FT-IR spectral studies

FT-IR spectra of the parent ligands and their Ru(II) complexes were recorded in a KBr disc in the region 4000-400 cm^{-1}. The main stretching frequencies of the IR spectra of the ligands and the complexes are indicated in Figs. SI 1-6 and selected characteristic frequencies are indicated in Table SI 1. Detailed comparison of the absorption peaks band around 1608-16037 cm^{-1} (s) cm^{-1}, and 1582-1592 cm^{-1} (s), which is assigned to −N=C− and −C=C− stretching vibrations of phenanthroline moiety in the free phenanthroline derivatives (L^{1-6}) exhibit slight shift, confirming coordination to the range around 1548-1626 and 1567-1599 cm^{-1}. The shift in stretching vibration absorption band of both C= Cand C= N, confirming coordination of Ru^{2+} ion via the nitrogen atoms of the heterocyclic ligand and is consistent with previously reported ruthenium-pyridyl stretching mode [1-3]. The coordination of the nitrogen atoms of the ligands was supported by the appearance of new weak bands at 452-531 cm^{-1} can be assigned to ν(RuN), confirming the coordination of both nitrogen atoms to ruthenium centre [4].

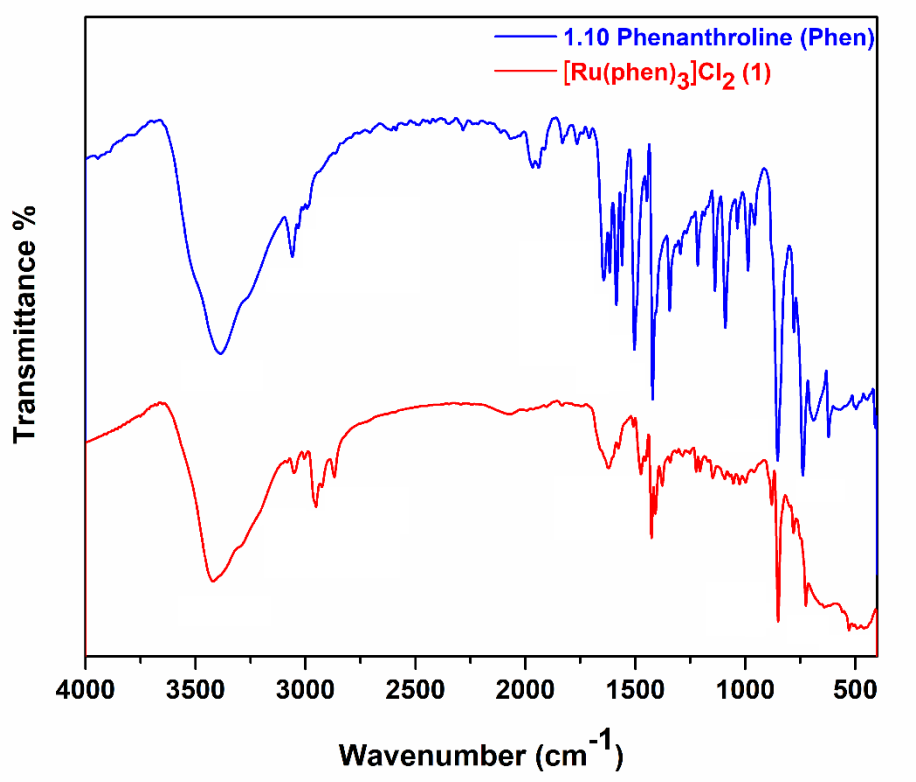

Fig. SI-1: FT-IR spectra of 1,10-phenanthroline (Phen) and $[Ru(Phen)_3]Cl_2$.

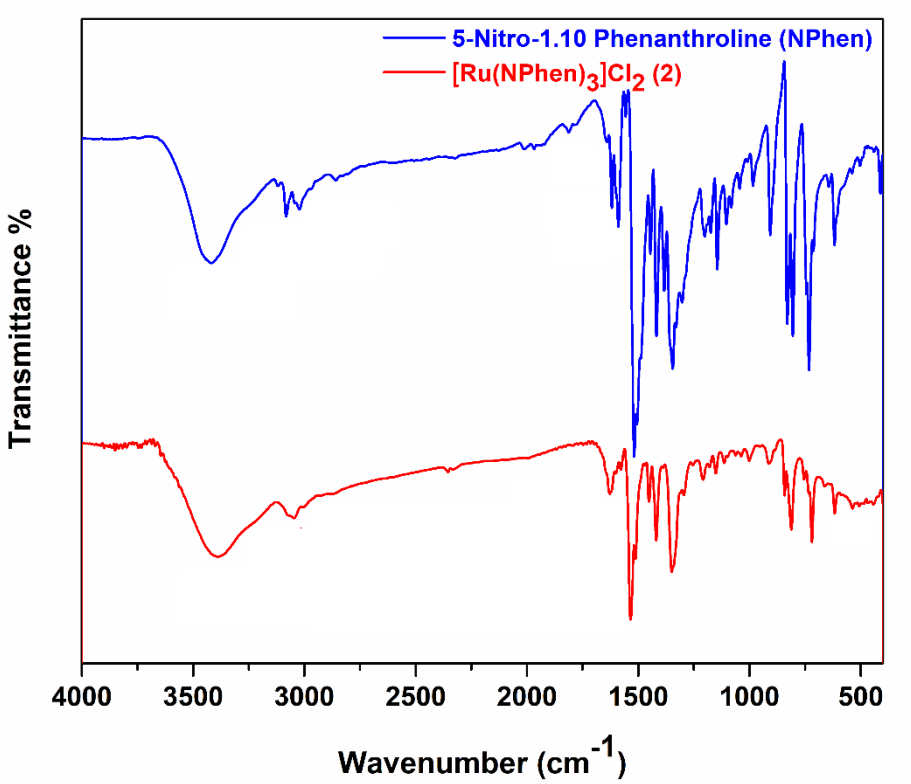

Fig. SI-2: FTIR spectra of 5-Nitro-1,10-phenanthroline (NPhen) and $[Ru(NPhen)_3]Cl_2$.

