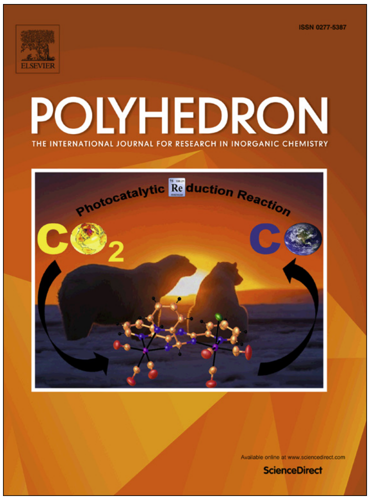

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Cyclometalated mono and dinuclear rhodium(III) and iridium(III) complexes with imidazolyl phenanthrolines: Synthesis and, photophysical and electrochemical characterization

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Abstract: Cyclometalated rhodium(III) and iridium(III) complexes were synthesized with imidazolyl modified phenanthroline ligands (**1** - **2**) of general formula $[M(ppy)_2(\mathbf{1})]Cl$ [M = Rh/Ir] and $[\{M(ppy)_2\}_2(\mathbf{2})]Cl_2$ [M = Rh/Ir] (**3** - **9**). All the compounds **1** - **9**, have been characterized spectroscopically to reveal their dependence on the solvent polarity and proticity of the environment. The photophysical details show that the ligands as well as the cyclometalated complexes have spectrum of variations depending on the immediate solvent environment and pH of the medium. Electrochemical studies show variation in the electrochemical behaviour due to the change of the metal centres.

1. Introduction

Cyclometalated iridium(III) complexes with polypyridyl based ancillary ligands exhibit rich photophysical properties. They are well addressed for their application as sensors,[1-5] in biological imaging, [6] light-emitting electrochemical cells,[7-11] organic light-emitting diodes,[12-20] catalysts for water splitting,[21-23] dye-sensitized solar cells (DSSCs)[24 -28] and organic transformations.[29 -35] In contrast, reports on photophysical properties of the cyclometalated rhodium(III) analogues are limited in literature.[4,29,30,36-47] Spectroscopic transitions in these systems are usually metal centered (MC) and ligand centered (LC), or through charge transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT) and corresponding oxidation and reduction processes are either metal or ligand centered. Ligand-field stabilization in these complexes depends on the oxidation state, nature of the cyclometalating ligand and d-orbitals. However, dissimilarity in photophysical behaviour between the cyclometalated iridium(III) and rhodium(III) complexes originates from the large difference in spin-orbit coupling (ξIr = 3909 cm^{-1} and ξRh = 1259 cm^{-1}) between these two metals. As a result, intersystem crossing from first excited singlet state to triplet state occurs efficiently in the iridium complexes. Hence, cyclometalated iridium(III) complexes are generally characterized by their long-lived triplet excited states. Iridium(III) complexes with strong-field cyclometalating ligands, such as phenylpyridine, usually emit from the admixture of spin-allowed metal-to-ligand charge-transfer, (^{1}MLCT) and π(ppy) - π^*(phen) ligand-to-ligand (^{1}LLCT) processes, whereas, the emission of rhodium(III) complexes are mainly ligand-based.[8,29-30,36-51] Cyclometalated rhodium complexes of phenylpyridines were recently explored for their catalytic properties.[52–55] Polynuclear transition metal complexes bridged through polypyridyl ligands are always interesting for their through-bridge electronic communication. Choice of the bridging ligand is crucial to design such systems. This is important from the structural viewpoint as well as for electronic coupling between the separated subunits.[56-75] Transition metal complexes containing polypyridyls are largely employed as energy donor or acceptor for fast and efficient energy transfer due to their rich photophysics and long-lived triplet excited states. Bis(imidazo[4,5-f][1,10]phenanthroline)s are well suited bridging ligands for this purpose.[76 - 82] They are fully conjugated, have two N$\cap$N-bidentate coordination sites, and possess protic sites (N-H) that induce pH-dependence. In addition, the photophysical properties can be modulated by incorporating two different cyclometalated subunits into the structure of this tetradentate system. The photoactive characteristic of one subunit can be coupled with the redox active centre in the other. Combined use of cyclometalated iridium(III) complexes and rhodium polypyridyl systems in homogeneous and heterogeneous photocatalytic processes have already been reported.[83 -85] The former acts as photosensitizer, and the latter serves as catalyst for proton induced reduction. The photophysical properties of a wide range of cyclometalated heteroleptic iridium(III) complexes with imidazolyl based phenanthroline as ancillary ligand have already been explored.[86 - 95]

In the present work, we have synthesised mononuclear, homo and hetero-dinuclear coordination complexes comprising of cyclometalated iridium and rhodium cores with polypyridyl ligands. In all the complexes the imidazolyl and bis-imidazolyl phenanthrolines bind to cyclometalated iridium and rhodium units as ancillary bidentate ligands. Photophysical characterization of the complexes was done to understand the electronic communication between the metal centres in homodinuclear and heterodinuclear complexes. Cyclic voltammetric measurements for the complexes were done to understand the electrochemical behaviour of the complexes and to understand the potential of heterodinuclear system in the catalytic processes.

2. Experimental

2.1. Chemicals and materials

The starting materials, $RhCl_3.3H_2O$, $IrCl_3.3H_2O$, 2-phenylpyridine, 8-aminoquinoline, 1-napthylamine and 1-methyl-2-imidazole carboxaldehyde were purchased from Sigma-Aldrich and used without further purification. All the solvents were dried by usual methods prior to use. The cyclometalated iridium(III) and rhodium(III) chloro bridged dimer $[Ir(ppy)_2Cl]_2$[96] and $[Rh(ppy)_2Cl]_2$,[97] 1,10-phenanthroline-5,6-dione,[98] 2-(4-formylphenyl)imidazo[4,5-f][1,10]phenanthroline(1),[78] and 2,2-p-Phenylene(imidazo[4,5-f][1,10]phenanthroline(2)[78] were synthesized according to the literature methods.

2.2. Synthesis of complexes

*2.2.1 Synthesis of [Rh(ppy)$_2$(**1**)]Cl* (**3**)

A mixture of $[Rh(ppy)_2Cl]_2$ (0.1 mmol), **1** (0.235 mmol), methanol (15 mL), dichloromethane (15 mL) and acetonitrile (15 mL) was refluxed for 5 h at 90̊ C that yielded a reddish orange solution. The product was purified by column chromatography with 5 to 10% (v/v) methanol in dichloromethane as eluent. A reddish orange compound was obtained after the eluent was dried. Yield: 72%. ESI-MS (*m/z*):

[M-Cl]$^+$: 735.137 (Calcd. 735.13). Elemental Analysis: Calcd. C: 65.42, H: 3.66, N: 10.90; Expt. C: 65.79, H: 3.87, N: 11.02; ^{1}H-NMR [$CDCl_3$]: δ 10.03 (s, 1H), 9.50 (d, 2H), 8.77 (d, 2H), 8.07 (d, 2H), 7.98 (d, 2H), 7.92 (d, 2H), 7.75 (m, 4H), 7.66 (q, 2H), 7.37 (d, 2H), 7.13 (t, 2H), 7.02 (t, 2H), 6.85 (t, 2H), 6.42 (d, 2H)(for more details see **Figure S8**). $\bar{\upsilon}_{max}$/cm^{-1}: 3423s (br), 2924m, 2360w, 1697s, 1605s, 1580s, 1480s, 1210m, 1118m, 758m, 732m.

