Mononuclear and binuclear ruthenium(III) polypyridyl complexes containing 2,6-bis(2'-benzimidazyl)-pyridine as co-ligand: Synthesis, spectroscopic properties and redox activity

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A series of complexes of the general formula \([\text{Ru Hbbip X Cit}]\), \([\text{Ru Hbbip (Xh)}_2]\)\(^+\) and \([\text{(Ru Hbbip Xh pyz)}_3]\)\(^+\); H2bbip = 2,6-bis-(2'-benzimidazyl) pyridine; pyz = pyrazine and X = 2,2'-bipyridine/1,10-phenanthroline have been synthesized and characterized by their elemental analysis, spectral (IR, \(^1\)H NMR, UV-visible and ESR) and redox data. Comparative luminescent behaviour of the complexes in the presence and absence of calf-thymus DNA has also been studied.

Photophysical and photochemical studies of polypyridine complexes of transition metals have shown impressive growth because of their ability to mediate electron and/or energy-transfer processes\(^1\). It has been realized that the energy and information carried by photons could be exploited more by photoinduced processes in suitably designed supramolecular (multicomponent) systems rather than in intermolecular photoreactions\(^2\).

However complexes of \([\text{Ru(bpy)}_3]\)\(^2\) family were found to be unsuitable from geometric isomerism\(^3\) viewpoint. Therefore, several researchers\(^4\) have focussed their attention on the complexes of the \([\text{Ru(tpy)}_3]\)\(^2\) family (tpy = 2,2':6,2''-terpyridine) inspite of the fact that it exhibits less favourable photophysical properties, in particular its lack of luminescence at room temperature owing to its much shorter excited state lifetime\(^5\). But the suitable substituents especially at 4’-position of terpyridine have been reported\(^6\) to display room-temperature luminescence. Thus in order to avoid isomeric complexities we selected a terpyridyl ligand where pyridine ring is attached to two benzimidazole groups through its 2,6-positions since benzimidazole ring has been reported to be involved in the strong intramolecular stacking interactions between the DNA strands\(^7\) and to induce bioactivity to the resulting complex\(^8\). Additional support for such selectivity was also based on the recent report by Bailey et al.\(^9\) that simple substitution in Ru(III) complexes with nitrogen ligands (NH\(_3\), imidazole, pyridine) potentiates the immuno suppressant activity and these could also function as antitumour drugs in view of an earlier report\(^10\) on Ru(III) imidazole complexes.

Taking all these points into consideration in addition to a current report\(^11\), the present work was undertaken on the synthesis and spectral studies of some mononuclear Ru(III) complexes and pyrazine-bridged Ru(II)/Ru (III) dinuclear complexes.

Materials and Methods

Solvents and starting material were purchased from Sigma-Aldrich and used without further purification but dimethylformamide was used after distillation. All the reactions were carried out under nitrogen. Aluminium oxide (Merck) was used for column chromatography and commercial (Fluka) tetrabutylammonium bromide was converted to pure tetrabutylammonium perchlorate (TBAP) by a reported procedure\(^12\).

Microanalysis (C, H, N) was performed on a Carlo Erba Elemental Analyzer 1108. FAB Mass data were collected on a Jeol SX-102 mass spectrometer at CDRI Lucknow, India. IR (KBr pellets) and UV-visible (DMSO) spectra were recorded on a Jasco FT IR 5300 spectrophotometer and a Cary 23 spectrophotometer respectively whereas ESR spectra, in solid state and in solution (DMSO) at room temperature and liquid N\(_2\) temperature, were recorded at Indian Institute of Technology, Mumbai, India. Electrochemical measurements were made using a electrochemical interface SI 1287 potentiostat, using a graphite disc as working electrode, platinum wire as
auxiliary electrode and Ag/Ag⁺ as reference electrode in a three-electrode configuration. Emission spectra (in CH₃CN) were measured using a Shimadzu spectrofluorophotometer RF-540.

