCl_3$-water. The combined organic phase was concentrated, washed with ethylacetate and dried under vacuo.

E.N.: 325 °C, MA: 916 g/ mol, FT-IR (cm^{-1}): 3243 (N-H), 2923 (C-H), 2160 (N = N), 1725 (C = O). ^{1}H-NMR (DMSO-d6): δ (ppm) = 4.8 (s, 4H, O-CH_2), 7.12–9.0 (m, 30H, ArH), 9.81 (s, 1H, HC = O), 13.75 (b, 2H, −NH).

Result and Discussion

Synthesis and Characterization

In this study novel polypyridine ligands and Ruthenium(II)-bridged complexes were synthesized. Firstly, 4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde (BA-PPY) polypyridine ligand was synthesized. Then schiff base polypyridine ligands; (E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine (PR-PPY), (E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine (FN-PPY) and different substitued ligands; 2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (BR-PPY), 2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (N3-PPY) were synthesized. Triazole containing polypyridine ligand 3,4-bis[(4-(metoxy)-1,2,3-triazole)1-methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)]benzaldehyde (BA-DIPPY) was synthesized as a part of 'click chemistry'. An outline of the synthesis of the polypyridine ligands were presented in Figs. 1 and 2. Except BA-DIPPY, Ruthenium(II) complexes of the ligands were synthesized with [$Ru(phen)_2Cl_2$] and [$Ru(bpy)_2Cl_2$] and the synthesis of 'bridged complexes' were completed.

4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde (BA-PPY) polypyridine ligand is a starting material for PR-PPY and FN-PPY schiff base polypyridine ligands (Fig. 1). BR-PPY was prepared by the condensation reaction between one equivalent of 1,10-phenanthroline-5,6-dione and one equivalent of 4-(bromomethyl) benzaldehyde in the presence of an excess of ammonium acetate in refluxing acetic acid. N3-PPY was prepared for the synthesis of triazole containing 3,4-bis[(4-(metoxy)-1,2,3-triazole)1-methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)]benzaldehyde (BA-DIPPY) polypyridine ligand (Fig. 2).

The heteroleptic mono- and dinuclear complexes; [$Ru(phen)_2$(4-((4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)methyl)benzaldehyde)] $(ClO_4)_2$, [$Ru(bpy)_2$(4-((4-(1H-imidazo[4,5-f][1,10] phenanthroline-2-yl)phenoxy)methyl)benzaldehyde)] $(ClO_4)_2$, [$Ru(phen)_2$((E)-N-(4-((4-(1H-imidazo [4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine)] $(ClO_4)_2$, [$Ru(bpy)_2$((E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine)] $(ClO_4)_2$, [$(Ru(phen)_2)_2$((E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy) methyl)benzylidene)-1,10-phenanthroline-5amine)] $(ClO_4)_4$, [$(Ru(bpy)_2)_2$((E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine)] $(ClO_4)_4$, [$Ru(phen)_2$(2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] $(ClO_4)_2$, [$Ru(bpy)_2$(2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] $(ClO_4)_2$, [$Ru(phen)_2$(2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)]$(ClO_4)_2$, [$Ru(bpy)_2$ (2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] $(ClO_4)_2$ were prepared by the reaction of the performed mono- and dipodal imidazo[4,5-f][1,10]-phenanthroline-cored ligands and [$Ru(phen)_2Cl_2$] and [$Ru(bpy)_2Cl_2$].$2H_2O$ in methanol (Fig. 3).