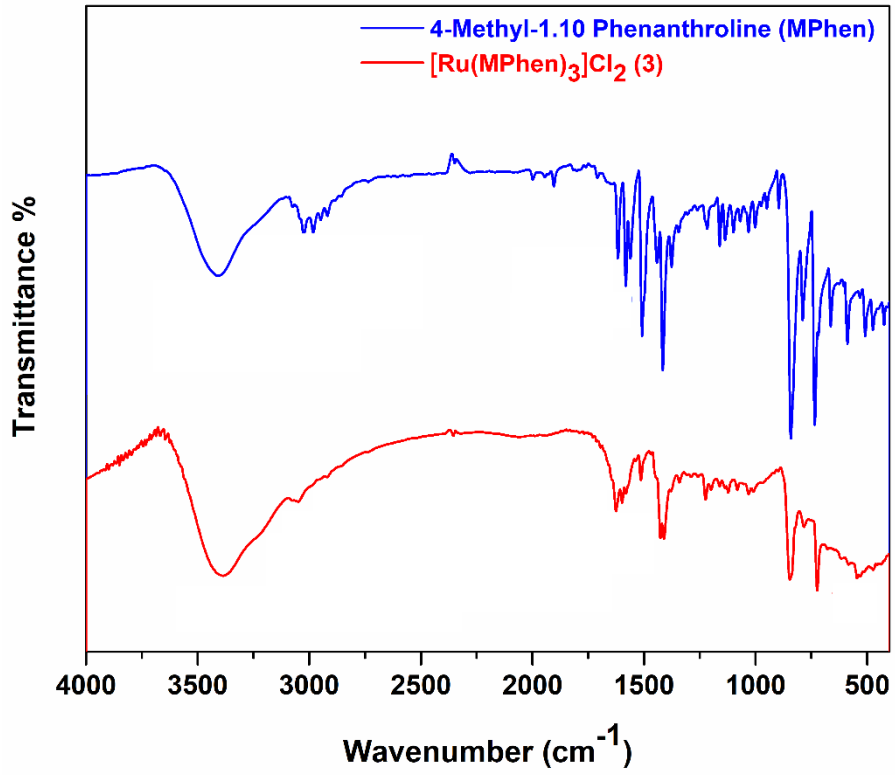

Fig. SI-3: FTIR spectra of 4-Methyl-1,10-phenanthroline (MPhen) and $[Ru(MPhen)_3]Cl_2$.

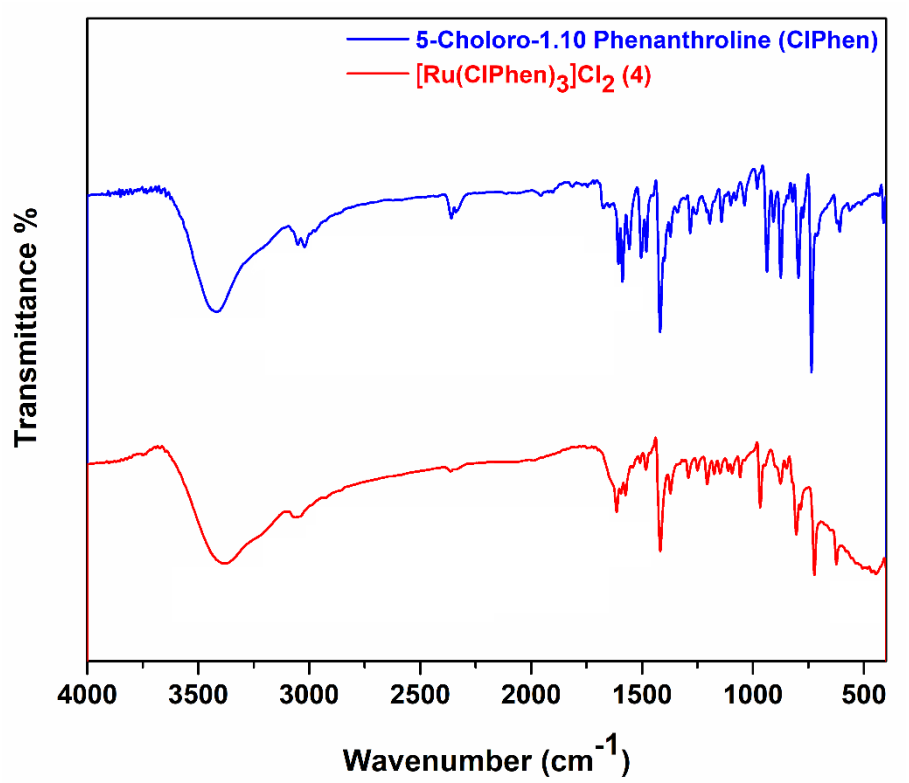

Fig. SI-4: FTIR spectra of 5-Choloro-1,10-phenanthroline (ClPhen) and $[Ru(ClPhen)_3]Cl_2$.

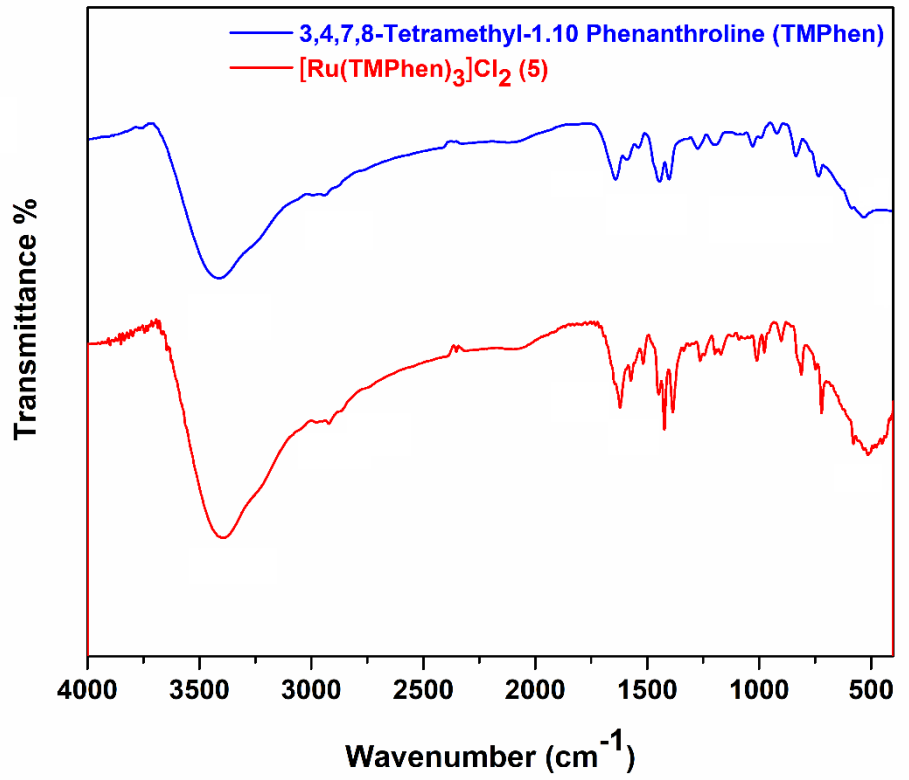

Fig. SI-5: FTIR spectra of 3,4,7,8-Tetraethyl-1,10-phenanthroline (TMPhen) and $[Ru(TMPhen)_3]Cl_2$.

