

Synthesis and Characterization of mono-, di- and trinuclear Ruthenium(II) complexes

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ABSTRACT : The synthesis of mono-, di- and trinuclear series of $[\{Ru(phen)_2(L1)\}(ClO_4)_2]$ (R1), $[\{Ru(phen)_2(L2)\}(ClO_4)_4]$ (R2) and $[\{Ru(phen)_2(L3)\}(ClO_4)_6]$ (R3) heteroleptic oligo-ruthenium(II) polypyridine complexes is undertaken. The synthesized organic precursors, 2-benzyloxy-1-formylnaphthalene (P1) and 1,4-bis(1-formyl-2-naphthylloxymethyl)benzene (P2), are characterized by single crystal X-ray diffraction pattern: Monoclinic P2₁/c. The divergent method has been adopted for synthesizing these heteroleptic oligo ruthenium(II) polypyridine complexes via pre-synthesized organic precursors and ligands followed by characterization.

Keywords: Imidazo[4,5-f][1,10]phenanthroline, heteroleptic oligoRuthenium(II) complexes, Supramolecules, Imidazole moiety

1 INTRODUCTION

The scientists are being exuberant of ruthenium (II) polypyridyl complexes for their properties of high stability in various redox stages, long-lived excited states and good photoluminescence efficiencies [1]. The sequel of these properties has influenced their outstanding performance in the wide range of applications such as artificial light harvester [2], photoluminescent sensors or switches [3], bioimaging [4], metal-lodendrimers [5], supramolecular [6], intramolecular energy and electron transfer agents [7]. In addition, these complexes have eminent properties as high cytotoxicity [8] accomplished with less noxious toward healthy tissues, various oxidation states under physiological conditions and photoreaction with DNA [9]. As the pH acts as a main influencer in the physiological function in various biological and chemical processes, the detection of the pH using these complexes is inevitable. Among various pH sensing entities the imidazole is one of the excellent pH sensing moiety and the orbital energy can be accessed easily by varying the pH. The imidazole containing ligands have been distinguished as characteristically poor π -acceptors and better π -donors whereas the pyridine-, pyrazine-, and pyrimidine based ligands have shown relatively low-lying π^* orbitals and therefore they act as good π -acceptors [10]. Hence, we have designed and synthesized the dendrimer based mono-, di- and trinuclear series of heteroleptic oligo ruthenium(II) polypyridine complexes. Most of them have been paid attention predominantly of containing ruthenium(II) centers in which the fluorescent groups are connected through little flexible ether linker to avoid the direct interaction with metal ions. This has led to drastic conformation change and to quenching of the fluorescence of the ruthenium

complexes. The heteroleptic ligand complexes exuded the special role in the wide range of applications due to the broadened MLCT absorption with increased intensity [11]. Almost all Ru(II) heteroleptic complexes reside in Kasha's rule [12] and exhibit a single emissive excited state. The desired spectroscopic, chemical and photophysical properties can easily be obtained by providing suitable ligand frameworks. Hence we have scrutinized the entire design into a well conjugated system which would lead us to modifying the polypyridine ligands and can give out distinguished properties of the modified complexes. Based on this, naphthalene units are covalently attached on to ligand framework in order to transfer efficiently the singlet excitation energy to the appended metal complex. Also, by increasing the extended conjugation of electron delocalisation in the triplet level by adding naphthalene unit through imidazole linker, the triplet lifetime of the complexes would be increased [13]. As the imidazole moieties stiffen the connection between the naphthyl moiety and the MLCT chromophore (Ru(II) coordination center) the redundant direct interactions between chromophores would be enabled. The most elegant way of identifying the position of metal coordination with the imidazole containing ligand is of the non emissive nature of coordinated imidazole when coordinated to the metal ions and the uncoordinated metal ion, particularly Ru(II) ion, would be a good emitter [14].

In this paper, we discuss about the synthetic strategy of heteroleptic oligo-Ru(II) complexes and their characterization for the pH-induced luminescent sensors and pH luminescent switches. Hence we deal the heteroleptic oligo-ruthenium (II) polypyridine complexes as a chromophore with ligands containing pH sensing imidazole moiety.

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2 EXPERIMENTAL SECTION

2.1 Materials and Reagents: 1,10-Phenanthroline monohydrate, ruthenium(III) chloride hydrate, 2-hydroxynaphthaldehyde and 1,4-bis(bromomethyl)benzene were purchased from Sigma Aldrich and used as received. 2,4,6-tris(bromomethyl)mesitylene, 1,10-phenanthroline-5,6-dione and $\text{Ru}(\text{phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ were synthesized according to method described in the literature [15].