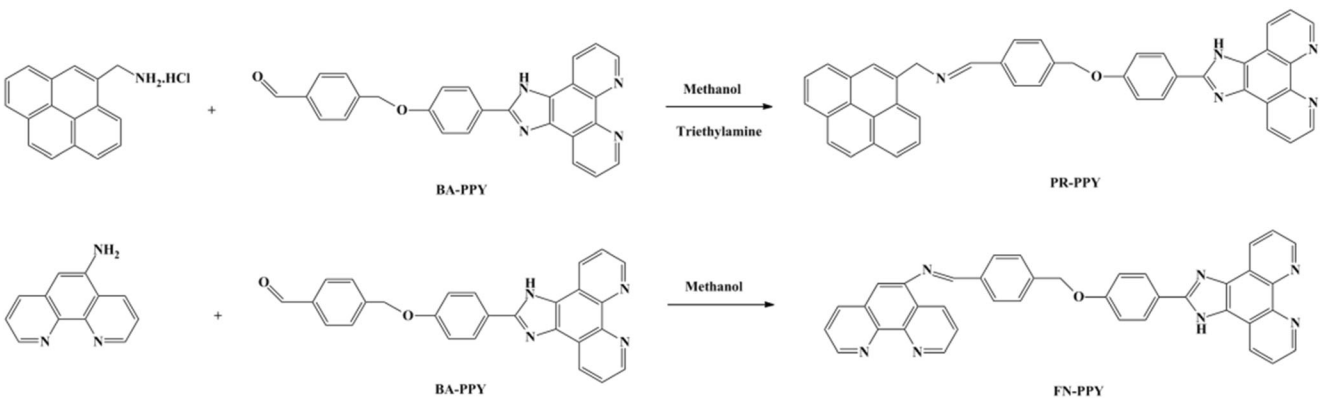

Fig. 1 Synthesis sheme of (PR-PPY) ve (FN-PPY) schiff base polypyridine ligands

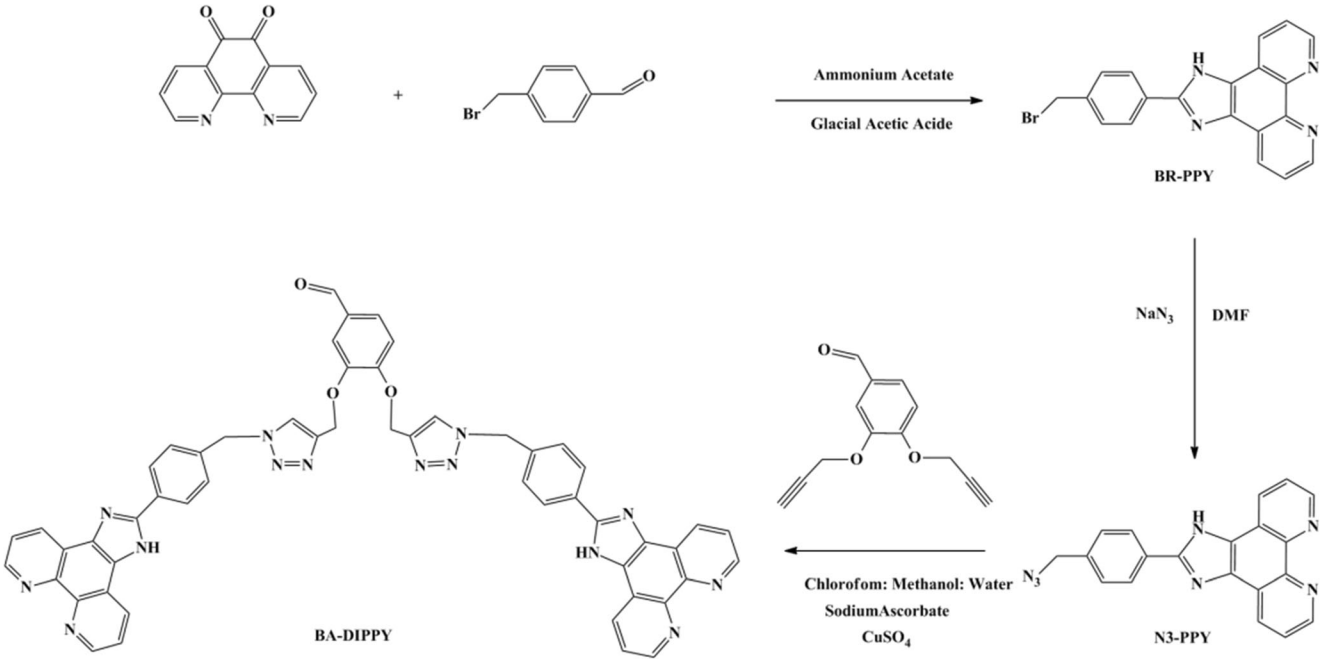

Fig. 2 Synthesis sheme of BR-PPY, N3-PPY, BA-DIPPY different substitued polypyridine ligands

The complexes were isolated as perchlorate salts and stable in air and in solution. All the ligands and Ruthenium(II)-bridged complexes were synthesized originally and characterized by ^{1}H-NMR spectroscopy, FT-IR spectroscopy, Elemental analysis and TG/DTA analysis. Their aborsption and emission studies were performed in acetonitrile medium by UV-Vis Spectrometer and Luminescence Spectrometer. The ^{1}H-NMR data and important FT-IR frequencies were given in experimental part and Tables 1 and 2.

4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde **(BA-PPY)** aldehyde-ended polypyridine ligand was synthesized originally. The ^{1}H-NMR spectrum of the monopodal ligand BA-PPY shows the chemical shifts at 8.95 and 8.2 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 7.8 ppm are assigned to the protons of the aromatic groups. Aldehyde HC = O band observed at 10.0 ppm. –NH group shows a chemical shift at 13.75 ppm and CH_2-O group shows a chemical shift at 5.4 ppm. In the FT-IR spectra of the ligand BA-PPY the peak at 3049 cm^{-1} comprises the both N-H and C-H bands. The peak at 1694 cm^{-1} belongs to the C = O stretching, the peak at 1208 cm^{-1} belongs to C-O-C ether bond and the peak at 804 cm^{-1} belongs to the pyridine groups.

Upon Ruthenium(II) coordination, obtained complexes of this ligand are [Ru(phen)$_2$(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde)] $(ClO_4)_2$, (RuP(BA-PPY)) and [Ru(bpy)$_2$(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzaldehyde)] $(ClO_4)_2$, (RuB(BA-PPY)). In the FT-IR spectra, the chemical shifts of the ligands shifted obviously. This is because of the coordination of phenanthroline nitrogen atoms to Ruthenium(II) leads to the electron deficiency of the phenanthroline group.

In the FT-IR spectra of the complex RuP(BA-PPY) the peak at 3068 cm^{-1} comprises the both N-H and C-H bands. The peak at 1660 cm^{-1} belongs to the C = O stretching and the peak at 804 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 540 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1049 cm^{-1} could be assigned to the counter anion ClO_4^-. In the FT-IR spectra of the complex RuB(BA-PPY) the peak at 3073 cm^{-1} comprises the both N-H and C-H bands. The peak at 1611 cm^{-1} belongs to the C = O stretching and the peak at 802 cm^{-1} belongs to the pyridine groups. The proof peak of the complexation observed at 540 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1073 cm^{-1} could be assigned to the counter anion ClO_4^-.

(E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine **(PR-PPY)**, fluorescent Schiff base polypyridine ligand was synthesized originally. The ^{1}H-NMR spectrum of the monopodal ligand PR-PPY shows the chemical shifts at 9.1 and 8.25 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 7.90 ppm are assigned to the protons of the aromatic groups. Schiff base imine HC = N band observed at 9.20 ppm. –NH group shows a chemical shift at 13.8 ppm. CH_2-O and CH_2-N groups show the chemical shifts at 5.2 and 5.4 ppm, respectively. In the FT-IR spectra of the ligand PR-PPY the peak at 3044 cm^{-1} comprises the both N-H and C-H bands. The peak at 1607 cm^{-1} belongs to the C = N stretching, the peak at 1250 cm^{-1} belongs to C-O-C ether bond and the peak at 813 cm^{-1} belongs to the pyridine groups.