*2.2.2 Synthesis of [Ir(ppy)$_2$(**1**)]Cl* (**4**)

The synthetic procedure is similar to that of **3**. A reddish orange compound was obtained on drying the eluent . Yield: 69%. ESI-MS (*m/z*): [M-Cl]$^+$:825.173 (Calcd. 825.19). Elemental Analysis: Calcd. C: 58.63, H: 3.28, N: 9.77; Expt. C: 59.10, H: 3.45, N: 9.23 ;^{1}H-NMR [$CDCl_3$]: δ 10.06 (s, 1H), 9.59 (broad, 2H), 8.79 (d, 2H), 8.13 (d, 2H), 8.02 (d, 2H), 7.94 (d, 2H), 7.73 (m, 6H), 7.38 (d, 2H), 7.10 (t, 2H), 6.99 (t, 2H), 6.85 (t, 2H), 6.42 (d, 2H) (for more details see **Figure S9**). $\bar{\upsilon}_{max}$/cm^{-1}: 3430m, 3043m, 2920m, 2850m, 1698s, 1607vs, 1582s, 1478s, 1383m, 757m, 730m.

*2.2.3 Synthesis of [Rh(ppy)$_2$(**2**)]Cl* (**5**)

A mixture of [Rh(ppy)$_2$(**1**)]Cl (0.0581mmol), 1,10-phenanthroline-5,6-dione (0.0762 mmol), glacial acetic acid (12 mL) and ammonium acetate (1.01 g, 13.12 mmol) was refluxed for 4 h at 110° C followed by cooling down to room temperature and dilution with distilled water. A precipitate appeared on neutralizing the solution with aqueous ammonia in a cooling bath. The resulting precipitate was filtered, washed first with water for several times and then with dichloromethane producing a brown coloured compound. Yield: 64%. ESI-MS (*m/z*): [M-Cl]$^{+:}$ 925.205 (Calcd. 925.20). Elemental Analysis: Calcd. C: 67.47, H: 3.57, N: 14.57; Expt. C: 66.96, H: 3.13, N: 14.89; ^{1}H-NMR [DMSO-d$_6$]: δ 9.09 (d, 2H), 9.03 (d, 2H), 8.98 (d, 2H), 8.59 (d, 2H), 8.37 (d, 2H), 8.28 (d, 2H), 8.01 (m, 4H), 7.95 (t, 2H), 7.87 (m, 4H), 7.47 (d, 2H), 7.12 (t, 2H), 7.08 (t, 2H), 7.03 (t, 2H), 6.34 (d, 2H)(for more details see **Figure S10**).. $\bar{\upsilon}_{max}$/cm^{-1}: 3403m (br), 2924m, 1605s, 1479m, 1449s, 1351s, 1121s, 810m, 757m, 740m.

*2.2.4 Synthesis of [Ir(ppy)$_2$(**2**)]Cl* (**6**)

The synthetic procedure is similar to that of **5.** A dark brown coloured compound was obtained as the final product. Yield: 61%. ESI-MS (*m/z*): [M-Cl]$^+$: 1015.23 (Calcd. 1015.26). Elemental Analysis: Calcd. C: 61.73, H: 3.26, N: 13.33; Expt. C: 62.94, H: 2.87, N: 13.67; ^{1}H-NMR [DMSO-d$_6$]: δ 9.09 (d, 2H), 9.01 (d, 4H), 8.59 (d, 2H), 8.40 (d, 2H), 8.26 (d, 2H), 7.95 (d, 4H), 7.86 (m, 6H), 7.50 (d, 2H), 7.06 - 7.00 (m, 4H), 6.95 (t, 2H), 6.32 (d, 2H) (for more details see **Figure S11**). $\bar{\upsilon}_{max}$/cm^{-1}: 3386s(br), 3060s, 1606s, 1581s, 1563s, 1478s, 1449s, 1397s, 758m, 740s.

*2.2.5 Synthesis of [{Rh(ppy)$_2$}2(**2**)]Cl$_2$* (**7**)

A mixture of **6** (0.047 mmol), [Rh(ppy)$_2$Cl]$_2$ (0.035 mmol) and acetonitrile/ dichloromethane/ methanol (1:1:1, v/v, 30 mL) was refluxed at 90° C for about 3 h. The resulting yellowish orange coloured solution was cooled down to room temperature. Subsequently, the compound was purified by thin layer chromatography with 10% methanol in dichloromethane mixture. A dark yellow compound was obtained on drying. Yield: 65%. ESI-MS (*m/z*): [M-2Cl]$^{2+}$/2: 713.13 (Calcd. 713.14), [M-2Cl-H$^+$]$^+$ = 1425.25 (calcd. [M-2Cl]$^+$ = 1426.29); Elemental Analysis: Calcd. C: 62.44, H: 3.45, N: 11.50; Expt. C:

62.76, H: 3.85, N: 11.20; ^{1}H-NMR [$CDCl_3$]: 9.74 (broad, 4H), 8.77 (s, 4H), 8.15 (d, 2H), 8.12 (d, 2H), 7.95 (d, 4H), 7.79 – 7.72 (m, 12H), 7.38 (t, 4H), 7.14 (t, 2H), 7.08 (t, 2H), 7.02 (t, 2H), 6.97 (t, 2H), 6.91 (t, 2H), 6.86 (t, 2H), 6.42 (d, 4H) (for more details see **Figure S12**)..$\bar{\upsilon}_{max}$/cm^{-1}: 3433s (br), 3043m, 2922m, 1606s, 1581m, 1479s, 1449m, 758m, 731m.