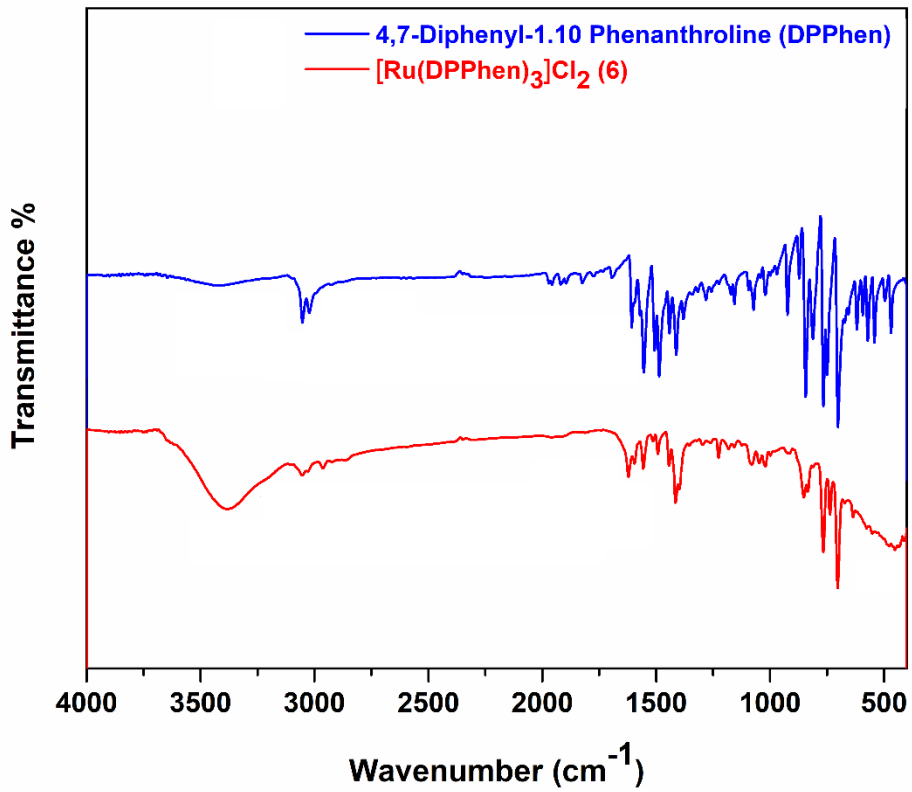

Fig. SI-6: FTIR spectra of 4,7-Diphenyl- 1,10-phenanthroline (DPPhen) and $[Ru(DPPhen)_3]Cl_2$.

Table SI-1: Infrared spectral data of the phenanthroline ligands and Ru(II) complexes.

Compound	$\nu_{C-H(Ar)}$	$\nu_{C=C}$	$\nu_{C=N}$	ν_{Ru-N}
Phen	3060, 3038, 2984	1647, 1615	1586	-
$[Ru(Phen)_3]Cl_2$		1629, 1584	1572	531
NPhen	3079, 3046, 3016	1637, 1620	1591	-
$[Ru(NPhen)_3]Cl_2$	3057, 3049, 2994	1633, 1608	1574	507
MPhen	3075, 3029, 2980	1619	1579	-
$[Ru(MPhen)_3]Cl_2$	3077, 3052, 3019	1626	1597	543
ClPhen	3058, 3023, 2966	1608	1588	-
$[Ru(ClPhen)_3]Cl_2$	3051, 3038, 2927	1615	1571	465
TMPhen	3034, 2955, 2876	1637	1582	455
$[Ru(TMPhen)_3]Cl_2$	3021, 2920, 2852	1623	1567	494
DPPhen	3054, 3022, 2933	1608	1592	-
$[Ru(DPPhen)_3]Cl_2$	3063, 3026, 2963	1622	1599	452

^{1}H NMR spectra

Proof of the bonding type of the ligands is also confirmed by comparing the ^{1}H NMR spectra of the ligands in normal DMSO-d_6, at room temperature deuterated solvent and their complexes. ^{1}H NMR spectrum of $[Ru(Phen)_3]Cl_2$ (Fig. SI-7) exhibit a singlet signal at 8.15, 8.45 and 8.83 ppm assigned to (H3(8), H4(H7) and H5(6), respectively. H3(8) protons appear as a triplet signal at 7.78 ppm. For $[Ru(NPhen)_3]Cl_2$ ^{1}H NMR spectrum (Fig. SI-8) exhibited three doublet signals at 8.35, 8.84, and 9.17 ppm which were assigned to H7, H2 and H9 protons, respectively. Additionally, two triplet signals were observed at 7.78 and 7.82 ppm which are ascribed to H8 and H3 protons, respectively. Finally, a singlet signal at 8.15 ppm is observed, which is attributed to H6 proton. In case of $[Ru(MPhen)_3]Cl_2$, ^{1}H NMR spectrum of (Fig. SI-9) exhibited a singlet signal at 2.76 which was assigned to aliphatic protons of CH_3 group. Besides, five doublet signals were shown at 7.54, 7.79, 8.45, 8.75 and 8.98 ppm, which are assigned to H3, H6, H7, H2 and H9, respectively. H8 signal appeared as a triplet signal at 7.95 ppm. ^{1}H NMR spectrum of $[Ru(ClPhen)_3]Cl_2$ (Fig. SI-10) exhibited a singlet signal at 7.52 due to H6 proton. Furthermore, four doublet signals due to H7, H4, H2, H9, were observed at 8.59, 8.88, 8.91 and 8.98 ppm. Also, two griplet signals at 7.72 and 7.91 ppm due to H8 and H3 protons, respectively. ^{1}H NMR spectrum of $[Ru(TMPhen)_3]Cl_2$ (Fig. SI-11) exhibited three singlet signals, two signals at 3.75 and 2.83 ppm ascribed to CH_3 protons at $C_4(C_7)$ and $C_3(C_8)$, respectively and the third signal at 8.48 ppm was assigned to H2 and H9 protons. The spectrum also showed a doublet signal at 7.73 ppm due to H5 and H6 protons. Finally, ^{1}H NMR spectrum of $[Ru(DPPhen)_3]Cl_2$ (Fig. SI-12) showed three doublet signals at 7.19, 7.76 and 8.87 ppm which were attributed to H3(H8), H5(H6) and H2(H9) protons, beside a multiplet signal at the range 7.36-7.55 ppm which are assigned to aromatic protons of substituted phenyl groups. The assignments of chemical shifts of the various types of protons in the ^{1}H NMR spectra of the reported Ru(II) complexes are collected in Table SI-2.

Table SI-2: ^{1}H NMR data of $[Ru(Phen)]^{2+}$(1), $[Ru(NPhen)_3]^{2+}$(2), $[Ru(MPhen)_3]^{2+}$(3), $[Ru(ClPhen)_3]^{2+}$(4), $[Ru(TMPhen)_3]^{2+}$(5), and $[Ru(DPPhen)_3]^{2+}$(6).