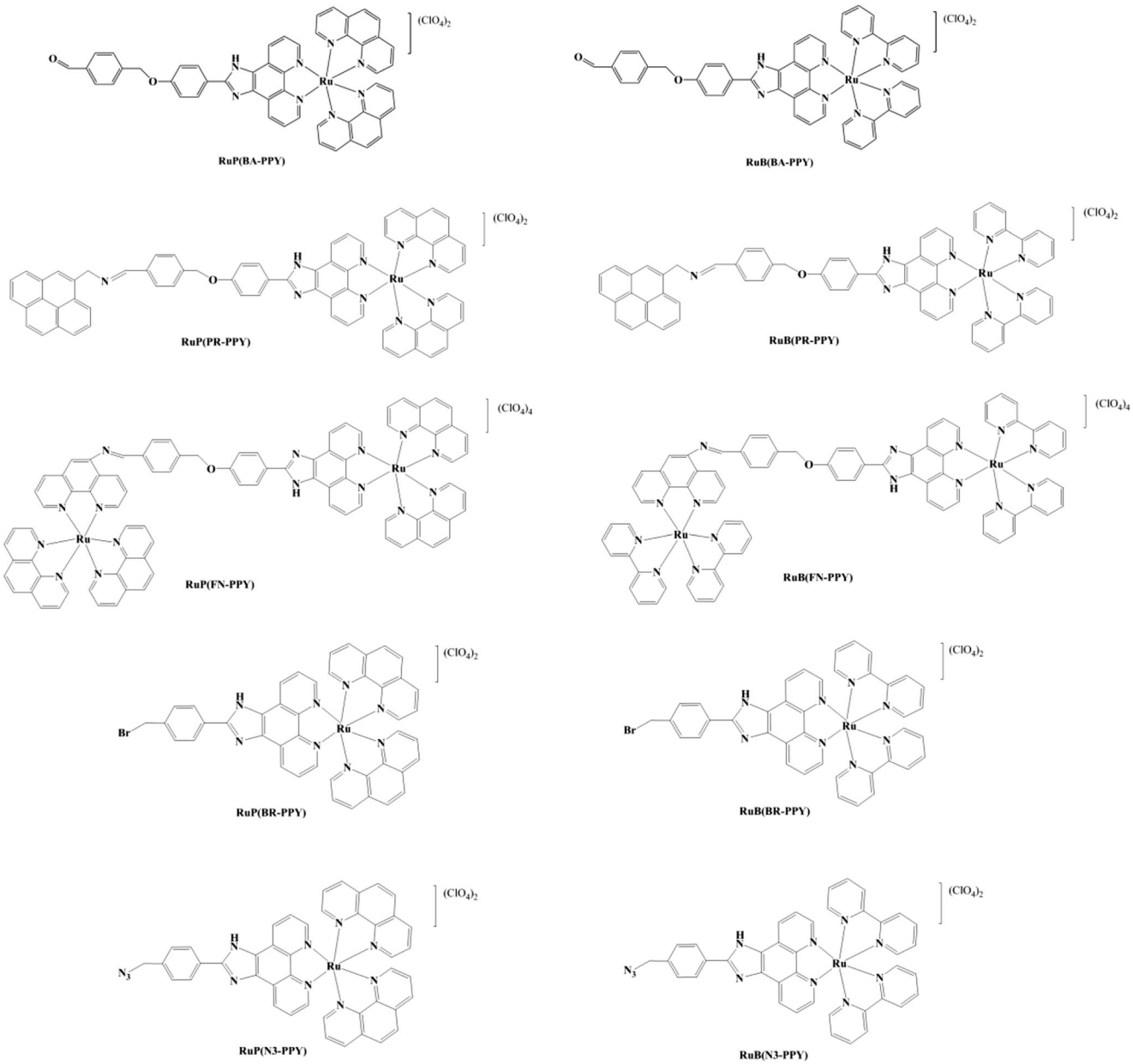

Fig. 3 The structure of Ruthenium(II)-bridged polypyridine complexes

In the FT-IR spectra of the complex $[Ru(phen)_2((E)$-N-(4-((4-(1H-imidazo [4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine)] $(ClO_4)_2$, RuP(PR-PPY), the peak at 3131 cm^{-1} comprises N-H bands and the peak at 2950 cm^{-1} comprises C-H bands. The peak at 1604 cm^{-1} belongs to the C = N stretching and the peak at

Table 1 ^{1}H-NMR characteristic chemical shift data of the ligands (ppm)

No	Ligand	Phen	Phenyl	O-CH_2	Br-CH_2	N_3-CH_2	C = O	N-CH_2	C = N	N-H
1	BA-PPY	8.95, 8.20	7.84	5.40			10.0			13.75
2	PR-PPY	9.1, 8.25	7.90, 7.55	5.20				5.40	9.20	13.80
3	FN-PPY	9.00, 8.15	7.80, 7.30	5.15					8.90	13.60
4	BR-PPY	8.90, 8.40	7.80, 7.60		5.15					13.75
5	N3-PPY	9.00, 8.30	7.80, 7.50			2.60				13.75
6	BA-DIPPY	8.85, 8.30	8.10, 7.25	4.80			9.81			13.75

Table 2 FT-IR characteristic frequencies of the ligands and complexes (cm^{-1})