*2.2.6 Synthesis of [{Ir(ppy)$_2$(**2**)Rh(ppy)$_2$}](PF_6)$_2$* (**8**)

8: was synthesised by refluxing [$Rh(ppy)_2Cl]_2$ (0.25 mmol) with **2** (0.25 mmol) in EtOH/dichloromethane mixture (2:1 v/v, 30 mL) for 4 h. The mixture was heated until the volume was reduced to 8 mL followed by addition of 10 mL water. The desired compound was precipitated by adding an excess of aqueous NH_4PF_6 to the solution. Filtration yielded a yellow coloured compound. Yield: 68%. ESI-MS (*m/z*): $[M\text{-}2PF_6]^{2+}/2$: 668.09 (Calcd. 668.12).$[M\text{-}2PF_6\text{-}H^+]^+$ = 1335.22; $^+$ (calcd. $[M\text{-}2PF_6]^+$ = 1336.24); Elemental Analysis: Calcd. C: 61.59, H: 3.40, N: 11.34; Expt. C: 61.78, H: 3.56, N: 12.02 ;^{1}H-NMR [DMSO-d_6]: δ 9.26 (d, 4H), 8.60 (s, 4H), 8.30 (d, 4H), 8.23 (d, 4H), 8.12 (t, 4H), 8.03 (d, 4H), 7.97 (t, 4H), 7.49 (d, 4H), 7.15 (t, 4H), 7.07 – 7.02 (m, 8H), 6.32 (d, 4H)(for more details see **Figure S13**). $\bar{\upsilon}_{max}$/cm^{-1}: 3430s(br), 1606s, 1578s, 1480s, 1451m, 846vs, 757s, 733m.

*2.2.7 Synthesis of [{Ir(ppy)$_2$}$_2$(**2**)]Cl_2* (**9**)

A mixture of [$Ir(ppy)_2Cl]_2$ (0.1 mmol), **2** (0.1 mmol) and acetonitrile/dichloromethane (1:1 v/v, 30 mL) was refluxed for 4 h at 90° C to obtain an orange coloured mixture. It was cooled down to room temperature and the solvent was evaporated using a rotary evaporator. The residue was purified by column chromatography (5% methanol in dichloromethane was used as eluent) yielding a brownish orange compound. Yield: 70%. ESI-MS (*m/z*): $[M\text{-}2Cl]^{2+}/2$: 758.12(calcd. 757.17).$[M\text{-}2Cl\text{-}H^+]^+$ = 1515.27 (Calcd. $[M\text{-}2Cl]^+$ = 1516.35); Elemental Analysis: Calcd. C: 58.85, H: 3.25, N: 10.84; Expt. C: 59.23, H: 3.27, N: 10.29; ^{1}H-NMR [$CDCl_3$]: δ 9.69 (broad, 4H), 8.73 (s, 4H), 8.09 (d, 4H), 7.94 (d, 4H), 7.71 (m, 12H), 7.38 (d, 4H), 7.05 (t, 4H), 6.95 (t, 4H), 7.85 (t, 4H), 6.41 (d, 4H) (for more details see **Figure S14**). $\bar{\upsilon}_{max}$/cm^{-1}: 3412s (br), 2924vs, 1605s, 1581s, 1477s, 1451s, 1377s, 758s, 729s.

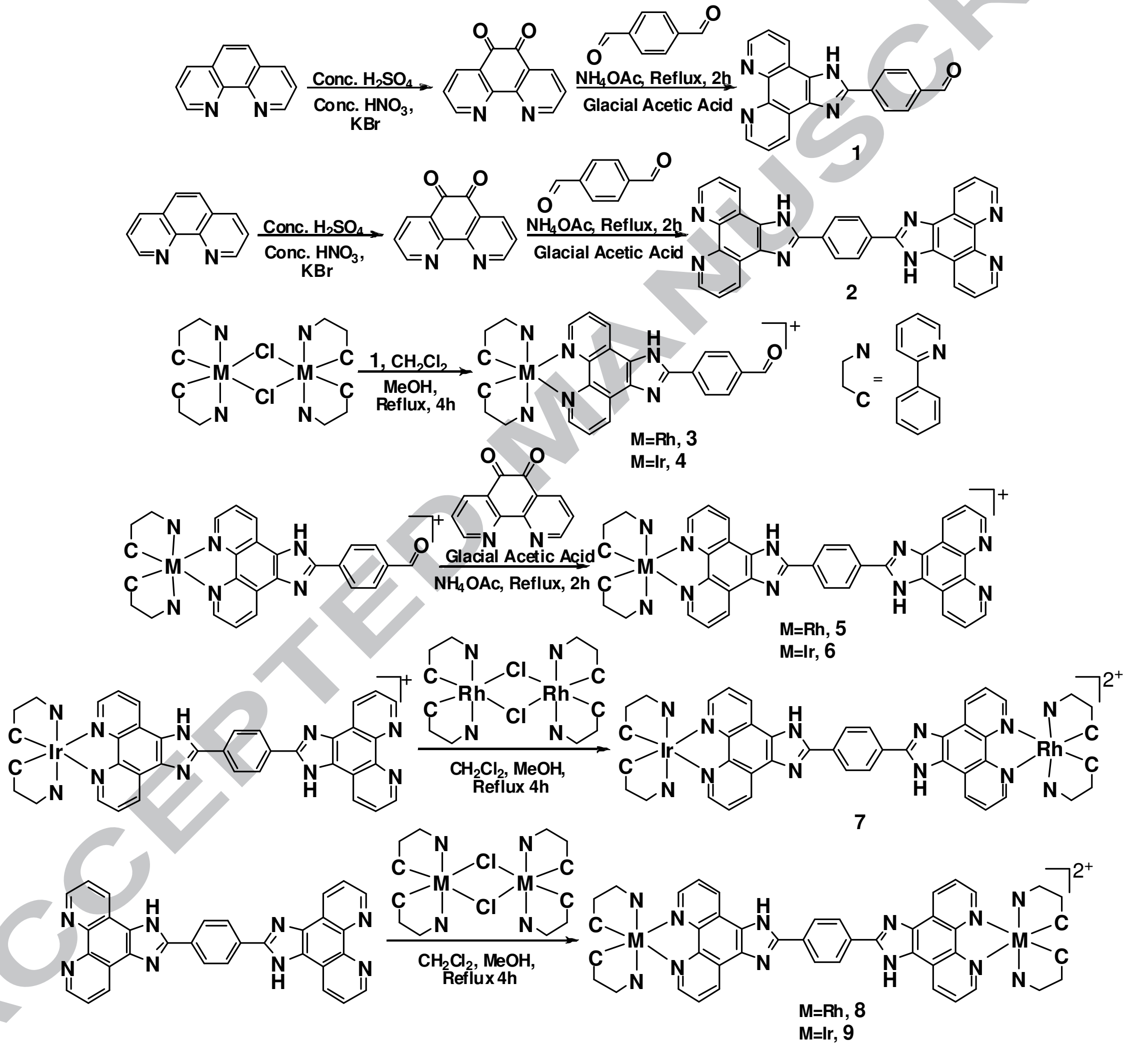
2.3 Physical measurements

Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN series. IR spectra were obtained on a Perkin-Elmer Spectrum RXI spectrophotometer with samples prepared as KBr pellets. Electronic spectra were recorded on a U-4100, HITACHI spectrometer. ^{1}H NMR spectra were obtained on a Bruker Avance III-500 NMR spectrometer using TMS as the internal standard. Electrochemical measurements were done using a PAR model 273 potentiostat. A platinum disk working electrode, a platinum wire auxiliary electrode and Ag/Ag+ (reference electrode) were used in a three electrode configuration. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. Fluorescence spectra were taken on a HORIBA JOBINYVON spectrofluorometer Fluoromax 4. Quantum yield data reported here were measured relative to quinine sulfate in 0.1 M H_2SO_4 (λex = 350 nm, Φ = 0.577). The integration of the emission spectra was obtained from the Fluoromax-4 instrument directly. The photoluminescence spectra were measured on a Horiba Jobin Yvon spectrometer equipped with a 150

W Xe lamp. Mass spectra were recorded on a Q-Tof Micromass spectrometer by positive-ion mode electrospray ionization.