**Synthesis of ligand**

2,6-Bis-(2′-benzimidazyl) pyridine (H₂bbip) was prepared from 2,6-pyridine dicarboxylic acid and o-phenylenediamine in acidic media following the reported procedure.⁸

**Synthesis of complexes**

[Ru H₂bbipCl₃] (I)—An ethanolic solution (5 ml) of RuCl₃ (0.1 mol, 2.07 g) was added to an ethanolic solution (10 ml) of H₂bbip (0.1 mol, 3.11 g) with stirring and the contents were then refluxed for 16 h. After keeping for 12 h in a refrigerator the brown precipitate obtained was filtered off and washed with ethanol and then recrystallized from water (I: I) as a brown powder, yield 35-40%; M.P. > 250°C; m/z 775 [M]. Found: C, 45.48; H, 3.47; N, 13.22. [Ru C₂₀H₁₇N₅Cl₃ PF₆] 2C₂H₅OH requires: C, 45.72; H, 3.69; N, 12.93%; vₘₐₓ cm⁻¹ (KBr) 3422 (-NH), 1602 (-C=C-aromatic), 1506 (-C=N). The insoluble part was dissolved in DMSO, and then precipitated and purified as described for compound 2. Finally it was crystallized from acetone by its slow evaporation; yield 25-30%; M.P. > 250°C; m/z 775 [M]. Found: C, 47.07; H, 3.88; N, 10.67 [Ru C₉₁H₇₇N₉O₂PF₆] .3C₂H₅OH requires: C, 46.87; H, 4.07; N, 10.93%; vₘₐₓ cm⁻¹ (KBr) 3437 (-NH), 1604 (-C=C-aromatic), 1510 (-C=N).

[Ru Hbbip bpy Cl][PF₆] (2)—An ethanolic solution (10 ml) of 2,2′-bipyridine (1 mmol; 156 mg) was added to the solution of 1 (1 mmol; 578.5 mg) dissolved in DMSO (5 ml) with stirring. The contents were then refluxed for 24 h. After cooling at room temperature, the residue left was discarded. To the filtrate, saturated methanolic solution of NH₄PF₆ was then added. Dark brown precipitate thus obtained was filtered and then purified on a column chromatograph using alumina as a column support and MeCN-saturated aqueous KN0₃ - water (7:1:0.5 v/v) as eluent. The eluate was evaporated to dryness and the residue thus obtained was dissolved in the minimum volume of acetonitrile followed by the excess addition of methanolic solution of NH₄PF₆. The solid product complex was then recrystallized from ethanol as a brown coloured crystalline complex. M.P. > 250°C; yield 35-40%; m/z, 750 [M]. Found: C, 47.93; H, 2.48; N, 11.55 [Ru C₉₁H₇₇N₉ClIPF₆] .H₂O requires: C, 47.02; H, 2.91; N, 12.38%; vₘₐₓ cm⁻¹ (KBr) 3425 (-NH), 1604 (-C=C-aromatic), 1527 (-C=N).

[Ru Hbbip bpy NO₃][PF₆] (3) and [Ru Hbbip (bpy)₂][PF₆] (4)—Complex 1 (1 mmol; 518.5 mg) and AgNO₃ (3 mmol; 570 mg) in acetone (50 ml) were refluxed and the mixture was then filtered to remove AgCl; DMF (100 ml) was then added to the filtrate and the excess of acetone was evaporated. To the resulting solution, a hot solution (80°C) of 2,2′-bipyridine (1 mmol; 156 mg) in DMF (100 ml) was slowly added under nitrogen. The contents were refluxed for 4 h. The excess DMF was then distilled off under reduced pressure. The residue was dissolved in excess of CH₃CN and insoluble part was filtered. To the filtrate, excess of methanolic NH₄PF₆ was added and the brown precipitate obtained was filtered and purified as described for compound 2. Finally it was crystallized from acetone by its slow evaporation; yield 25-30%; M.P. > 250°C; m/z 775 [M]. Found: C, 49.60; H, 3.22; N, 10.66. [Ru C₉₁H₇₇N₉P₂F₁₁] .3C₂H₅OH requires: C, 49.0; H, 3.91; N, 10.50%; vₘₐₓ cm⁻¹ (KBr) 3427 (-NH), 1601 (-C=C-aromatic), 1507 (-C=N).
acetone was distilled out followed by the dropwise addition of a hot solution of pyrazine (0.5 mmol; 0.04 g) in DMF (50 ml). The contents were then refluxed for 6 h. DMF was distilled out in vacuo and the residue thus obtained was dissolved in CH3CN (20 ml) and was precipitated by the excess addition of NH4PF6. The purification was done as stated earlier for 2, M.P. > 250°C; yield 40-45%; m/z; 1649 [M]. Found: C, 46.58; H, 3.71; N, 11.89%. IR max cm⁻¹ (KBr) 3379 (-NH), 1604 (-C=C-aromatic), 1649 (-C=C-aromatic), 1506 (-C=N).