Complex	^{1}H NMR data (400 MHz, ppm DMSO-d_6, TMS)
$[Ru(Phen)]^{2+}$ (1)	δ: 8.83 (d, H2&9, J = 6.4 Hz) ; 8.45 (d, H5&6 J = 13.8 Hz)); 7.78 (t H3&8, J 24.1 Hz); δ 8.15 ((d, H4&7 J = 13.2 Hz).
$[Ru(NPhen)_3]^{2+}$ (2)	δ: 8.84 (d, H2, J = 8.4 Hz); 7.82 (t, H3, J = 9.5 Hz); 8.67 (d, H4, J = 8.3 Hz); 8.15 (s, H6); 8.35 (d, H7, J =11.7 Hz); 7.78 (t, H8, J = 11.8. Hz); 9.17 (d, H9, J = 6.1 Hz).
$[Ru(MPhen_3]^{2+}$ (3)	δ: 8.75 (d, H2, J =5.6 Hz); 7.54 (d, H3, J =7.4 Hz); 8.26 (d, H5, J = 9.7 Hz); 7.79 (d, H6, J =10.4 Hz); 8.45 (d, H7, J =11.2 Hz); 7.95 (t, H8, J =14.1 Hz); 8.98 (d, H9, J =9.6 Hz); 2.76 (s, CH_3)
$[Ru(ClPhen)_3]^{2+}$ (4)	δ: 8.91 (d, H2, J =15.7 Hz); 7.91 (t, H3, J =14.7 Hz); 8.88 (d, H4, J =7.8 Hz); 7.52 (s, H6); δ 8.50 (d, H7); 7.72 (t, H8, J =13.75 Hz); 8.98 (d, H9, J =12.3 Hz)
$[Ru(TMPhen)_3]^{2+}$ (5)	δ: 8.48 (s, H2&9), 7.73 (d, H5&6, J = 10.7 Hz) ; 2.75 (s, CH_3 (C4,C7); 2.83 (s CH_3(C3,C8).
$[Ru(DPPhen)_3]^{2+}$(6)	δ: 8.87 (d, H2&H9, J = 9.3 Hz); 7.19 (d, H3&H8, J = 12.7 Hz); 7.76 (d, H5, H6, J = 8.7 Hz); 7.36-7.55 (m, Ph-H)

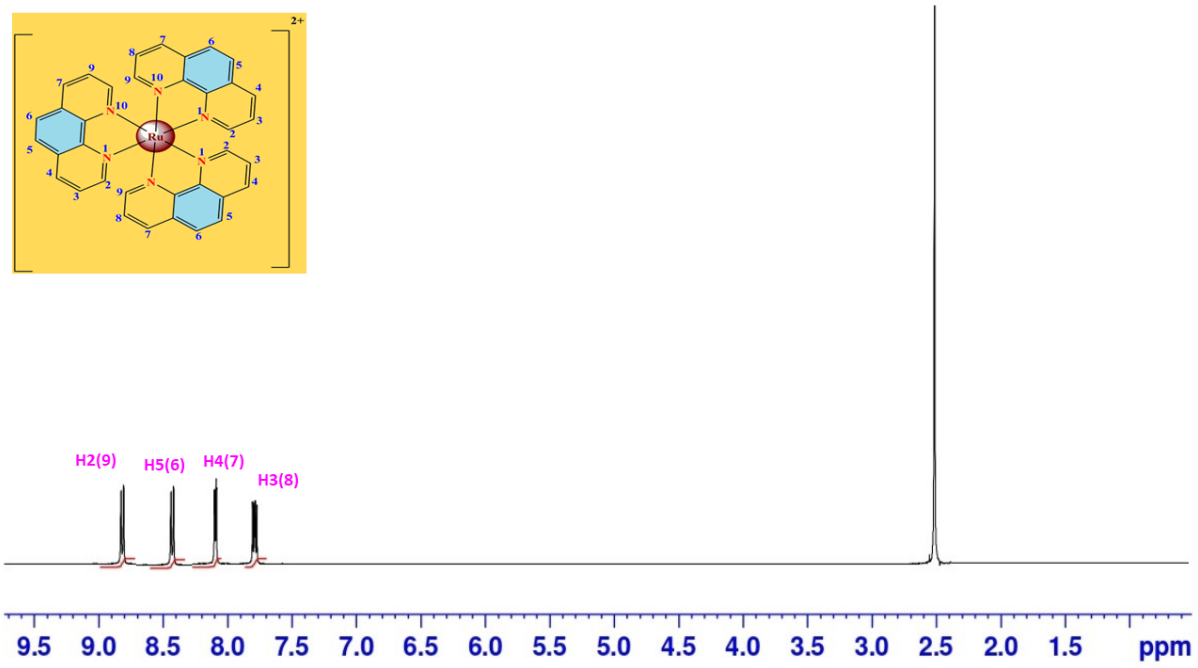

Fig. SI-7: ^{1}H NMR spectrum of $[Ru(Phen)_3]Cl_2$.

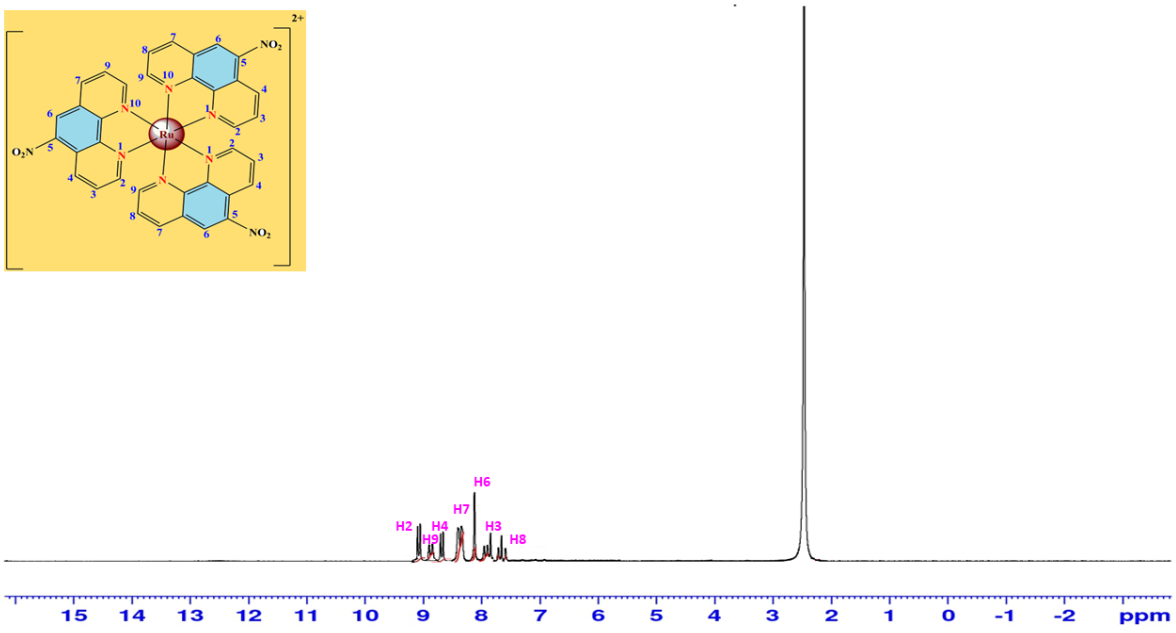

Fig. SI-8: ^{1}H NMR spectrum of $[Ru(NPhen)_3]Cl_2$.

