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# Luminescent bis-tridentate ruthenium(II) and osmium(II) complexes based on terpyridyl-imidazole ligand: synthesis, structural characterization, photophysical, electrochemical, and solvent dependence studies<sup>†</sup>

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Homo- and heteroleptic bis-tridentate ruthenium(II) and osmium(II) complexes of compositions  $[(tpy-PhCH_3)Ru(tpy-HImzPh_3)](ClO_4)_2$  (1),  $[(H_2pbbzim)Ru(tpy-HImzPh_3)](ClO_4)_2$  (2) and  $[M(tpy-HImzPh_3)_2](ClO_4)_2$  [M = Ru<sup>II</sup> (3) and Os<sup>II</sup> (4)], where tpy-PhCH<sub>3</sub> = *p*-methylphenyl terpyridine, H<sub>2</sub>pbbzim = 2,6-bis(benzimidazole-2-yl)pyridine and tpy-HImzPh<sub>3</sub> = 4'-[4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenyl]-[2,2':6',2'']terpyridine, have been synthesized and characterized by using standard analytical and spectroscopic techniques. These compounds were designed to increase the room temperature excited-state lifetimes of bisterpyridine-type ruthenium(II) and osmium(II) complexes. The X-ray crystal structures of two homoleptic complexes 3 and 4 have been determined and show that both the compounds crystallized in orthorhombic form with space group Fddd. The photophysical and redox properties of the complexes have been thoroughly investigated. All the complexes display moderately strong luminescence at room temperature with lifetimes in the range of 6–35 ns. The complexes are found to undergo one reversible oxidation in the positive potential window (0 to +1.6 V) and one irreversible and two successive quasi-reversible reductions in the negative potential window (0 to -2.0 V). The influence of solvents on the photophysical properties of the complexes have also been investigated in detail.

# Introduction

Ruthenium(II) and osmium(II) complexes with polypyridyl ligands are potentially useful in many important areas of research such as photochemical conversion of solar energy, catalytic conversion of water to molecular oxygen and molecular electronic devices because of their unique combination of spectroscopic, photophysical, photochemical and electrochemical properties.<sup>1-3</sup> These properties can often be tuned by modification of the ligand structures and by introducing co-ligands in the complexes. Among the most widely studied complexes, particularly popular are the ruthenium complexes derived from the bipyridine-type of ligands because of their excellent photo-redox properties.<sup>1-3</sup> However, the synthesis of tris(bpy)-type complexes is hampered by the mixtures of diasteromers that form due to its  $\Delta$  and  $\Lambda$  enantiomers and by the fac and mer isomers generated by mono-substituted bpy ligands.<sup>1,4</sup> In contrast to [Ru(bpy)<sub>3</sub>]<sup>2+</sup> type complexes, structurally more appealing [Ru(tpy)<sub>2</sub>]<sup>2+</sup> type complexes give linear rod-like assemblies when substituted at the 4'-position of the tpy ligands.<sup>5</sup> However, usually such complexes are practically non-luminescent at room temperature and their excited state lifetimes ( $\tau = 0.25$ ns) are also very short.<sup>6</sup> Consequently, lots of effort has been devoted to design and synthesize tridentate polypyridine ligands that can produce ruthenium(II) complexes with enhanced excitedstate lifetimes at room temperature. Most of the approaches aim to increase the energy gap between the radiative <sup>3</sup>MLCT and quenching <sup>3</sup>MC states. Stabilization of the <sup>3</sup>MLCT state can be achieved by substitution of the tpy ligands by electron-withdrawing groups,<sup>7</sup> introducing a coplanar hetero-aromatic moiety,8 incorporation of organic chromophore etc. Indeed, such approaches have produced complexes that have longer emission lifetimes compared to the parent compounds.9-11 A second approach is to destabilize the <sup>3</sup>MC state by using cyclometalated ligands.<sup>12</sup> One can also modify the terpyridine directly, by replacing the pyridines with other heterocyclic rings to enlarge the bite angle of the tridentate ligand.13

To this end, we report herein a new series of bis-tridentate ruthenium(II) and osmium(II) complexes by using a 4'-[4-(4,5-diphenyl-1H-imidazol-2-yl)-phenyl]-[2,2':6',2'']terpyridine (tpy-HImzPh<sub>3</sub>) system, wherein a triphenyl-imidazole motif has been fused at the 4'-position of 2,2':6',2'' terpyridine. Several homo- and heteroleptic complexes have been synthesized (shown in Chart 1) for fine-tuning of their photophysical and redox properties.