2.2 Physical measurements: NMR spectra were recorded on a Bruker Avance III 500MHz multi nuclei solution NMR spectrometer with deuterated solvents and all chemical shifts are given relative to TMS. Mass spectra were recorded on a Micromass Quattro-II Triple Quadrupole ESI Mass spectrometer. Single crystal XRD patterns were obtained using Bruker X8 KAPPA APEXII single crystal X-ray diffractometer.

2.3 Synthesis of organic precursors

2-benzyloxy-1-formylnaphthalene (P1) : To a solution of 2-hydroxynaphthaldehyde (2.24 g, 13 mmol) in acetonitrile, cesium carbonate (4.25 g, 13 mmol) was added and stirred for 15 min under nitrogen atmosphere. To the above reaction mixture, a solution of benzyl chloride (1.5 ml, 13 mmol) in acetonitrile was added dropwise for 15 min and refluxed for 2 days under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and flash-evaporated. The resulting crude solid was washed thoroughly with ethanol and tetrahydrofuran (THF). The obtained solid was dissolved in chloroform and washed with copious amount of water. The organic extract was dried over the sodium sulfate and filtered. The chloroform extract was flash evaporated and the resulting product was recrystallized in hot chloroform-ethanol (1:1) mixture to obtain colourless (3 g, 11.4 mmol, 88% yield) crystals. The ORTEP diagram of this compound obtained from single crystal XRD data is shown in Fig. (1)[16]. ^1H NMR (500MHz, CDCl_3 , 298K): δ 5.3 (2H, s), 7.32 (1H, d), 7.36 (4H, d), 7.4 (1H, t), 7.44 (1H, t), 7.61 (1H, t), 8.01 (1H, d), 9.28 (1H, d), 10.97 (1H, s). ^{13}C NMR (125MHz, CDCl_3 , 298K): 71.56, 114.7, 117.3, 124.9, 125, 127.4, 128.23, 128.43, 128.74, 128.82, 129.9, 131.6, 135.97, 137.45, 163.181, 192.047. ESI MS: m/z 263.13[M+H] $^+$.

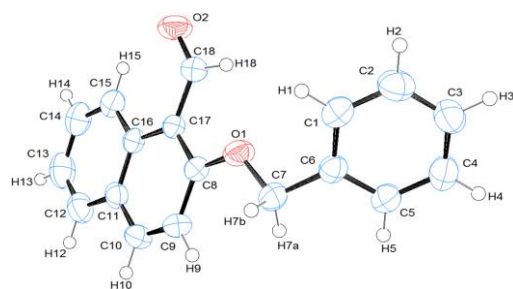


Figure 1. ORTEP diagram for organic precursor P1

1,4-Bis(1-formyl-2-naphthylloxymethyl)benzene (P2) : To a solution of 2-hydroxynaphthaldehyde (2.09 g, 12.1 mmol) in dry DMF, potassium carbonate (1.7 g, 12.1 mmol) was added and stirred for 30 min under nitrogen atmosphere. A solution of 1,4-bis(bromomethyl)benzene (1.6 g, 6 mmol) in DMF was added dropwise for 20 min to the above reaction mixture and stirred at 70°C for 2 days under nitrogen atmosphere. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The resulting crude product was dissolved in dichloromethane and washed thoroughly with water. Finally the organic extract was dried over sodium sulfate and filtered. The dichloromethane extract was flash evaporated and the resulting product was recrystallized in hot ethanol to obtain colorless (2.2 g, 4.93 mmol, 81.3% yield M.Pt 235°C) crystals. The ORTEP diagram of this compound obtained from single crystal XRD data is shown in Fig. (2) [17]. ESI MS: m/z 274 [M-C $_{11}$ H $_7$ O $_2$] $^+$, 469 [M+Na] $^+$.