3. Results and Discussion

The Bis(imidazo[4,5-f][1,10]phenanthroline system as bridging ligand has been chosen judiciously as, cyclometalated iridium(III) complexes with N∩N polypyridyl as ancillary ligands are luminescent in nature.[36-40, 99 - 100] The synthesis of complexes **3, 4** and **8 - 9** have been done by refluxing [M(ppy)$_2$Cl]$_2$ (M = Ir, Rh) with **1 - 2** or **5 - 6** in dichloromethane: acetonitrile (1:1) solution at 60^{o}C for 4 h (**Scheme 1**).



Scheme 1. Synthetic details of ligands **1** - **2** and complexes **3** - **9**, with procedures starting from 1,10-phenanthroline as ligand and [Ir(phenylpyridine)$_2$Cl$_2$]as metal precursor.

Complexes **5** and **6** has been synthesized by treating phen-5, 6-dione with **3**, **4** in glacial acetic acid in presence of ammonium chloride respectively. Complex **7** has been synthesized by refluxing [Rh(ppy)$_2$Cl]$_2$ with **6** in dichloromethane: acetonitrile (1:1) solution. Except, complex **8** (precipitated as

PF_6 salt), the complexes **3 – 7** and **9** have been obtained as chloride salt. The synthesized compounds were purified by standard techniques and characterized by ^{1}H NMR, mass spectrometry and infrared (IR) spectroscopy. ESI-MS data depict the composition of the complex as shown in **Scheme 1** and ^{1}H NMR spectra of the complexes (**Figure S8 – S14**) confirm the structural aspect of the complexes quite well. Despite, several attempts to get good quality crystals, the quality of the crystals was very poor and could not be solved.

3.1. Spectral features in the ground electronic state

Ligands **1** and **2** display absorption bands at around 375 nm and 284 nm in common organic solvents (**Figure 1**). Bands at 375 nm get blue shifted with increase in solvent polarity for **1**. Ligand **2** has an insignificant blue shift but is more structured compared to **1**. The higher energy absorption bands **1** and **2** show high extinction coefficient ($\varepsilon \approx 2.7 - 12 \times 10^4$ $M^{-1}cm^{-1}L$) around 290 nm and hence can be assigned to the spin allowed ligand-centered transitions within the π-conjugated system ($^1\pi \rightarrow \pi^*$). The TDDFT of ligands **1** and **2** help us to correlate the spectral data and the electronic transition along with the main orbital contributions of the transition of **1** and **2** are given in (**Table 1**) and the frontier orbital surface diagrams are shown in **Figure 2.**

Fig. 1 Absorption spectra of ligands **1** and **2** in solvents of different polarities

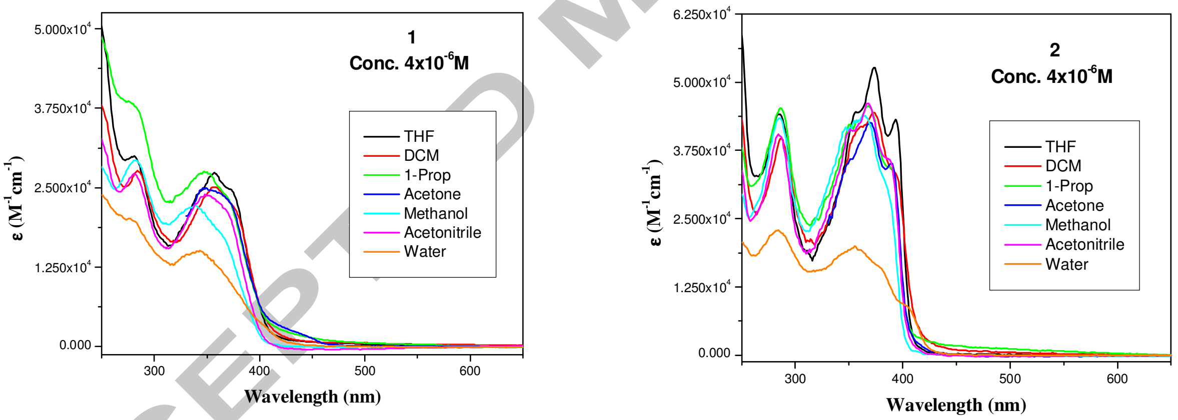
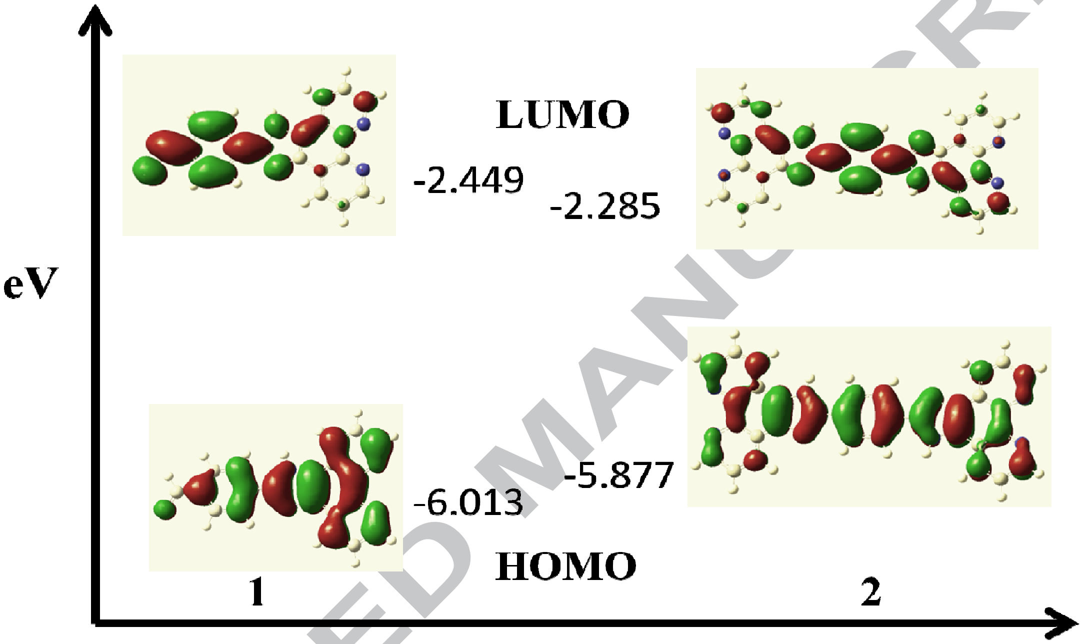