[RuII Hbbip phenpyz phen Hbbip RuIII] (PF6)4C2H5OH (8) — It was prepared using the same procedure as described above for compound 7 except that 1,10-phenanthroline was used instead of 2,2'-bipyridine; M.P. > 250°C; yield 35-40%; m/z; 1262 [M-3PF6]4+. Found: C, 47.58; H, 3.47; N, 12.15 [RuII(C5H46N10P13F18)]·5C2H5OH requires: C, 45.98; H, 4.04; N, 11.92%; v max cm⁻¹ (KBr) 3422 (-NH), 1604 (-C=C-aromatic), 1508 (-C=N).

[RuII Hbbip phen pyz phen Hbbip RuIII] (PF6)4 (9) — To an ethanolic solution of Hbbip (2 mmol, 0.622 g), an ethanolic solution (5 ml) of RuCl3 (1 mmol; 0.207) was added with stirring followed by the addition of two drops of N-ethylmorpholine. The rest of the procedure was the same as used for compound 1: yield 50-60%; Found: C, 58.73; H, 4.40; N, 16.62. [RuII(C5H46N10)] requires: C, 59.34; H, 4.10; N, 16.88%; v max cm⁻¹ (KBr) 1620 (-C=C-aromatic), 1506 (-C=N); 1H NMR (90 MHz, 293 K, DMSO-d6) δ 8.46-8.00 (m, bpy + Ar), 8.77-8.33 (m, bpy + Ar), 7.73-7.33 (m, bpy + Ar).

[RuII Hbbip bpy Cl][PF6]4 (10) — It was prepared and purified by the same method as used for compound 2 except that a few drops of N-ethylmorpholine were added to the reaction mixture; yield 30%; 1H NMR (90 MHz, 293 K, DMSO-d6) δ 8.46-8.00 (m, py + bpy + Ar), δ 7.73-7.33 (m, bpy + Ar).

Results and Discussion

[Ru Hbbip bpy NO3]3, [Ru Hbbip (phen)2]3+, [Ru Hbbip (bpy)]3+, [Ru Hbbip (bpy)2(py)]3+ and [Ru Hbbip (phen)2(py)]3+ were prepared according to the literature method. Reported procedure was also followed for the preparation of compound [RuII Hbbip bpy Cl]. This compound was prepared to get the structural support for 1H NMR spectral data. The positions of protons δ (ppm) correspond well with the proposed structure and were assigned in view of earlier reports. The 1H NMR signals in the spectrum of compound [RuII (bipy)]3+ also corresponded well with the reported value.

IR spectra — The FTIR spectra (KBr) showed the characteristic ligand vibrations at 1595 and 1527 cm⁻¹ assigned as ν-C=C and ν-C=N respectively. In complexes, the peak observed at 1595 cm⁻¹ (pyridyl + C=C-aromatic) shifted to 1601-1624 cm⁻¹ whereas peaks at 1527 cm⁻¹ (C=N) shifted to 1510-1506 cm⁻¹.

A peak observed at 3470 cm⁻¹ in the spectrum of ligand (Hb2bip) due to vNH shifted to 3437-3379 cm⁻¹ in the spectra of its complexes showing that coordination with the metal had occurred. However, a peak observed in still higher region (= 3600 cm⁻¹) in the spectra of the complexes was considered to be due to vOH of solvents (C2H5OH/H2O) present in the complexes. A strong and sharp vibration observed at ~840 cm⁻¹ in the spectra of all complexes was assigned as v(PF6)3.

ESR spectra — The ESR spectrum of [Ru Hbbip bpy Cl]3+ (Fig. 1) showed broad signals at 298 K and 77 K in solid state. However, the spectrum at 77 K was better resolved. The solution (DMSO) spectrum at 298 K showed a set of three peaks (g1, g2, g3) but at 77 K an additional set of three peaks (g′1, g′2, g′3) was also observed. This observation showed that there could be two different sets of coordinating environment around Ru(III). It could only be possible either (i) due to impurity of the initial compound or (ii) due to the formation of a new compound. The first possibility was discarded on the basis that no such peaks were observed in the initial compound. Thus, the second possibility is quite likely as there is an evidence that chloride ions are easily substituted by DMSO so the weak peaks observed in the spectrum (Fig. 1) might be the result of partial substitution of chloride ion by DMSO. The g values calculated from the peaks of major set were found as g1 = 2.334, g2 = 2.052, g3 = 2.021 but from the weaker peaks these values were found as g′1 = 2.448, g′2 = 2.174 and g′3 = 1.930. Since the possibility of substitution occurs only at low temperature (77 K) isolation of new product at 298 K was not possible.