No	Ligand-Complexes	N-H	C = N	C = O	Pyridine	M-N	ClO_4	C-O-C	C-Br	N = N = N
1	BA-PPY	3049		1694	804			1208		
2	PR-PPY	3044	1607		813			1250		
3	FN-PPY	3024	1608		802			1242		
4	BR-PPY	3081	1744		800				689	
5	N3-PPY	3081	1735		804					2150
6	BA-DIPPY	3243		1725	809			1225		
7	RuP(BA-PPY)	3068		1660	804	540	1049			
8	RuB(BA-PPY)	3073		1611	802	540	1073			
9	RuP(PR-PPY)	3131	1604		711	580	1060			
10	RuB(PR-PPY)	3027	1604		721	580	1060			
11	RuP(FN-PPY)	3402	1650		750	580	1033			
12	RuB(FN-PPY)	3310	1606		722	580	1069			
13	RuP(BR-PPY)	3480	1633		715	530	1085		690	
14	RuB(BR-PPY)	3402	1610		716	530	1090		692	
15	RuP(N3-PPY)	3350	1601		723	502	1038			2010
16	RuB(N3-PPY)	3501	1602		726	502	1084			2015

711 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 580 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1060 cm^{-1} could be assigned to the counter anion ClO_4^-. In the FT-IR spectra of the complex $[Ru(bpy)_2((E)$-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-pyrene-4-amine)] $(ClO_4)_2$, RuB(PR-PPY), the peak at 3027 cm^{-1} comprises N-H bands and the peak at 2980 cm^{-1} comprises C-H bands. The peak at 1604 cm^{-1} belongs to the C = N stretching and the peak at 721 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 580 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1060 cm^{-1} could be assigned to the counter anion ClO_4^-.

(E)-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine **(FN-PPY)**, fluorescent Schiff base polypyridine ligand was synthesized originally. The ^{1}H-NMR spectrum of the monopodal ligand FN-PPY shows the chemical shifts at 9.0 and 8.15 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 7.8 ppm are assigned to the protons of the aromatic groups. Schiff base imine HC = N band observed at 8.9 ppm. –NH group shows a chemical shift at 13.6 ppm. CH_2-O group shows the chemical shift at 5.15 ppm, respectively. In the FT-IR spectra of the ligand FN-PPY the peak at 3024 cm^{-1} comprises the both N-H and C-H bands. The peak at 1608 cm^{-1} belongs to the C = N stretching, the peak at 1242 cm^{-1} belongs to C-O-C ether bond and the peak at 802 cm^{-1} belongs to the pyridine groups.

In the FT-IR spectra of the complex $[(Ru(phen)_2)_2((E)$-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine)] $(ClO_4)_4$, RuP(FN-PPY), the peak at 3402 cm^{-1} comprises N-H bands and the peak at 2922 cm^{-1} comprises C-H bands. The peak at 1650 cm^{-1} belongs to the C = N stretching and the peak at 750 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 580 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1033 cm^{-1} could be assigned to the counter anion ClO_4^-. In the FT-IR spectra of the complex $[(Ru(bpy)_2)_2((E)$-N-(4-((4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)methyl)benzylidene)-1,10-phenanthroline-5amine)] $(ClO_4)_4$, RuB(FN-PPY) the peak at 3310 cm^{-1} comprises N-H bands and the peak at 2921 cm^{-1} comprises C-H bands. The peak at 1606 cm^{-1} belongs to the C = N stretching and the peak at 722 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 580 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1069 cm^{-1} could be assigned to the counter anion ClO_4^-.

2-(4-(Bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, BR-PPY, bromomethyl-substitued polypyridine ligand was synthesized originally. The ^{1}H-NMR spectrum of the monopodal ligand BR-PPY shows the chemical shifts at 8.9 and 8.4 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 7.8 ppm are assigned to the protons of the aromatic groups. –NH group shows a chemical shift at 13.75 ppm and CH_2-Br group shows a chemical shift at 5.15 ppm. In the FT-IR spectra of the ligand BR-PPY the peak at 3081 cm^{-1} comprises the both N-H and C-H bands. The peak at 1744 cm^{-1} belongs to the C = N stretching, and the peak at 800 cm^{-1} belongs to the pyridine groups.

In the FT-IR spectra of the complex $[Ru(phen)_2$(2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,

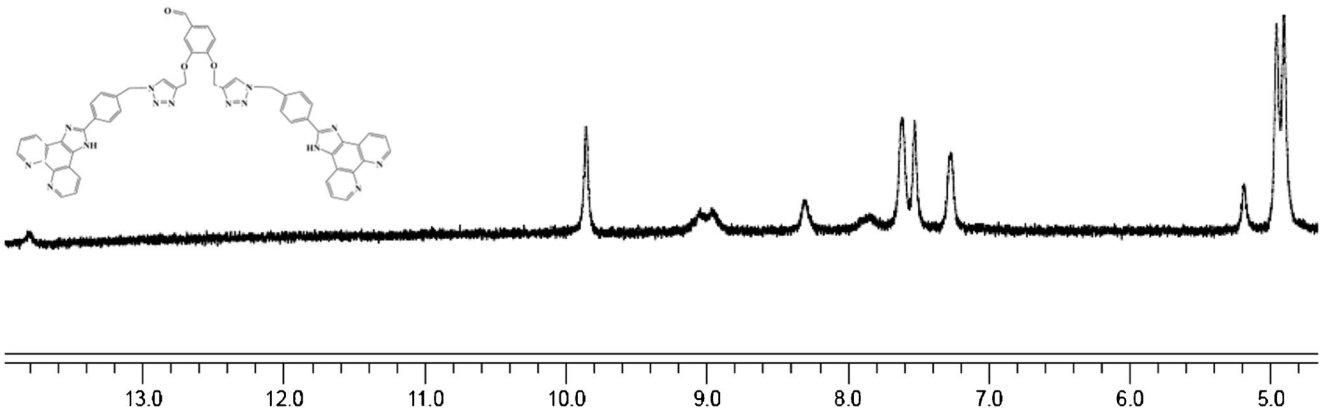

Fig. 4 ^{1}H-NMR spectrum of BA-DIPPY

10]phenanthroline)] $(ClO_4)_2$, RuP(BR-PPY), the peak at 3480 cm^{-1} comprises the both N-H and C-H bands. The peak at 1633 cm^{-1} belongs to the C = N stretching and the peak at 715 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 530 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1085 cm^{-1} could be assigned to the counter anion ClO_4^-. In the FT-IR spectra of the complex $[Ru(bpy)_2$(2-(4-(bromomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] $(ClO_4)_2$, RuB(BR-PPY) the peak at 3402 cm^{-1} comprises the both N-H and C-H bands. The peak at 1610 cm^{-1} belongs to the C = N stretching and the peak at 716 cm^{-1} belongs to the pyridine groups. The proof peak of the complexation observed at 530 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1090 cm^{-1} could be assigned to the counter anion ClO_4^-.