Table 1: The correlation of electronic spectral data with the theoretically calculated spectral assignment

Compound (Dichloromethane)	Absorption (nm)	Calculated (nm, force constant)	Key transition (expt.)
1	377, 357, 284	370.46 (f=0.4175) 362.64 (f=0.0156) 299.26 (f=0.0592)	HOMO -> LUMO (87%) HOMO -1 -> LUMO (86%) HOMO -> LUMO +2 (33%)

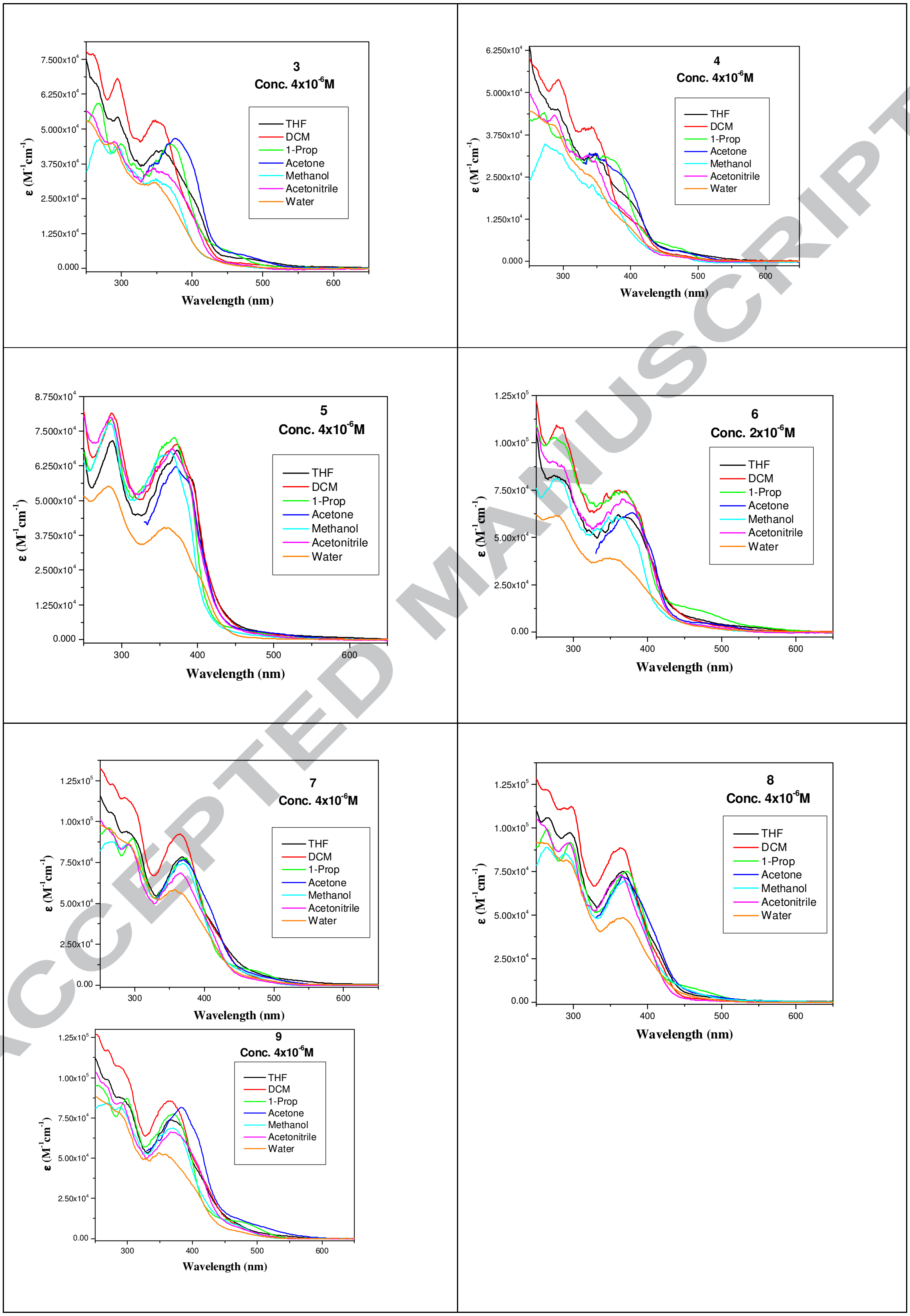
2	371, 354, 314, 287	374.59 (f=1.0825) 350.03 (f=0.0029) 311.50 (f=0.0089) 295.67 (f=0.2363)	HOMO -> LUMO (89%) HOMO - 2 -> LUMO (68%) HOMO -> LUMO+3 (37%) HOMO-6 -> LUMO (54%)

Fig 2. The frontier orbital diagrams of HOMO and LUMO for the compounds **1** and **2**



The absorption spectral studies show that the complexes **3 - 9** absorb at around 290 nm, 350 nm and 470 nm in common organic solvents (**Figure 3**). It is interesting to note that, ε of the high energy bands increases sharply once the phenyl pyridine ligands are first introduced in **3**. This can be attributed to π_{ppy} - π^*_{phen} ligand-to-ligand (^{1}LLCT) charge transfer.[101] The absorption bands around 390 nm have $\varepsilon \approx 2.5 - 9 \times 10^4$ $M^{-1}cm^{-1}L$ **(Table S1)**. Increase in absorption at this wavelength (390 nm) is presumably due to the contribution from the admixture of spin-allowed metal-to-ligand charge transfer.[14] The weak band around ~470 nm with low ε (≈ $0.2 - 10\times10^3$ $M^{-1}cm^{-1}L$, **Table S1**), can be assigned to spin-forbidden ^{3}MLCT and ^{3}LLCT transitions.[102-104] Summarily, the basis of the above assignments are: (i) the high extinction coefficients of the bands, which are consistent with π - π* transitions in polypyridine metal complexes and (ii) similar ppy-centered bands in the protonated ppy and other rhodium(III) and iridium(III) cyclometalated compounds.[29-30, 36 - 51] It is perceivable that influence of 5d and 4d metal ions are quite similar on the absorption spectra of the complexes (**3 - 9**).

Fig. 3 Absorption spectra of **3-9** in solvents of different polarities.