UV-visible — Solution (DMSO) UV/vis spectra of the complexes (10⁻⁵ M) were recorded in the region 200-800 nm and the spectral data are listed in Table 1.
Table 1—UV/vis and luminescent data

<table>
<thead>
<tr>
<th>Complexes</th>
<th>λ nm (ε d m³ mol⁻¹ cm⁻¹)</th>
<th>λₓₓₓ (nm)</th>
<th>λₓₓₓ (nm)</th>
<th>λₓₓₓ (nm)</th>
<th>Emission quenching %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>620 (34000), 328 (110000), 310 (100000), 290 (190000), 244 (95000)</td>
<td>620</td>
<td>740</td>
<td>740</td>
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<td>2</td>
<td>540 (5000), 448 (23000), 416 (22000), 328 (76000), 290 (58000), 244 (60000)</td>
<td>455</td>
<td>520</td>
<td>518</td>
<td>19.6</td>
</tr>
<tr>
<td>3</td>
<td>568 (9000), 490 (34000), 328 (31000), 290 (23000), 244 (24000)</td>
<td>500</td>
<td>600</td>
<td>595</td>
<td>22.4</td>
</tr>
<tr>
<td>4</td>
<td>568 (5000), 490 (16000), 328 (140000), 310 (100000), 290 (90000), 244 (95000)</td>
<td>455</td>
<td>595</td>
<td>595</td>
<td>13.2</td>
</tr>
<tr>
<td>5</td>
<td>560 (11000), 508 (34000), 328 (90000), 290 (78000), 244 (80000)</td>
<td>500</td>
<td>592</td>
<td>590</td>
<td>23.6</td>
</tr>
<tr>
<td>6</td>
<td>500 (10000), 444 (35000), 420 (36000), 328 (90000), 310 (80000), 290 (65000), 244 (70000)</td>
<td>455</td>
<td>595</td>
<td>595</td>
<td>10.6</td>
</tr>
<tr>
<td>7</td>
<td>568 (5000), 448 (15000), 416 (140000), 328 (50000), 310 (40000), 290 (30000), 244 (35000)</td>
<td>450</td>
<td>610</td>
<td>605</td>
<td>41.5</td>
</tr>
<tr>
<td>8</td>
<td>548 (22000), 484 (67000), 328 (100000), 310 (90000), 290 (80000), 244 (85000)</td>
<td>480</td>
<td>595</td>
<td>585</td>
<td>48.9</td>
</tr>
<tr>
<td>9</td>
<td>500 (11500), 480 (12000), 328 (80000), 310 (40000), 290 (30000), 244 (35000)</td>
<td>450</td>
<td>600</td>
<td>595</td>
<td>31.5</td>
</tr>
<tr>
<td>10</td>
<td>500 (16000), 480 (17000), 328 (90000), 310 (80000), 290 (70000), 244 (72000)</td>
<td>450</td>
<td>515</td>
<td>515</td>
<td>20.6</td>
</tr>
</tbody>
</table>

* in CH₃CN 10⁻⁴ M concentration

*calculated with respect to \( \frac{\text{Emission max(-DNA)} - \text{Emission max(+DNA)}}{\text{Emission max(-DNA)}} \times 100 \)

Two intense peaks observed at λ 244 and 322 nm were found to originate from a ligand centred transition but in the spectrum of [Ru H₂bbip Cl₁] a very broad peak observed at λₓₓₓ 620 nm (ε = 34000) was assigned to a transition from the ligand (H₂bbip) π* orbital to metal π orbital (LMCT) in view of an earlier report on Ru (III) complexes. Upon substitution of chloride ions by 2,2'-bipyridine/1,10-
phenanthroline, the LMCT transition shifted to lower wavelengths as a shoulder at 500-568 nm. Additionally, the intense absorption observed at \( \lambda > 500 \) nm was assigned to the metal (d\( ^* \)) to \( \pi^* \) (2,2'-bipy/1,10-phenanthroline) transitions (MLCT).