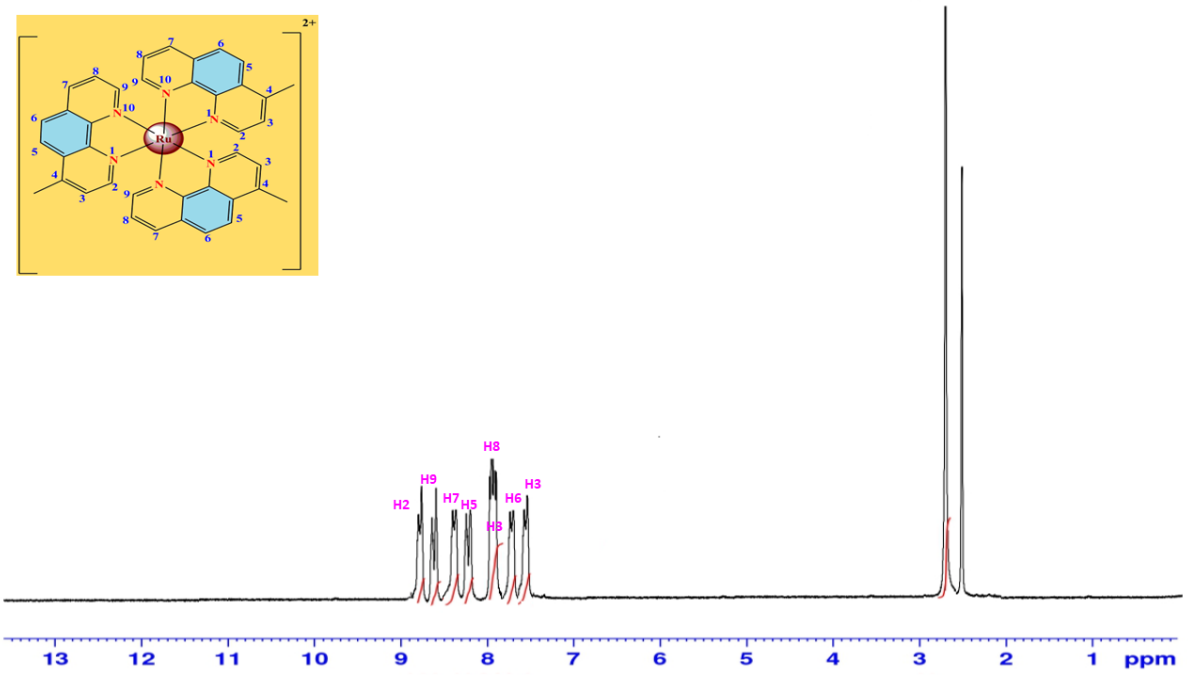

Fig. SI-9: ^{1}H NMR spectrum of $[Ru(MPhen)_3]Cl_2$.

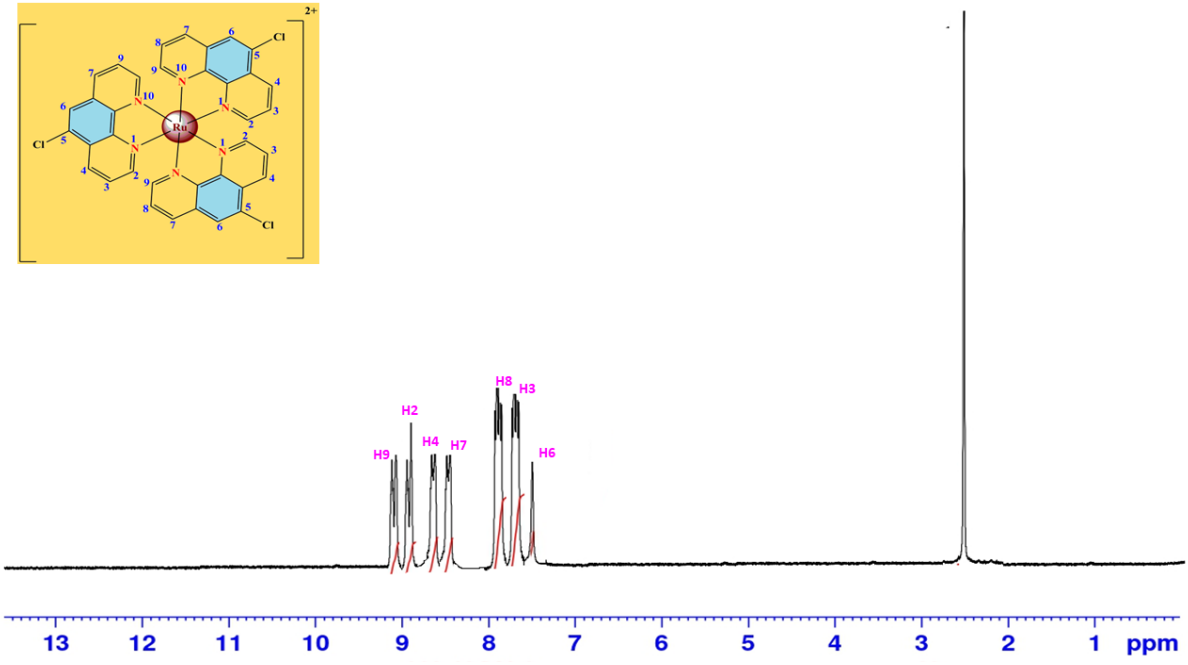

Fig. SI-10: ^{1}H NMR spectrum of $[Ru(ClPhen)_3]Cl_2$.