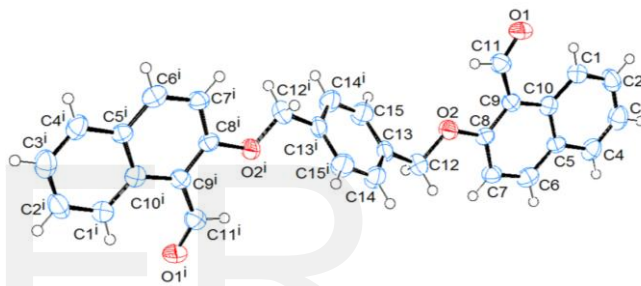
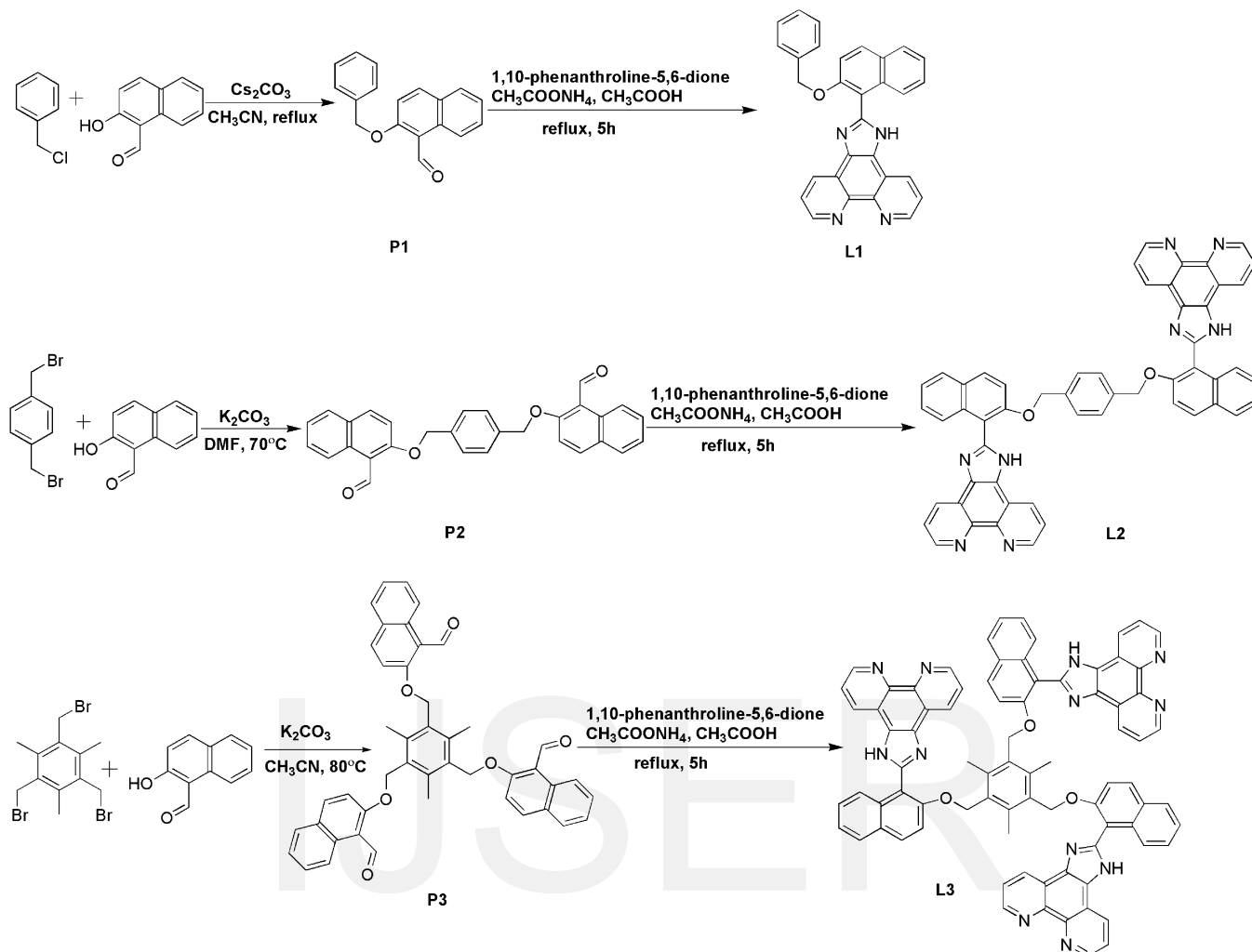