However, in the spectrum of 10 two absorptions observed at \( \lambda_{max} \) 480 and \( \lambda_{max} \) 500 nm were assigned as MLCT transitions from filled metal \( t_{2g} \) orbital to the two different \( \pi^* \) acceptor orbitals since no shoulder was observed at higher wavelength sides as observed in the spectrum of Ru(III) complex. Similar spectral behaviour was also observed for the complex 9 in agreement with the earlier report.

In the case of the dinuclear mixed valence complexes containing 2,2'-bipyridine as a terminal ligand, a shoulder observed at \( \lambda_{max} \) 568 nm was assigned to the MLCT transitions from Ru(II) to pyrazine as reported earlier. It is obscured by d-d-transition. Two peaks observed at 416 and 448 nm were assigned to MLCT transitions. These are due to the transitions from metal to two different acceptor levels in H-2bip and bpy; however, the absorption intensity observed in each case was found to be lower than that obtained from the sum of the absorbances (\( \varepsilon \) values) observed in case of the separate mononuclear Ru(II) and Ru(III) complexes. Thus, it could be inferred from this observation that there is loss of energy during the charge transfer between the two oxidation states. Similar spectral behaviour was also observed for the complexes containing 1,10-phenanthroline as terminal ligands.

To support this energy transfer between two oxidation states of ruthenium centres near-IR-spectra of these complexes were also recorded.

Near infrared spectra—The near-IR-spectra recorded for the complexes 7 and 8 showed (Fig. 2) two intervalence charge-transfer bands at 1450, 1550 and 1470, 1570 nm respectively and the values were found to be consistent with those reported for similar mixed valence dimetallic complexes.

Since these complexes were prepared using Ru(III) precursors and out of mentioned coordination centres one was getting reduced so it was considered probable that the solvent (DMF) might be reducing one of the ruthenium ions from III \( \rightarrow \) II state. In order to check this, [Ru(III) Hbip bpy Cl\( ^+ \)]\(^{14+} \) and [Ru(II) Hbip bpy Cl\( ^+ \)]\(^{2+} \) (2 and 10) in 1:1 ratio were refluxed together in DMF using similar method as used for the synthesis of complexes 7-8. It was found that Ru(III) centre was getting reduced. The product thus isolated was identified as 11 since its \( ^1H \)-NMR spectrum (Fig. 3) was found to be well resolved as compared to the broad spectrum obtained for its precursor complex 2. Furthermore, complex 11 did not show any band in near-IR region, whereas complex 7 which is proposed to contain Ru\( ^{II} \)-Ru\( ^{III} \) ions showed the band in near-IR region. Thus, this complex was considered to contain Ru\( ^{II} \)-Ru\( ^{II} \) ions. However, similar reduction did not occur when the above reaction was carried out in the presence of acetone as a solvent.

Thus on the basis of IR, \(^1H \) NMR, UV/vis, ESR, FAB mass and elemental analysis data the proposed
structures for the complexes are depicted in Fig. 4.

Room temperature emission spectra — From the emission wavelengths of the complexes (Table 1) obtained after the excitation of their solutions (DMSO, \(10^{-5} M\)) to \(\lambda = 450-620\) nm, it was observed that the complex \([\text{Ru}^{	ext{II}}(\text{bbip})_2]\) luminesces at \(\lambda_{\text{max}} = 600\) nm whereas it has been reported that the complex \([\text{Ru}^{	ext{II}}(\text{terpy})_2]^2+\) is non-luminescent at room temperature. Thus the substitution of benzimidazole group at 2, 6 positions of pyridine ring resulted into the formation of a luminescent Ru(II) complex at room temperature.

Furthermore, addition of calf-thymus DNA (2 mg/10 ml) in tris phosphate buffer (0.5 \(M, \text{pH} = 7.1\)) solution to the complexes resulted in the quenching of luminescent intensity by 13.2-48.9% along with a blue shift in the \(\lambda_{\text{max}}\) by 2-10 nm.

It is worth mentioning that luminescent behaviour of the complexes was studied on a preliminary level and the quenching of luminescence is comparative to each other.
Redox properties—Electrochemical properties of the complexes have been studied in acetonitrile solution by cyclic voltammetry (CV) and they have been found to be active in the potential range ±2 V Ag/Ag⁺. Representative voltammograms for the complexes 2, 7 and 11 are shown in Fig. 5 and the redox potential data are given in Table 2.