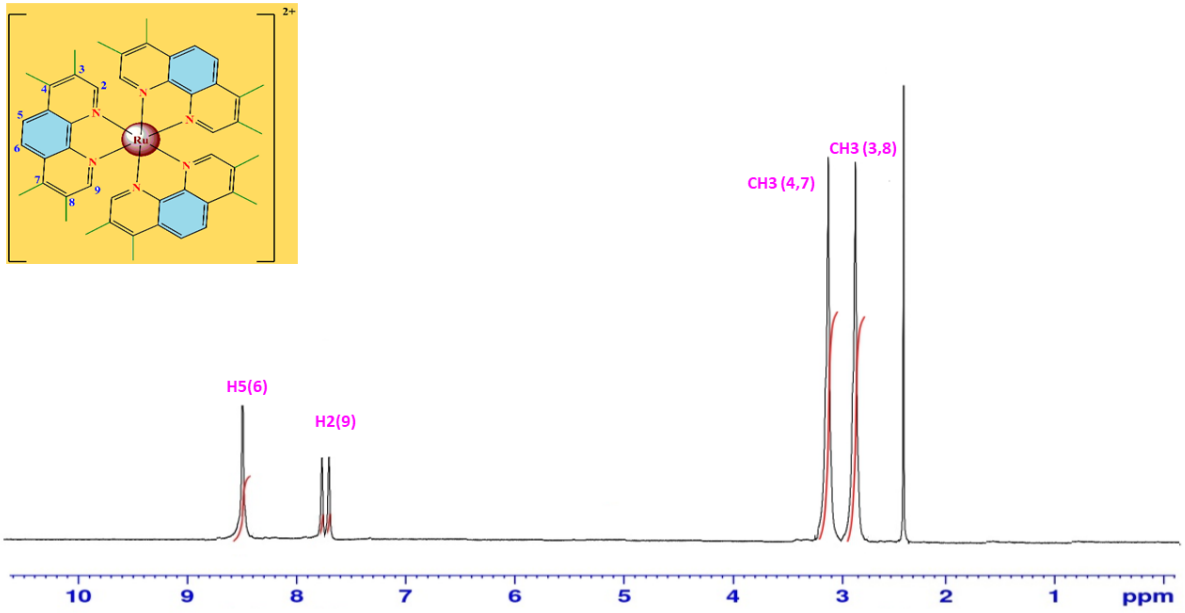

Fig. SI-11: ^{1}H NMR spectrum of $[Ru(TMPhen)_3]Cl_2$.

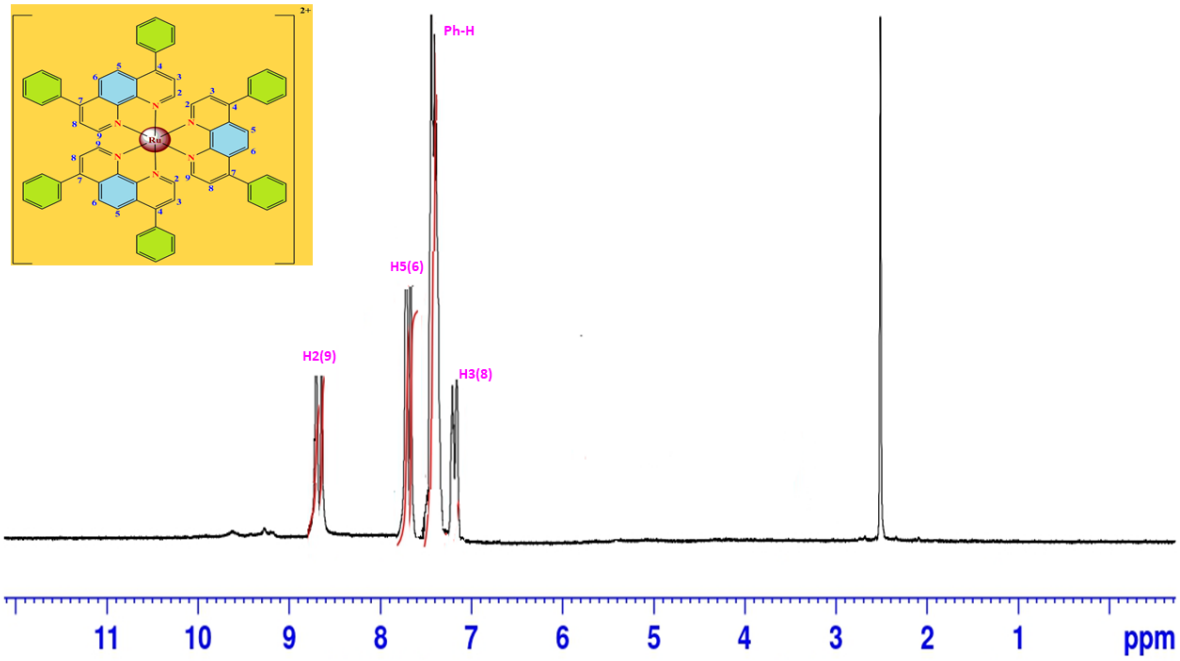

Fig. SI-12: ^{1}H NMR spectrum of $[Ru(DPPhen)_3]Cl_2$.

ESI-Mass spectra

Electrospray ionization mass spectrometry (ESI-MS) studies were carried out in the positive mode and in the range of *m/z* 50-1150. The mass spectra were measured in MeOH:H_2O (50:50) solution and confirmed the formula proposed for all synthesized complexes (Figs. SI-13-18). The mass spectra of the complexes displayed m/z = 642.5 (52%), 777.6 (81 %), 683.5 (78%), 745.1 (44 %), 899.1 (80 %) and 1098.1 (79 %) which are corresponding to $[Ru(Phen)_3 - 2Cl]^+$, $[Ru(NPhen)_3 - 2Cl]^+$, $[Ru(MPhen)_3 - 2Cl]^+$, $[Ru(ClPhen)_3 - 2Cl]^+$, $[Ru(TMPhen)_3 - 2Cl]^+$ and $[Ru(DPPhen)_3 - 2Cl]^+$, fragments, respectively.

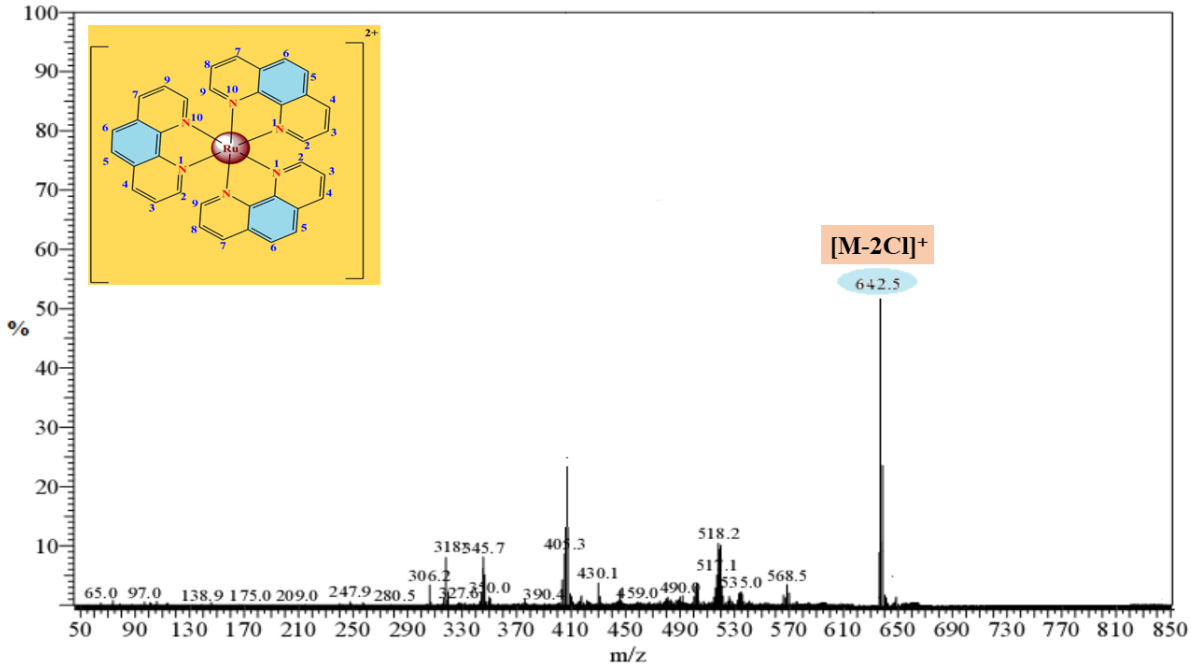

Fig. SI-13: ESI-Mass spectrum of $[Ru(Phen)_3]Cl_2$.