Figure 2. ORTEP diagram for organic precursor P2

2,4,6-Trimethyl-1,3,5-tris(1-formyl-2-naphthylloxymethyl)benzene (P3): A solution of 2-hydroxynaphthaldehyde (1.9 g, 11.3 mmol) in dry acetonitrile was slowly added to a suspension of potassium carbonate (1.6 g, 11.3 mmol) in acetonitrile and stirred for 30 min under nitrogen atmosphere. Another solution of 2,4,6-tris(bromomethyl)mesitylene (1.5 g, 3.76 mmol) in dry acetonitrile was added dropwise for 20 min to the above reaction mixture and stirred at 80°C for 3 days under nitrogen atmosphere. The reaction mixture was cooled to room temperature (30 °C) and flash evaporated. The resulting crude product was dissolved in chloroform and washed thoroughly with water and the extracted organic layer was dried over sodium sulfate and filtered. The chloroform extract was flash evaporated and the resulting product was recrystallized in dichloroform-ethanol (1:1) mixture to obtain white product (2 g, 3 mmol, 79% yield). ^1H NMR (500MHz, CDCl_3 , 298K): δ 10.84 (3H, s), 9.3 (3H, d), 8.16 (3H, d), 7.84 (3H, d), 7.66 (3H, t), 7.54 (3H, t), 7.47 (3H, d), 5.45 (6H, s), 2.57 (9H, s). ^{13}C NMR (125MHz, CDCl_3 , 298K): δ 16.34, 66.8, 113.69, 117.29, 124.94, 125.04, 128.28, 130.02, 131.59, 134.68, 135.97, 137.65, 163.43, 191.89. ESI MS: m/z 695 [M+Na] $^+$.



Scheme 1. Synthesis of organic precursors and organic ligands.

2.4 Synthesis of organic ligands

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

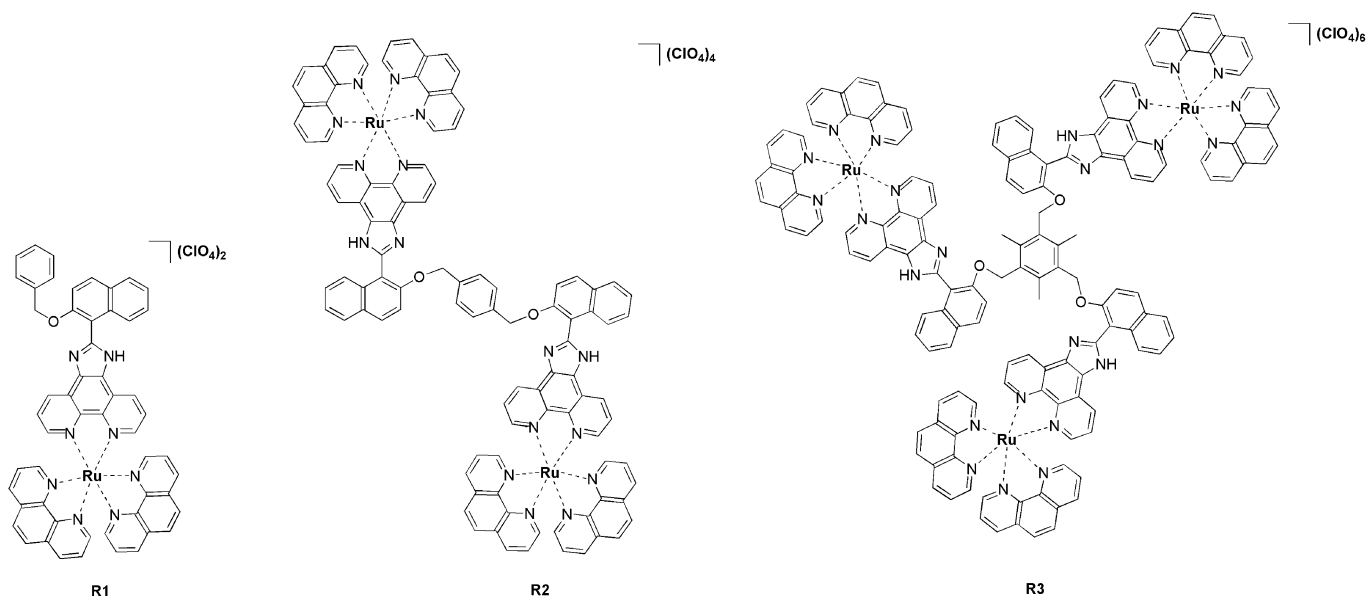
(L1): To a solution of 1,10-phenanthroline-5,6-dione (1.2 g, 5.7 mmol) and ammonium acetate (8.7 g, 114 mmol) in hot glacial acetic acid was added a solution of P1 (1.5 g, 5.7 mmol) in glacial acetic acid slowly for 30 min with stirring, refluxed for 5 h, cooled to room temperature, and poured in water. Then aqueous ammonia (25%) was added slowly with stirring whereupon a pale yellow compound precipitated out. The product was filtered, washed with copious amount of water and dried *in vacuo* (1.9 g, 4.2 mmol, 73.4% yield). ¹H NMR (500MHz, CDCl₃, 298K): δ(ppm) 5.28 (s, 1H), 7.4(multiplet, 5H), 7.6(d, H), 7.74(t, 2H), 7.83(t, 2H), 7.85(d, 1H), 7.96(d, 1H), 9.05(d, 2H), 9.12(d, 2H). ¹³C NMR (125MHz, CDCl₃, 298K): δ (ppm) 72.764, 114.38, 116.88, 124.13, 124.79, 126.83, 128.1, 128.22, 128.34, 128.85, 129.2, 130.03, 132.14, 132.64, 135.98, 147.57, 154.86, 157.07. ESI MS: m/z 453.20[M+H]⁺.