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<sup>†</sup> Electronic supplementary information (ESI) available: X-ray crystallographic file in CIF format for compounds **3** and **4** and Fig. S1–S5. CCDC reference numbers 842087 and 842088. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11645b



Chart 1

As will be seen, the most striking feature of these bis-tridentate complexes is their fairly strong room temperature luminescence and appreciable long excited state lifetimes.

# Experimental

# Materials

Reagent grade chemicals obtained from commercial sources were used as received. Solvents were purified and dried according to standard methods. 4'-Formyl-2,2':6',2"-terpyridine (tpy-PhCHO), 2,6-bis(benzimidazole-2-yl)pyridine (H<sub>2</sub>pbbzim) and the ligand 4'-[4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenyl]-[2,2':6',2"] terpyridine (tpy-HImzPh<sub>3</sub>) were synthesized according to the literature procedures.<sup>14</sup> [(tpy-PhCH<sub>3</sub>)RuCl<sub>3</sub>] and [(H<sub>2</sub>pbbzim)RuCl<sub>3</sub>] were prepared by reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O with tpy-PhCH<sub>3</sub> and H<sub>2</sub>pbbzim, respectively in 1:1 molar ratio in refluxing ethanol.

# Synthesis of the metal complexes

The complexes were prepared under oxygen and moisture free dinitrogen using standard Schlenk techniques.

Caution! Perchlorate salts of the metal complexes used in this study are potentially explosive and, therefore, should be handled with care in small quantities.

**[(tpy-PhCH<sub>3</sub>)Ru(tpy-HImzPh<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (1).** A mixture of Ru(tpy-PhCH<sub>3</sub>)Cl<sub>3</sub> (75 mg, 0.14 mmol), AgBF<sub>4</sub> (92 mg, 0.47 mmol) and 30 mL Me<sub>2</sub>CO was refluxed with continuous stirring for 2 h. After the solution cooled down to room temperature, the precipitated AgCl was removed by filtration. 30 mL

of EtOH was added to the filtrate and the Me<sub>2</sub>CO was removed by rotary evaporation. To the resulting solution was added finely powdered tpy-HImzPh<sub>3</sub> (80 mg, 0.15 mmol) and the mixture was refluxed for 10 h with continuous stirring. During cooling down to room temperature an orange-red compound precipitated. The compound was filtered, washed with cold EtOH followed by ether and then dried under vacuum. The compound was purified by silica-gel column chromatography with elution with CH<sub>3</sub>CN. The eluate was rotary evaporated to a small volume and was then added to an aqueous solution of NaClO<sub>4</sub> when a red microcrystalline compound deposited. The compound was finally recrystallized from CH<sub>3</sub>CN-MeOH (1:1) mixture in the presence of a few drops of 10<sup>-4</sup> M HClO<sub>4</sub> (105 mg, yield: 65%). Anal. calcd. for C<sub>58</sub>H<sub>44</sub>N<sub>8</sub>Cl<sub>2</sub>O<sub>9</sub>Ru: C, 59.59; H, 3.79; N, 9.58. Found: C, 59.56; H, 3.82; N, 9.55. <sup>1</sup>H NMR data {300 MHz, DMSO- $d_6$ ,  $\delta$  (ppm)}: 12.97 (s, 1H, NH imidazole), 9.53 (s, 2H, H3'), 9.45 (s, 2H, H3"), 9.11 (t, 4H, J = 8.0 Hz, H6), 8.58 (d, 2H, J = 8.4 Hz, H8), 8.45 (d, 2H, J = 8.3 Hz, H7, 8.36 (d, 2H, J = 8.0 Hz, H8') 8.09-8.03 (m, 100)4H, H4), 7.62–7.43 (m, 16H, 4H3 + 2H7'+10HPh), 7.38–7.26 (m, 4H5), 2.53 (s, 3H, CH<sub>3</sub>). ESI-MS (positive, CH<sub>3</sub>CN) m/z = 476.09(100%) [(tpy-PhCH<sub>3</sub>)Ru(tpy-HImzPh<sub>3</sub>]<sup>2+</sup>. UV-vis [CH<sub>3</sub>CN;  $\lambda_{max}$ , nm (ɛ, M<sup>-1</sup>cm<sup>-1</sup>)]: 494 (43970), 382(sh) (22130), 310 (89910), 283 (77770).