2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (N3-PPY), azidomethyl-substitued polypyridine ligand was synthesized originally. The ^{1}H-NMR spectrum of the monopodal ligand N3-PPY shows the chemical shifts at 9.0 and 8.3 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 7.78 ppm are assigned to the protons of the aromatic groups. –NH group shows a chemical shift at 13.70 ppm and CH_2-N_3 group shows a chemical shift at 2.6 ppm. In the FT-IR spectra of the ligand N3-PPY the peak at 3080 cm^{-1} comprises the both N-H and C-H bands. The peak at 2150 cm^{-1} belongs to the N = N stretching and the peak at 1735 cm^{-1} belongs to the C = N stretching, and the peak at 804 cm^{-1} belongs to the pyridine groups.

In the FT-IR spectra of the complex $[Ru(phen)_2$(2-(4-(azidomethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] $(ClO_4)_2$, RuP(N3-PPY), the peak at 3350 cm^{-1} comprises the both N-H and C-H bands. The peak at 1601 cm^{-1} belongs to the C = N stretching and the peak at

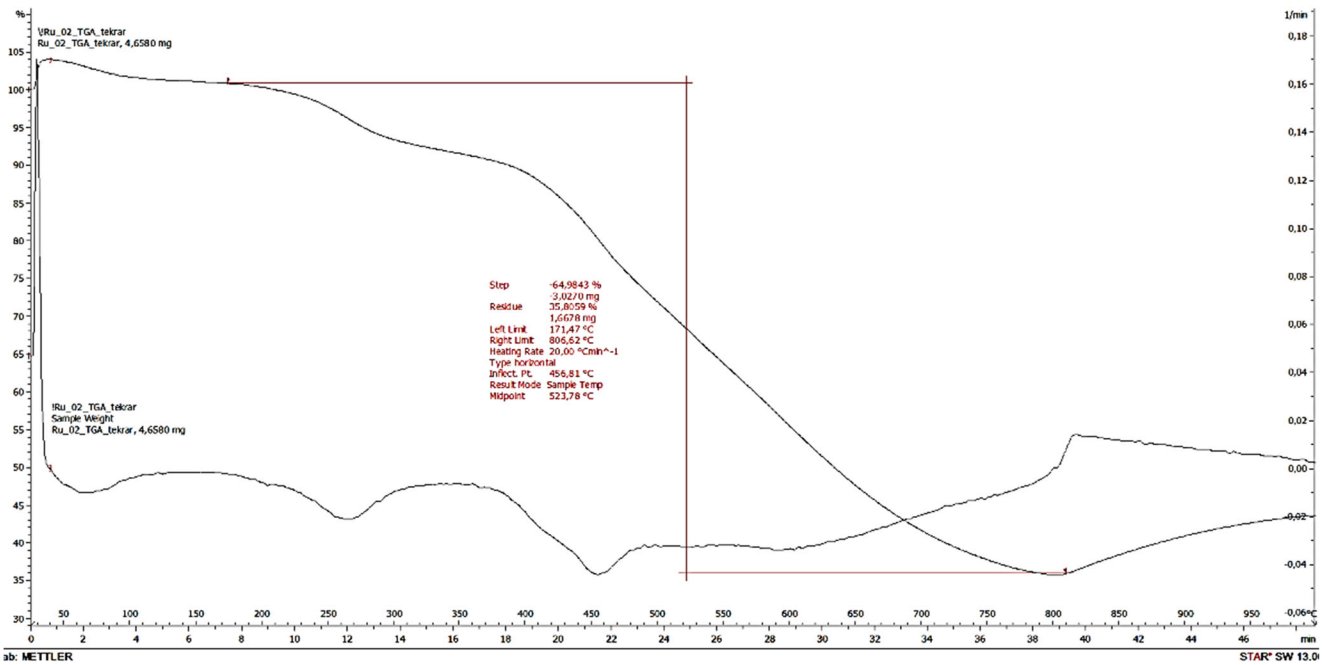

Diagram 1 TG/ DTA diagram of RuP(PR-PPY) polypyridine complex

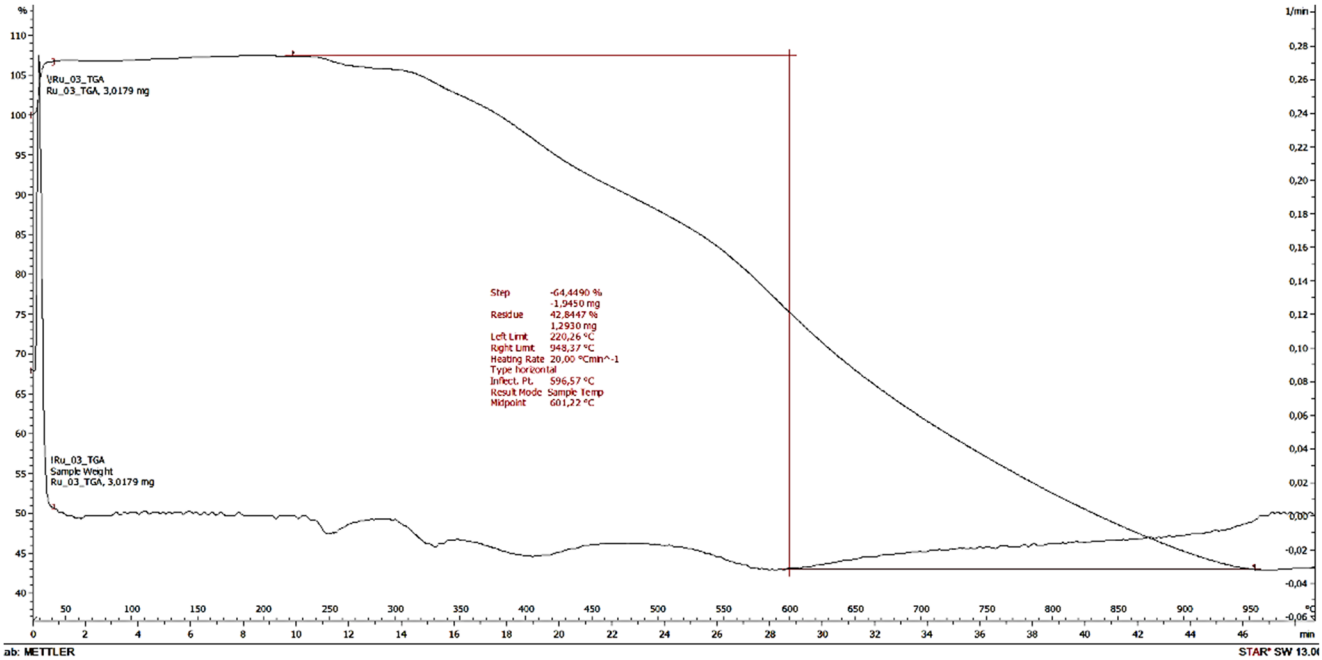

Diagram 2 TG/ DTA diagram of RuB(PR-PPY) polypyridine complex

723 cm^{-1} belongs to the pyridine groups. In addition, The proof peak of the complexation observed at 502 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1038 cm^{-1} could be assigned to the counter anion ClO_4^-. In the FT-IR spectra of the complex $[Ru(bpy)_2(2\text{-}(4\text{-}(azidomethyl)phenyl)\text{-}1H\text{-}imidazo[4,5\text{-}f][1,10]phenanthroline)](ClO_4)_2$, RuB(BA-PPY) the peak at 3501 cm^{-1} comprises the both N-H and C-H bands. The peak at 1602 cm^{-1} belongs to the C = N stretching and the peak at 726 cm^{-1} belongs to the pyridine groups. The proof peak of the complexation observed at 502 cm^{-1} which could be assigned to Ru(II)-N stretching. A strong bands at 1084 cm^{-1} could be assigned to the counter anion ClO_4^-.