1,4-Bi(2-oxymethyl-1-yl(1H-imidazo-2-yl)[4,5-f][1,10]phenanthroline)naphthyl)benzene (L2)

This ligand was synthesized in a manner similar to that described for L1, with P2 (1.3 g, 2.9 mmol) instead of P1 (1.5 g, 5.7 mmol). The compound was obtained as a pale yellow product (1.9 g, 2.3 mmol, 79% yield). ¹H NMR (500MHz, DMSO-d₆, 298K): δ(ppm) 13.56 (2H, s), 9.02 (4H, d), 8.84 (4H, d), 8.06 (2H, d), 7.94 (4H, d), 7.80 (4H, t), 7.58 (4H, t), 7.45 (4H, d), 7.23 (2H, s), 5.21 (4H, s). ¹³C NMR (125MHz, DMSO-d₆, 298K): δ(ppm) 70.57, 114.98, 115.55, 123.77, 124.63, 125.02, 127.54, 127.93, 128.52, 128.91, 129.92, 132.05, 133.63, 136.89, 143.89, 147.19, 148.17, 155.39. ESIMS: m/z 274.40[M-C₂₃H₁₃N₄O-C₁₂H₆N₃]⁺, 362.47[M-C₃₁H₂₁N₄O]⁺, 450.47[M-C₂₄H₁₅N₄O]⁺, 827.27 [M]⁺.

2,4,6-Trimethyl-1,3,5-tris(2-oxymethyl-1-yl(1H-imidazo-2-yl)[4,5-f][1,10]phenanthroline)naphthyl)benzene (L3)

This ligand was synthesized in a manner similar to that described for L1, with P3 (1.3 g, 1.9 mmol) instead of P1 (1.5 g, 5.7 mmol). The compound was obtained as pale yellow product (1.7 g, 1.4 mmol, 70% yield). ¹H NMR (500MHz, DMSO-d₆, 298K): δ(ppm) 13.45



Scheme 2. Structure of series of Ru(II) heteroleptic complexes.

(3H, s), 8.89(6H, d), 8.65 (6H, d), 7.80 (3H, d), 7.68(6H, d), 7.51 (6H, t), 7.23 (6H, t), 7.11 (3H, d), 4.6 (6H, s), 2.18(9H, s). ^{13}C NMR (125MHz, DMSO- d_6 , 298K): δ (ppm) 15.35, 70.35, 116.01, 118.78, 123.66, 123.76, 124.74, 127.67, 128.25, 128.60, 130.10, 131.88, 132.02, 133.63, 135.67, 143.88, 148.15, 148.20, 155.20. ESIMS: m/z 1243.40[M+H] $^+$.

2.5 Synthesis of heteroleptic Ru(II) complexes

[[Ru(phen) $_2$ (L1)](ClO $_4$) $_2$ (R1): To a hot solution of L1 (1.2 g, 2.7 mmol) in ethylene glycol (20 ml) under stirring Ru(phen) $_2$ Cl $_2$ ·2H $_2$ O (1.7 g, 3 mmol) was added slowly and then refluxed for 2 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature, poured into copious amount of water and filtered. An aqueous solution of sodium perchlorate was added slowly to the filtrate with stirring where dark reddish precipitate separated out. The precipitate was filtered, dried and recrystallized in hot methanol (2.6 g, 2.34 mmol, 88% yield). ESIMS: m/z 1012 [M-ClO $_4$] $^+$, 778 [(M-2)-(ClO $_4$ +C $_{17}$ H $_{13}$ O)] $^+$, 702 [M-(2ClO $_4$ +C $_{15}$ H $_5$ O)] $^+$, 503 [(M+2)-(2ClO $_4$ +C $_{29}$ H $_{21}$ N $_2$ O)] $^+$, 412 [M-(2ClO $_4$ +C $_{25}$ H $_{16}$ N $_6$ Ru)] $^+$.