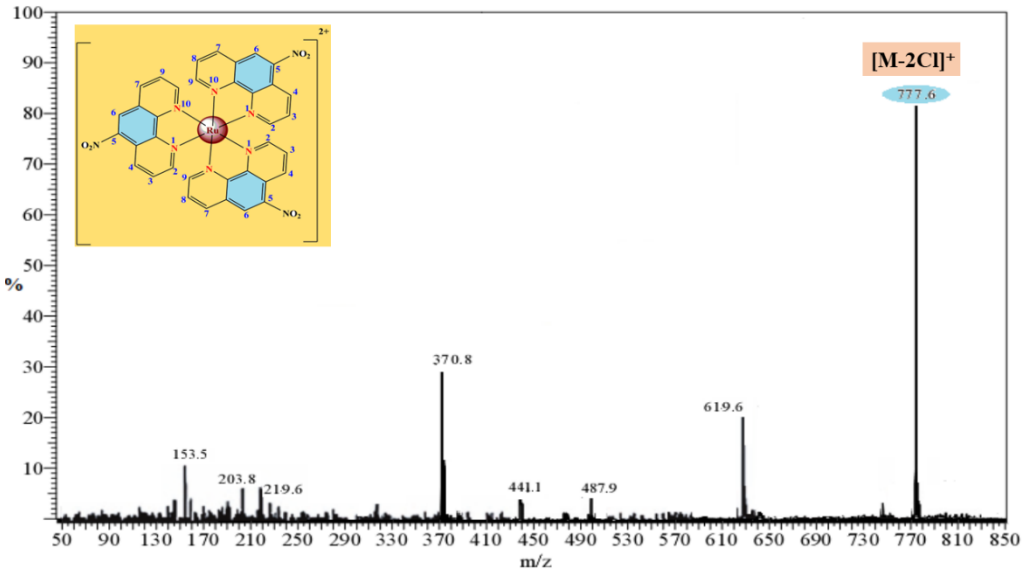

Fig. SI-14: ESI-Mass spectrum of $[Ru(NPhen)_3]Cl_2$.

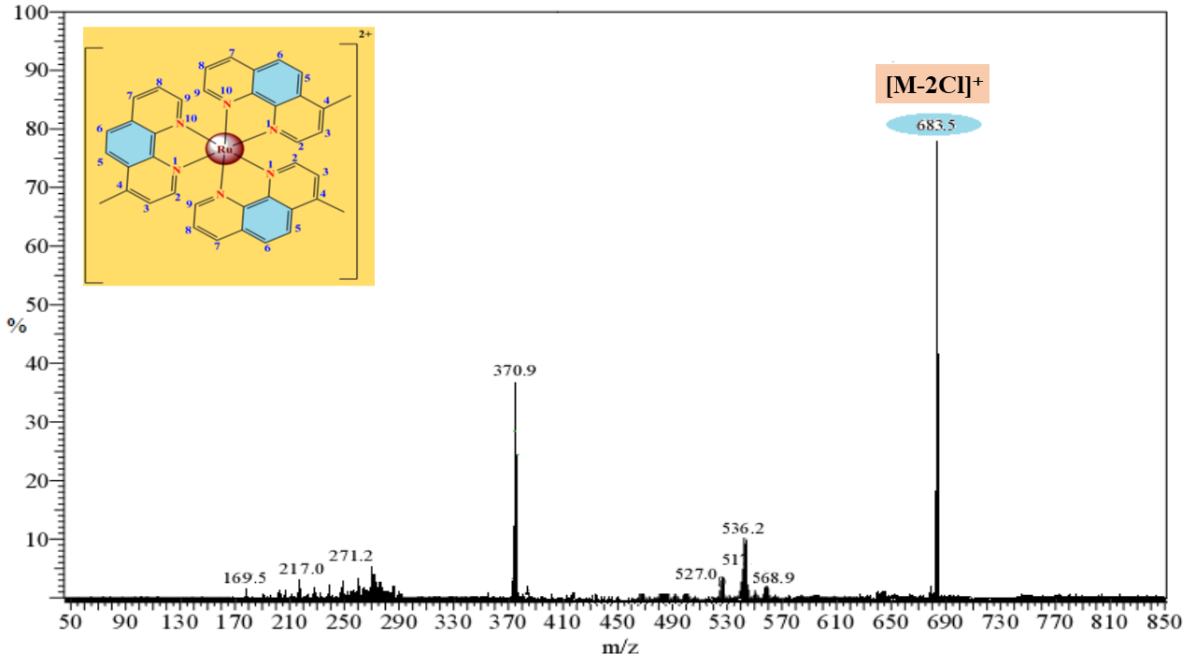

Fig. SI-15: ESI-Mass spectrum of $[Ru(MPhen)_3]Cl_2$.