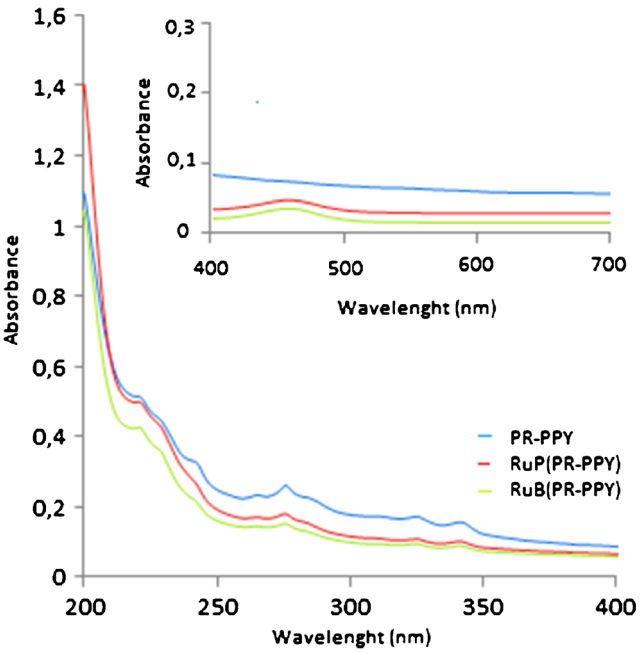

Fig. 5 Electronic absorption spectra of pyrene-appended polypyridine ligand PR-PPY and Ruthenium(II) complexes in acetonitrile medium at room temperature

3,4-bis[(4-(metoxy)-1,2,3-triazole)1-methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline)] benzaldehyde (BA-DIPPY) aldehyde-ended triazole containing polypyridine ligand was synthesized originally as a part of 'click chemistry'. As seen in Fig. 4, the ^{1}H-NMR spectrum of the monopodal ligand BA-DIPPY shows the chemical shifts at 8.85 and 8.30 ppm are assigned to the protons of the phenanthroline ring. The chemical shifts around 8.10–7.25 ppm are assigned to the protons of the aromatic groups. Aldehyde HC = O band observed at 9.81 ppm. –NH group shows a chemical shift at 13.75 ppm and CH_2-O group shows a chemical shift at 4.8 ppm. In the FT-IR spectra of the ligand BA-DIPPY the peak at 3243 cm^{-1} comprises the both N-H and C-H bands. The peak at 1725 cm^{-1} belongs to the C = O stretching, the peak at 1225 cm^{-1} belongs to C-O-C ether bond and the peak at 809 cm^{-1} belongs to the pyridine groups.

Magnetic and Thermal Properties

The magnetic susceptibility measurements of the Ruthenium(II)-bridged polypyridine complexes shows that all the complexes have diamagnetic property. It is seen that the complexes are represented by the electronic structure of $t_2g^6eg^0$. The magnetic data for the complexes show good harmony with the high spin d^6 metal ion in an octahedral structure [23].