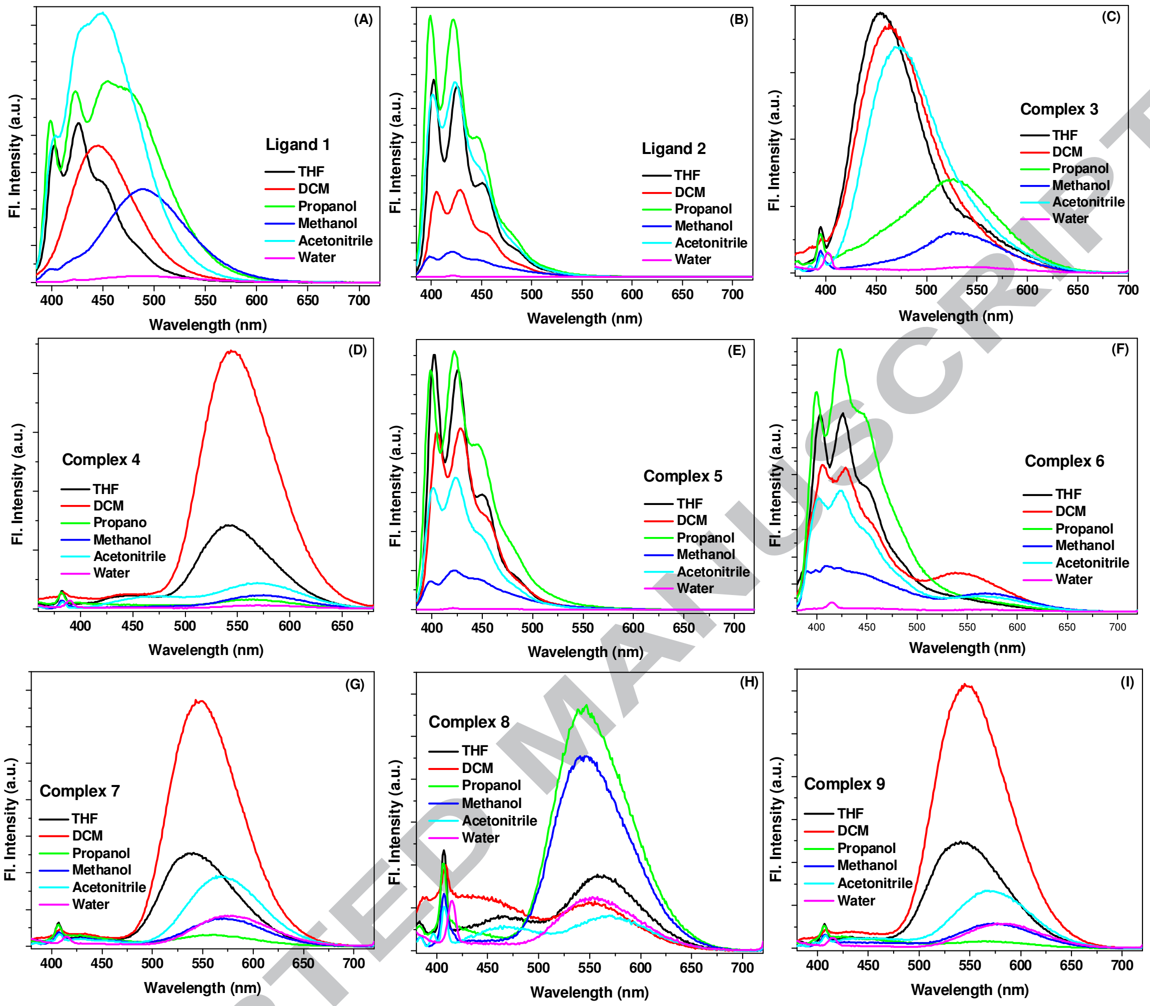
3.2. Emission spectral characteristics

The fluorescence spectra of **1** – **9** and an image of the emission of the compounds (solvent: dichloromethane, λ_{ex} = 366 nm) are shown in **Figure 4**. Characteristic locally excited (LE) and charge transfer (CT) state emissions were observed from **1** in solvents of different polarity. The benzaldehyde moiety in ligand **1** attracts the electron cloud facilitating intramolecular charge transfer (ICT) in solvents of higher polarity. LE emission occurs at lower wavelengths showing bands at at 401, 425 nm and 445 nm. The reason behind appearance of a single structureless band at 425 nm in dichloromethane is unknown. In protic solvents, such as propanol, methanol and water, **1** shows ICT emission at ~490 nm. However, acetonitrile, which is polar and aprotic in nature, does not show ICT. Hence, it is apparent that for **1**, ICT is promoted in polar protic solvents. The –CHO group in **1** can form hydrogen bond with protic solvents that results into enhancement of its electron withdrawing ability. Ligand **2**, on the other hand, shows emission only from the LE state in all the solvents. Symmetric nature of **2** makes it relatively insensitive to solvent polarity and hence no ICT band is observed in this case.

Complexes **3** and **4** were synthesized using the ligand **1** with cyclometalated rhodium and iridium core respectively. Due to the difference in photophysical characteristics of iridium(III) and rhodium(III),[29-30,36-51] the CT (^{3}MLCT) emission is prominent in complex **4**. Complex **3** shows intense ligand-based emission (^{3}LC) peak at 453, 464 and 471 nm in THF, DCM and acetonitrile. However, the emission maximum shifts towards 540 nm in propanol, methanol and water probably contribution of MLCT increases in these solvent. The emission from ^{3}MLCT in complex **4** dominates irrespective of the nature of solvent because of the presence of 5d electrons in iridium(III) in contrast to 4d electrons in rhodium(III) due to large shift in the spin-orbit coupling constant (ζ/cm^{-1}: Rhodium: 1259; Iridium 3909). This phenomenon renders intersystem crossing much easier for the iridium(III) complex. Thus, CT emission in **3** is aided by hydrogen bonding between the –CHO group in of the ligand and the protic solvents. In **4**, MLCT becomes more labile and hence ICT emission is observed readily in all the solvents. Emissions from **5** and **6** are quite similar to **2,** with a less intense MLCT based emission observed only in the cyclometalated iridium complex **6** (λ_{max} = 560 nm).

The complexes **7** to **9** constitute the cyclometalated dinuclear complexes with imidazolyl phenanthroline bridging ligand. The emission spectra of **7**, **8** and **9** are clearly MLCT based and emit in the range 540 – 580 nm. In **8**, although MLCT based emission is prominent but LLCT based emission is also observed at around 400 – 415 nm. Similar spectral characteristic is observed for **7** and **9** presumably due to the presence of iridium(III). The corresponding fluorescence quantum yields for the complexes in various solvents are given in **Table 2**. The image of the complexes shown in cuvette irradiated at 366 nm, completely in agreement with the experimental observation.

Fig. 4. A. Fluorescence spectra of (A-I) **1-9** in solvents of different polarities. Excitation wavelength for **1** - **9** is 350 nm. B.