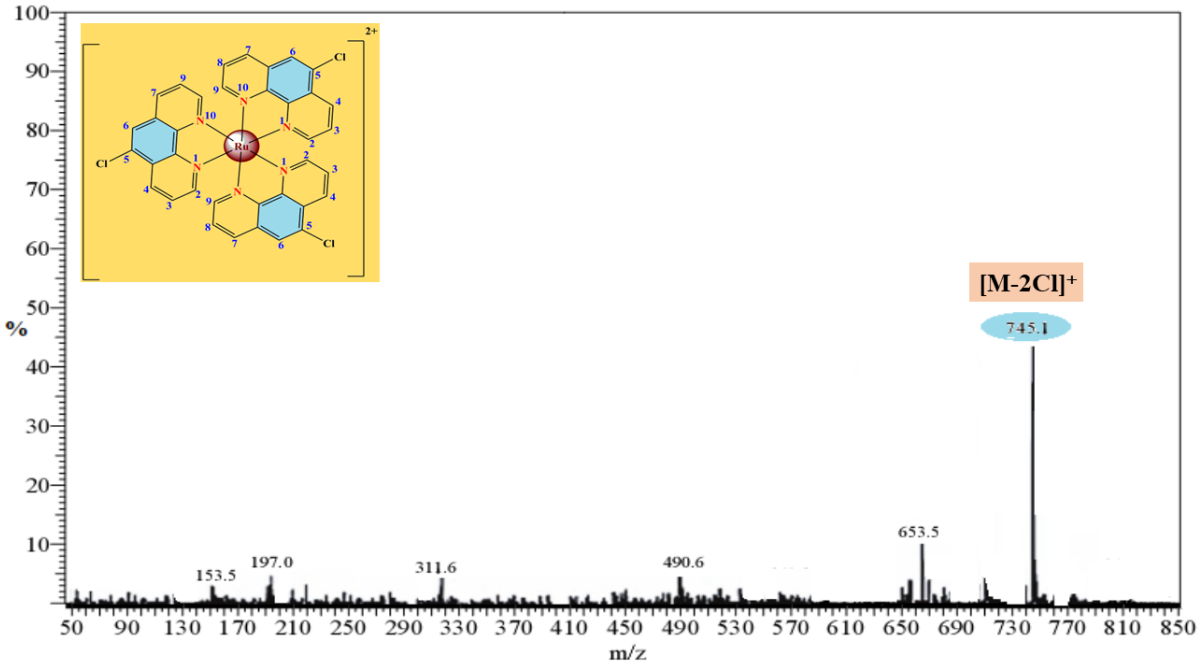

Fig. SI-16: ESI-Mass spectrum of $[Ru(ClPhen)_3]Cl_2$.

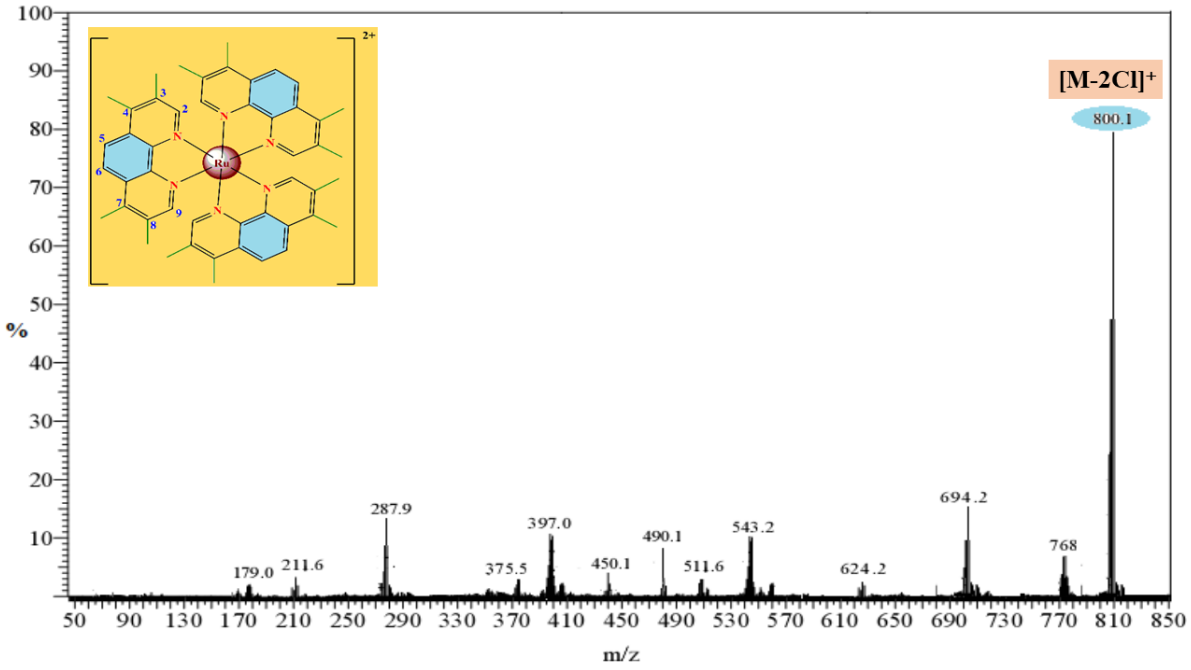

Fig. SI-17: ESI-Mass spectrum of $[Ru(TMPhen)_3]Cl_2$.

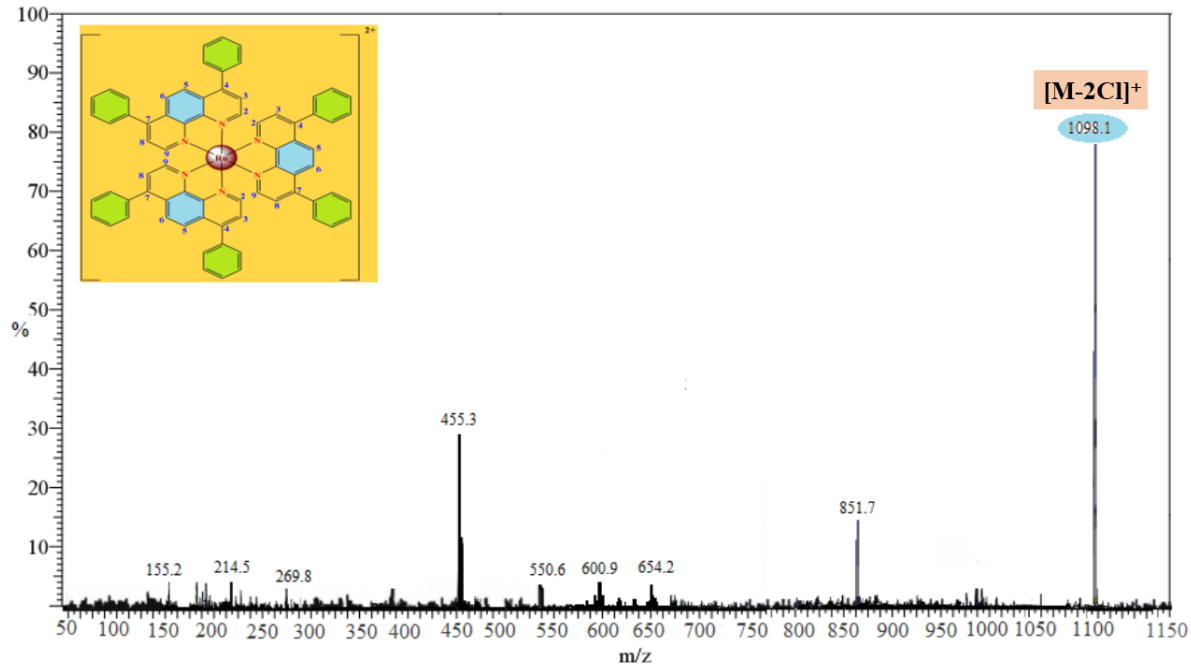

Fig. SI-18: ESI-Mass spectrum of $[Ru(DPPhen)_3]Cl_2$.

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