Oxidation—A single oxidation peak observed from Ru(III) complex 1 at 1.4 V attributable³⁴,¹⁷ to Ru(III) → Ru(IV) oxidation is shifted to lower potential at 1.25 V in the CV of 2,2’-bipyridine/1,10-phenanthroline substituted complexes (2-6). This could be possible in view of greater π* accepting behaviour of 2,2’-bipyridine/1,10-phenanthroline as compared to chloride ions. Furthermore, when the complex 2 was reduced chemically the resulting complex 10 gave an oxidation potential at 1.16 V.

In the case of mixed valence complexes (7 and 8) two successive oxidation peaks observed at 0.43, 1.06 and 0.5; 1.20 V respectively were found to lie at a higher potential than those reported for the famous Creutz-Taube complex¹⁷. It could happen most likely due to enhanced energy gap between π* (ligand) - metal (d) orbitals.

However, the observation of two oxidation peaks at 0.45 and 0.80 V in the dinuclear Ru(II)/Ru(II) complex 11 could be explained in terms of electronic communications¹⁹ between ruthenium centres since
Table 2—Electrochemical data*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal oxidation</th>
<th>Ligand reduction (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.40</td>
<td>-0.50, -1.00, -1.62, -1.80</td>
</tr>
<tr>
<td>2</td>
<td>1.25</td>
<td>-0.63, -1.29, -1.42, -1.75</td>
</tr>
<tr>
<td>3</td>
<td>1.25</td>
<td>0.90, -1.56, -1.80, -1.96</td>
</tr>
<tr>
<td>4</td>
<td>1.25</td>
<td>-0.88, -1.25, -1.88</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>-0.63, -1.37, -1.63, -1.88</td>
</tr>
<tr>
<td>6</td>
<td>1.25</td>
<td>-0.90, -1.50, -1.825, -1.89</td>
</tr>
<tr>
<td>7</td>
<td>0.43, 1.06</td>
<td>-0.75, -1.45, -1.88</td>
</tr>
<tr>
<td>8</td>
<td>0.50, 1.20</td>
<td>-0.63, -1.50, -1.88, -1.96</td>
</tr>
<tr>
<td>9</td>
<td>1.17</td>
<td>-0.93, -1.45, -1.88</td>
</tr>
<tr>
<td>10</td>
<td>1.16</td>
<td>-0.75, -1.25, -1.87</td>
</tr>
<tr>
<td>11</td>
<td>0.45, 0.80</td>
<td>-0.75, -1.68, -1.90</td>
</tr>
</tbody>
</table>

*Conditions: Solvent acetonitrile; supporting electrolyte, TBAP (0.1 M), working electrode, graphite disc; auxiliary electrode, platinum; reference electrode Ag/Ag⁺; solute concentration -10⁻³ M, \( E_{1/2} = 0.5 \left( E_{pa} + E_{pc} \right) \) where \( E_{pa} \) and \( E_{pc} \) are anodic and cathodic peak.

the coordinating environment of both centres is similar.

**Terminal ligand reductions**—As shown in Table 2 all complexes showed three to four successive reduction peaks at -0.5 to -0.9 V, -1.00 to -1.56 V, -1.42 to -1.62 V and -1.8 to -1.96 V which are in accordance with the reported values for \( \text{H}_2\text{bbip} \), \( 2,2'\text{-bipyridine} \) and \( 1,10\text{-phenanthroline} \) ligands.

The present studies show that the tridentate ligand (\( \text{H}_2\text{bbip} \)) provides an opportunity to make selective substitution of only two chloride ions in the complex by \( 2,2'\text{-bipyridine}/1,10\text{-phenanthroline} \) leaving the space for the creation of ligand (pyrazine) bridged dinuclear Ru\(^{II}\)-Ru\(^{II}\)/Ru\(^{II}\)-Ru\(^{III}\) complexes. Also, mixed valence dinuclear complexes could be prepared using DMF as a solvent for their photophysical and electrochemical studies.

Benzimidazole substituted ligand (\( \text{H}_2\text{bbip} \)) makes the ruthenium complex luminescent even at room temperature. The quenching of luminescence on addition of calf-thymus DNA provides additional opportunity to look into the bioactive behaviour of the complexes.

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