[[Ru(phen) $_2$ (L2)](ClO $_4$) $_4$ (R2): This complex was synthesized in a similar manner to that described for R1, with L2 (1.1 g, 1.3 mmol) instead of L1 (2.4 g, 1.1 mmol, 84% yield). ESIMS: m/z 1976 [M-H $_8$ ClO $_8$] $^+$, 1831[M-(3ClO $_4$ +H $_2$ O)] $^+$, 1712 [(M-2)-(4ClO $_4$ +2H $_2$ O)] $^+$, 1202 [M-C $_{55}$ H $_{40}$ N $_8$ O $_2$ Ru] $^+$, 974 [M-2ClO $_4$] $^{2+}$, 707 [M-C $_{63}$ H $_{41}$ N $_8$ Cl $_4$ O $_{18}$ Ru] $^+$, 554 [M-C $_{73}$ H $_{46}$ Cl $_4$ N $_{10}$ O $_{18}$ Ru] $^+$, 503 [M-C $_{77}$ H $_{48}$ C $_{14}$ N $_{10}$ O $_{18}$ Ru] $^+$, 412 [M-(4ClO $_4$ +C $_{55}$ H $_{37}$ N $_8$ ORu)] $^{2+}$.

[[Ru(phen) $_2$ (L3)](ClO $_4$) $_6$ (R3): This complex was synthesized in a manner similar to that described for R1, with L3 (1.2 g, 1 mmol) instead of L1 (2.5 g, 0.7 mmol, 80% yield). ESIMS: m/z

3089 [M-(ClO $_4$ +H $_2$ O)] $^+$, 2971 [M-(2ClO $_4$ +3H $_2$ O)] $^+$, 2411 [M-(6ClO $_4$ +H $_2$ O+C $_{12}$ H $_{10}$ N $_2$ O)] $^+$, 2395 [M-(3ClO $_4$ +3H $_2$ O+C $_{31}$ H $_{20}$ N $_6$)] $^+$, 1105 [M-(6ClO $_4$ +3H $_2$ O+C $_{23}$ H $_{16}$ N $_4$ O)] $^{2+}$, 1005 [M-C $_{13}$ H $_{14}$ N $_2$ O)] $^{3+}$, 923 [(M-3)-(4ClO $_4$ +3H $_2$ O)] $^+$, 823 [M-(5ClO $_4$ +3H $_2$ O+ C $_{12}$ H $_{13}$ N $_2$ O)] $^{3+}$, 753 [M+(6ClO $_4$ +3H $_2$ O+C $_{13}$ H $_{16}$ N $_2$ ORu)] $^{3+}$, 751[M-(6ClO $_4$ +3H $_2$ O+C $_{21}$ H $_{15}$ N $_4$)] $^{3+}$, 708 [M-(2ClO $_4$ + C $_{12}$ H $_{16}$ N $_2$ O)] $^{4+}$, 503 [M-(3ClO $_4$ +3H $_2$ O+C $_{23}$ H $_{10}$ N $_4$ O)] $^{5+}$, 412 [M-(5ClO $_4$ +H $_2$ O+C $_{15}$ H $_{13}$ N $_2$ O)] $^{6+}$.

3 Conclusion : We have disclosed dendrimer based novel series of naphthalene containing imidazo[4,5- f][1,10]phenanthroline oligo ruthenium(II) polypyridine complexes through divergent method. The organic precursors and ligands are synthesized and characterized by X-ray diffraction studies and the ligands are complexed with Ru(II) metal ions. These oligo ruthenium(II) complexes with the acidic imidazole moieties have a capability to do well in anion sensing applications. Also, the applications of these complexes as pH luminescence sensors, for intercalation and photocleavage of DNA and for cytotoxicity against cancer cells as anticancer agents are under investigation.

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- [17] Crystallographic data for compound P2 in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC982183. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].