B. Visible emission of ligands **1-2** and complexes **3-9** in dichloromethane (λ_{ex} = 366 nm)

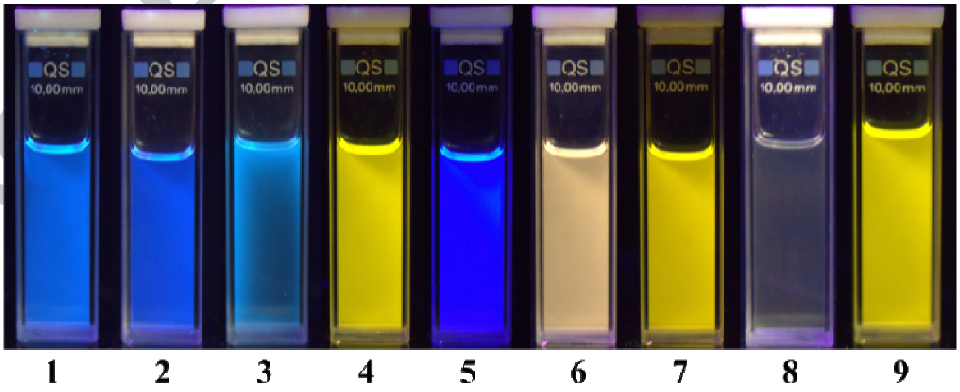


Table 2. Fluorescence quantum yield of the complexes in solvents of different polarities measured with respect to that of quinine hemisulfate in 0.1M H_2SO_4

Complex	THF	DCM	Propanol	Methanol	Acetonitrile	Water
3	0.0103	0.0171	0.0131	0.0080	0.0165	0.0063
4	0.0164	0.0978	0.0042	0.0084	0.0108	0.0067
5	0.1471	0.1480	0.2583	0.0356	0.1596	0.0017
6	0.0215	0.0413	0.0242	0.0192	0.0237	0.0053
7	0.0142	0.0679	0.0025	0.0088	0.0263	0.0048
8	0.0039	0.0023	0.0074	0.0067	0.0012	Negligible
9	0.0200	0.0956	0.0020	0.0072	0.0284	0.0056

3.3. Time resolved fluorescence measurements

Time resolved fluorescence decay data from the ligands and the metal complexes could be fitted by a double exponential function indicating coexistence of two excited state species in all the solvents. The compounds were excited at 340 nm. The 450 nm and 425 nm emissions were monitored for **1** and **2**, respectively. The nanoseconds component in the fit is attributed to the LE state and the picoseconds one to the CT state (**Table 3**).

Table 3. Time-resolved fluorescence decay data for the ligands **1** and **2** in different solvents. The samples were excited at 340 nm and the 450 nm and 425 nm emissions were monitored. Values in parentheses are the percentage contributions to the fits and χ^2 values indicate goodness of the fits.

Ligand	Solvent	τ_1 (ns)	τ_2 (ps)	χ^2
1	THF	2.89 (87)	821 (14)	1.28
	DCM	1.67 (89)	641 (11)	1.11
	Acetonitrile	1.71 (90)	547 (10)	1.18
	Methanol	1.04 (13)	2010 (87)	1.14
	Water	2.41 (31)	570 (69)	1.18
2	THF	2.24 (71)	425 (29)	1.07
	DCM	1.79 (74)	709 (26)	1.19
	Acetonitrile	1.55 (91)	478 (9)	1.09
	Methanol	1.79 (94)	709 (6)	1.19
	Water	1.77 (95)	442 (5)	1.06

This is because percentage contribution of the slower component is greater than the faster one in low polarity solvents, whereas, in water (higher polarity) the contribution gets reverted. It is known that solvents with higher polarity promote CT which explains the result for **1.** However, in **2** we found that the LE state is the major contributor in all the solvents. This is probably due to the absence of a strong electron withdrawing group at an appropriate position as that in **1**. The data from the time-resolved fluorescence experiment corroborate well with the findings from the steady state measurements for **1** and **2**.

Cyclometalated dinuclear rhodium and iridium complexes are known to show slow decay because of intersystem crossing (ISC) to the triplet states.[76-79] Hence, we measured the phosphorescent lifetimes of **7**, **8** and **9** as given in **Table 4**. Although the triplet state phenomena need further studies, but the data indicate that ISC is better exhibited in **7** in low polarity solvents. In case of **8** the trend reverses and for **9** ISC equally less favourable in all sorts of solvents. This is again due to the presence of rhodium(III) in the complexes **7** and **8**, where ISC is not favourable like iridium.[29-30, 36 – 51]

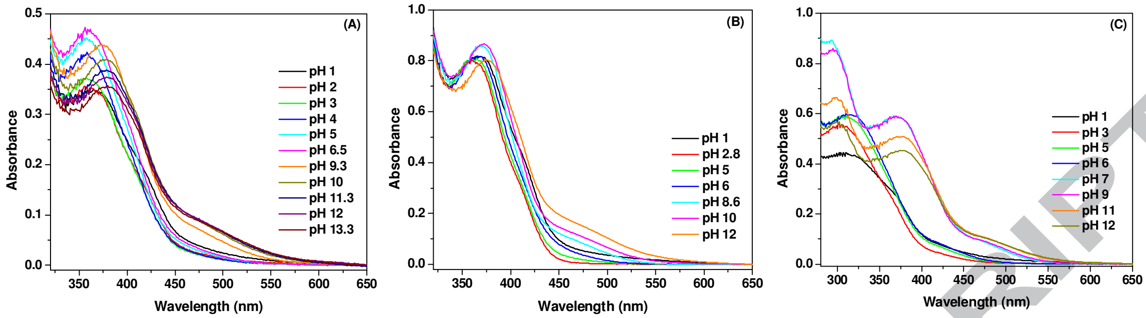
Table 4. Phosphorescence lifetimes (μs) of **7**, **8** and **9**. The values in parentheses are the percentage fit

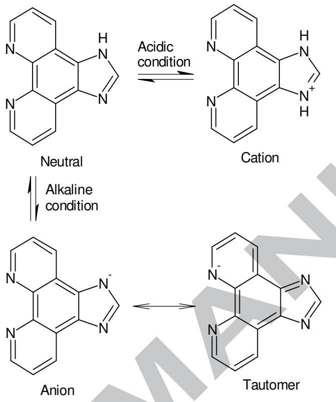
Complex	THF(% Fit)	DCM(% Fit)	ACN(% Fit)	Propanol(% Fit)	Methanol(% Fit)
7	10.1 (99.9)	9.8 (99.8)	9.8 (99.9)	7.9 (90.9)	9.2 (94.9)
8	9.1 (86)	6.2 (38.6)	9.1 (73.8)	9.4 (99.5)	9.3 (99)
9	10.1 (99.8)	11.3 (99.6)	9.9 (99.8)	9.7 (99.7)	9.4 (99)