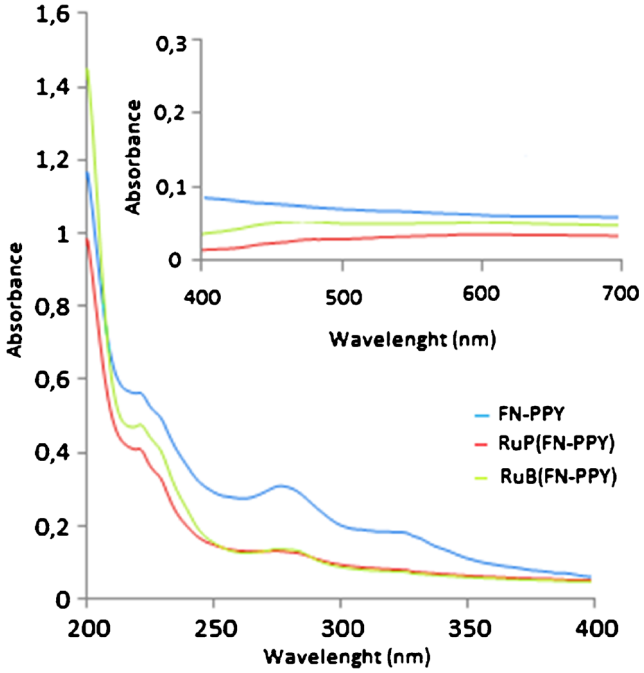

Fig. 6 Electronic absorption spectra of phenanthroline-appended polypyridine ligand FN-PPY and Ruthenium(II) complexes in acetonitrile medium at room temperature

The complexes **RuP(PR-PPY)**, **RuB(PR-PPY)** have also been thermally investigated and their plausible degradation schemes are presented in Diagram 1 and 2. The thermograms of the complexes show about five-step weight losses at the temperature 40 to 1000 °C. The first weight loss at 50 to 170 °C was attributed to the removal of physically adsorbed water, the second region between 250 to 350 °C was due to removal of coordinated water. The third region between 250 to 500 °C was due to the combustion of amine and oxygen-carrying functionalities, those not used for attachment of the Ruthenium(II) complex. The forth region at 400 to 650 °C was related to the perchlorate removal. And fifth region at 450 to 900 °C was attributed to the decomposition of the ligands of the Ruthenium complexes. The residues were carbon black, some metal oxides and chlorides as RuO_2, Ru_2O_3, $RuCl_3$ [24]. The observed weight losses for all complexes are in good harmony with the calculated values.

Photophysical Properties

Electronic Absorption Spectra

The Uv-Vis absorption spectra of polypyridine ligands and their Ruthenium(II)-bridged complexes have been recorded in acetonitrile solution, at a working concentration of 1×10^{-6} mol/L between 200 and 800 nm. The ligand PR-PPY and the complexes RuP(PR-PPY) and RuB(PR-PPY) exhibit absorption bands in the UV region at 200–300 nm and the ligands FN-PPY and the complexes RuP(FN-PPY) and RuB(FN-PPY) exhibit absorption bands at 200–270 nm. These bands are attributed to intraligand π–π* transitions (ILCT) centered on the 2,2-bipyridine / 1,10-phenanthroline ligands. The shoulders appearing at 328–345 nm for the complexes of PR-PPY ligand and 276–324 nm for the complexes of FN-PPY ligand are attributed to the imidazo[4,5-*f*][1,10]phenanthroline-centered transition. The complexes RuP(PR-PPY), RuB(PR-PPY, RuP(FN-PPY) and RuB(FN-PPY) exhibit a broad absorption bands at 485, 475, 476, and 453 nm, respectively, assignable to the spin-allowed MLCT (d_π–π*) transition (Figs. 5 and 6).

Maximum wavelenghts (λ_{max}) and maximum absorbance values (A_{max}) and calculated molar absorptivity values (**ε**) are given in Table 3, (**$\varepsilon = A_{max}/l.C$** (**l** = 1 cm) for the Podal ligands and complexes (a) and for the Schiff base ligand and complexes. According to the molar absorptivity values, pyrene and phenanthroline chromophore-appended Schiff base compounds have strong molar absorptivity.

The singlet excited state of a metal-to-ligand charge transfer transition (MLCT) consists of overlapping d_π(Ru)-π*(bpy) / d_π(Ru)-π*(L) components. The MLCT

Table 3 Maximum wavelenghts (λ_{max}) and maximum absorbance values (A_{max}) and calculated molar absorptivity values (ε) of the Podal ligands and complexes (1×10^{-4} M) (a) and Schiff base ligand and complexes (1×10^{-6} M) (b) in acetonitrle medium

(a)

	λ_{max} (278 nm)	ε ($M^{-1}.cm^{-1}$)		λ_{max} (265 nm)	ε ($M^{-1}.cm^{-1}$)
O-DIPPY	0.1184	1184	RuP(O-DIPPY)	0.1001	1001
P-DIPPY	0.1166	1166	RuP(P-DIPPY)	0.1056	1056
TZ-PPY	0.1506	1506	RuP(TZ-PPY)	0.1193	1193

(b)

	λ_{max} (275 nm)	ε ($M^{-1}.cm^{-1}$)
PR-PPY	0.2575	257,500
FN-PPY	0.3087	308,700
RuP(PR-PPY)	0.1802	180,200
RuP(FN-PPY)	0.1315	131,500
RuB(PR-PPY)	0.1521	152,100
RuB(FN-PPY)	0.1368	136,800