3.4. Effect of pH on the photophysics of 7-9

The absorption spectra of **7**, **8** and **9** are shown in **Figure 5** collected at different pH in aqueous medium. The complexes were dissolved in water using dimethylsulfoxide (DMSO) as co-solvent to acquire a final concentration of 6 μM. **7** and **8** show an intense absorption at 360 nm and a weak shoulder at ~410 nm in low pH (acidic condition), whereas **9** shows absorption bands at 307 nm and 370 nm. Up to pH 6 we observed enhancement in the lower wavelength band along with a concomitant decrease of the shoulder. This helped us to attribute the lower wavelength band to the neutral benzimidazolyl species and the shoulder to its cationic form. The spectral features in all the three cases show an abrupt shift in the absorption spectrum as the medium acquires pH > 6. The sudden change observed is due to ionization of the imidazolyl group at around pH 5.5. Under alkaline condition, **7** and **8** show an intense peak at 370 nm and a weak shoulder at 480 nm. The peak at 370 nm is due to the normal anionic form of the benzimidazolyl moiety and the shoulder at 480 nm is for its tautomer (**Scheme 2**).[105] In **9**, all the three species coexist at all pH. **Figure 6** presents the fluorescence spectral changes for **7**, **8** and **9** under different pH from acidic to alkaline conditions. All the complexes show emission at three wavelengths. Emission in the lowest wavelength with very low fluorescence yield could be due to the benzimidazolyl cationic species. In **7** the emission from this species decreases with increase in solution pH.

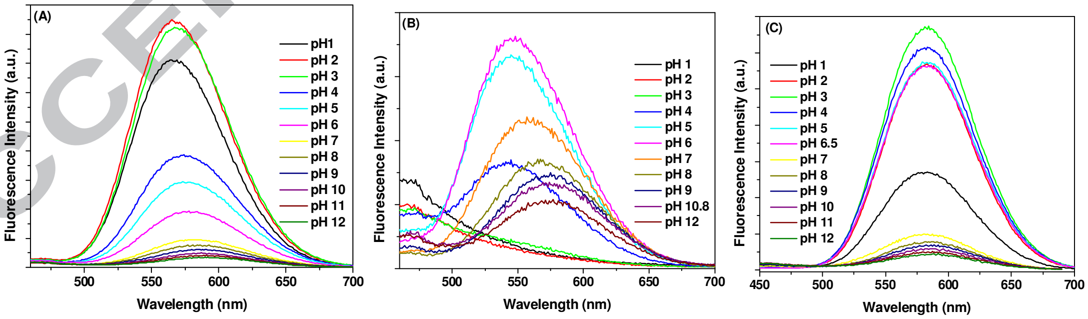
Fig. 5 Absorption spectra of (A) **7**, (B) **8** and (C) **9** at different pH.





Scheme 2 Molecular structure of the chromophoric part of the ligands (**1** and **2**) under different pH conditions.

Fig. 6 Fluorescence spectra of (A) **7**, (B) **8** and (C) **9** at different pH of the medium. The samples were excited at 370 nm.



The fluorescence spectra of **8** at different pH are quite different from the rest as we could see ligand-centered emission from the cationic species up to pH 3 that decreases in intensity as the pH increases from 1 to 3. There is a red shift in the emission maximum to 550 nm with further increase in pH of the medium. The intensity of emission increases until pH 6 followed by a decrease. An intense band is observed for **7** (λ_{max} =565 nm) at pH = 2 decreases with increase in pH. For **8** and **9** the bands appear at 550 nm and 580 nm are considered to be due to the neutral form of the benzimidazolyl moiety. Over pH 6 we observed a profuse reduction in intensity of the band with a bathochromic shift. We attribute this band to the anionic form of the benzimidazolyl moiety. All the three species coexist for **9**. The findings match well with those observed from the absorption studies. The behavioural difference between **8** with **7** and **9** could be due the presence of rhodium metal at both sides of the bridging ligand. Rhodium being more redox active than iridium, can diffuse the electron density to phenylpyridine moiety easily. In case of the iridium(III) complex, however, the bridging ligand bear the impact of the change in pH more than in complex **8**.

3.6. Cyclic voltammetry

The complexes **3**, **4**, **7**, **8** and **9** were subjected to a scan from -2.00 to 2.00V to understand the redox behaviour (**Table 5**). Due to extremely poor solubility we could not record the cyclic voltammograms for **5** and **6**. The rhodium complexes **3**, **7** and **8** have similarity in their first oxidation potentials >1.42 V (3 = 1.53V, 7 = 1.42V, 8 = 1.46V) attributed to the M(III) - M(IV) oxidation, whereas, purely homonuclear iridium complexes **4** and **9** have their first oxidation around ~1.07V(Ir(III)-Ir(IV).[106] Interestingly, complex **7**, which contain both the metals shows peaks quite similar to the rhodium complexes **3** and **8**. The Ir(III)-Ir(IV) oxidation is not visible in complex **7** which may be due to the current height of the rhodium oxidation peak. In addition to the metal centered peaks, the other oxidation and reduction peaks are certainly ligand based.

Table 5. The redox potential of complexes **3** - **4** and **7** - **9**.

Complex	Redox potential (V)	
	E_{ox}	E_{red}
3	0.67, 1.019, 1.53	-1.048, -1.33, -1.75
4	1.07, 1.33 (90 mV)[a], 1.84	-0.79, -1.24, -1.54 (80 mV)[a]
7	0.66, 0.92, 1.42	-0.99, -1.44
8	0.63, 1.46	-0.80, -1.29, -1.46, 1.72 (100 mV)[a]
9	1.08, 1.35, 1.62	-0.78, 1.26, -1.63

[a] $\Delta Ep = E_{pa} - E_{pc}$ in mV

4. Conclusions

In summary, we have synthesized three homodinuclear and heterodinuclear cyclometalated rhodium(III) and iridium(III) complexes. To have a better understanding on the photophysical and electrochemical properties of the systems the mononuclear precursors were also synthesized and studied in detail. The effect of ligand emission on the purely rhodium based complexes over MLCT based emission and pronounced effect of MLCT-based emission for iridium based complexes can be visualized very prominently on excitation at 366 nm. It is quite interesting to note that, the photophysical property of the heterodinuclear complex behaves like pure iridium based complexes. Conversely, the electrochemical property of the heterodinuclear complex is quite similar to the rhodium analogue. We are working on the device fabrication with heterodinuclear system, where well established electrochemical character of rhodium

5. Supplementary materials: [Figure **S1-S7**: ESI-MS of the complexes. Figure **S8** - **S14**: ^{1}H NMR of the complexes. **Table S1**: Molar extinction coefficients of ligand **1-2** and complex **3-9**

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Cyclometalated mono and dinuclear rhodium(III) and iridium(III) complexes with imidazolyl phenanthrolines: Synthesis, photophysical and electrochemical characterization

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Homonuclear and heterobinuclear cyclometalated rhodium(III) and iridium(III) complexes **3 - 9** were synthesized with imidazolyl modified phenanthroline ligands. The detail photophysical studies reveal that the emission behaviour of the rhodium complexes is greatly influenced by ligand emission behaviour.