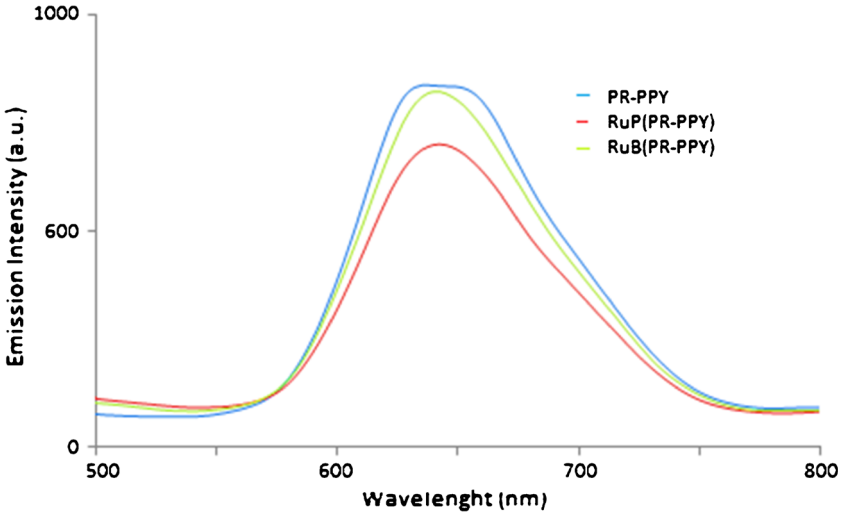

Fig. 7 Fluorescence spectra of pyrene-appended polypyridine ligand PR-PPY and Ruthenium(II) complexes in acetonitrile medium at room temperature with the concentration of 1×10^{-6} M

bands of the complexes RuB(PR-PPY) and RuB(FN-PPY) with bpy as ancillary ligands (λmax =475 and 453 nm, respectively) and that of the complexes RuP(PR-PPY) and RuP(FN-PPY) with phen as ancillary ligands (λmax = 485 and 476 nm, respectively) are bathochromically shifted with respect to that of $[Ru(bpy)_3]^{2+}$ (λmax = 451 nm) and $[Ru(phen)_3]^{2+}$ (λmax = 446 nm) which can be attributed to the extension of the π-framework in the ligands. The MLCT absorption maxima of the four complexes are redshifted compared with that of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ [25] because pyrene and phenanthroline-appended polypyridine ligands have larger π-frameworks.

Fluorescence Spectra

The fluorescence spectra of the polypyridine ligands and complexes have been recorded in acetonitrile solution at a working concentration of 1×10^{-6} mol/L with excitation wavelenght 275 nm in the range 200 and 800 nm.

The emission maxima of the pyrene-appended polypyridine ligand PR-PPY is observed at λems = 616 nm and the phenanthroline-appended polypyridine ligand FN-PPY is observed at λems = 668 nm. And the emission maxima of the mononuclear complexes RuP(PR-PPY) and RuB(PR-PPY) are observed at λems = 646 nm. The emission maxima of the dinuclear complexes RuP(FN-PPY) and RuB(FN-PPY) are observed at λems = 685 nm.

When look at their fluorescence spectra, it can be observed that the fluorescence intensities of the ligands are higher than their metal complexes (Figs. 7 and 8). This is because of quenching effect of Ruthenium(II) metal on chromophore groups. The emission of Ruthenium(II) species is assigned to the MLCT state involving the bridging ligand as the acceptor site and the emitting MLCT state of the acceptor ligand does not extend over to the core of the bridging ligand, but it only involves the phenyl group directly connected to the imidazo[4,5-*f*][1,10]phenanthroline moiety.

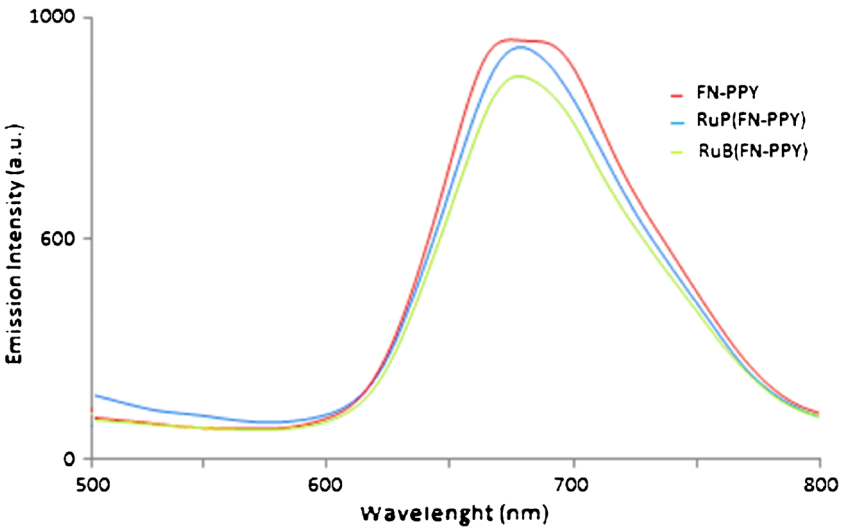

Fig. 8 Fluorescence spectra of phenanthroline-appended polypyridine ligand FN-PPY and Ruthenium(II) complexes in acetonitrile medium at room temperature with the concentration of 1×10^{-6} M

Conclusion

In this context, novel different substitued polypyridine ligands are presented. Pyrene-appended polypyridine ligand PR-PPY and phenanthroline-appended polypyridine ligand FN-PPY are synthesized by means of Schiff base condesation reaction. BA-PPY has been reacted with 1-pyrene(methylamine) hydrochloride for PR-PPY formation and 1,10-phenanthroline-5amine for FN-PPY formation. BA-PPY is also a novel polypyridine ligand. These highly fluorescent Schiff base polypyridine ligands have remarkable photophysical behaviours. And also, all ligands contain a potential N,N-donor group capable of coordinating with the Ruthenium(II) metal. The BA-DIPPY polypyridine ligand has been synthesized by part of 'Click Chemistry'. As mentioned in experimental part the synthesis steps contain different substitued novel BR-PPY and N3-PPY polypyridine ligands, respectively. The characterization were performed by UV-Vis Spectroscopy, Fluorescence Spectroscopy, FT-IR Spectroscopy, ^{1}H-NMR Spectroscopy, Elemental Analysis, TG/DTA Analysis, Magnetic Susceptibility.

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