 $[(H_2pbbzim)Ru(tpy-HImzPh_3)](ClO_4)_2 \cdot H_2O(2).$  [(H\_2pbbzim)-RuCl<sub>3</sub>] (75 mg, 0.14 mmol) was suspended in 20 mL of ethylene glycol and heated at ~100 °C with continuous stirring. To the suspension, tpy-HImzPh<sub>3</sub> (80 mg, 0.15 mmol) was added and the reaction mixture was heated overnight at 200 °C. The resulting solution was then cooled down to room temperature and the perchlorate salt of the complex was precipitated by pouring the solution into an aqueous solution of NaClO<sub>4</sub>·H<sub>2</sub>O (1.0 g in 5 mL of water). The precipitate thus obtained was filtered, washed with water and then dried under vacuum. The compound was then purified by silica gel column chromatography using a mixture of CH<sub>3</sub>CN and 10% aqueous KNO<sub>3</sub> (10:1) as the eluent. The desired compound was obtained by rotary evaporation of the combined eluates and subsequent anion exchange reaction with NaClO<sub>4</sub>·H<sub>2</sub>O. The compound was finally recrystallized from a  $CH_3CN-H_2O(2:1)$  mixture in the presence of a few drops of  $10^{-4}$ M HClO<sub>4</sub> (90 mg, yield: 56%). Anal. calcd. for  $C_{55}H_{40}N_{10}Cl_2O_9Ru$ : C, 57.09; H, 3.48; N, 12.10. Found: C, 57.07; H, 3.51; N, 11.98. <sup>1</sup>H NMR data {300 MHz, DMSO- $d_6$ ,  $\delta$  (ppm)}: 15.02 (s, 2H, NH imidazole), 13.03 (s, 1H, NH imidazole), 9.65 (s, 2H, H3'), 9.05 (d, 2H, J = 8.0 Hz, H6), 8.78 (d, 2H, J = 7.9 Hz, H8), 8.73 (d, 2H, J = 8.3 Hz, H10), 8.63 (t, 1H, J = 8.0 Hz, H9), 8.50 (d, 2H, J =8.2 Hz, H7), 7.96 (t, 2H, J = 7.7 Hz, H4), 7.68–7.43 (m, 14H, 2H3 + 2H11 + 10HPh), 7.30–7.23 (m, 4H, 2H5 + 2H12), 7.03 (t, 2H, J = 7.6 Hz, H13), 6.09 (d, 2H, J = 8.2 Hz, H14). ESI-MS (positive, CH<sub>3</sub>CN)  $m/z = 470.06 (100\%) [(H_2 \text{pbbzim})\text{Ru}(\text{tpy-HImzPh}_3)]^{2+};$ 938.08 (5%) [(pbbzim)Ru(tpy-HImzPh<sub>3</sub>)]. UV-vis [CH<sub>3</sub>CN;  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>)]: 491 (24700), 347 (54800), 332 (53220), 314 (57720), 283 (42450).

[Ru(tpy-HImzPh<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (3). A mixture of tpy-HImzPh<sub>3</sub> (110 mg, 0.21 mmol) and RuCl<sub>3</sub>·3H<sub>2</sub>O (26 mg, 0.10 mmol) in 20 mL of ethylene glycol was stirred under reflux at 180 °C for 18 h. The resulting deep red solution was added to an aqueous solution of NaClO<sub>4</sub>·H<sub>2</sub>O and stirred for 10 min, when a red microcrystalline compound deposited. The precipitate

was filtered, washed several times with cold water and then dried under vacuum. The compound was then purified by silica gel column chromatography using CH<sub>3</sub>CN as the eluent. The eluate was reduced to a small volume followed by the addition of an aqueous solution of NaClO<sub>4</sub>·H<sub>2</sub>O when a red micro crystalline compound deposited. The precipitate was collected and washed several times with cold water. Further purification was carried out by recrystallization from a mixture of CH<sub>3</sub>CN and MeOH (1:5, v/v) in the presence of a few drops of aqueous  $10^{-4}$  M HClO<sub>4</sub> (70 mg, yield: 52%). Anal. calcd. for C<sub>72</sub>H<sub>54</sub>N<sub>10</sub>Cl<sub>2</sub>O<sub>10</sub>Ru: C, 62.15; H, 3.91; N, 10.06. Found: C, 62.13; H, 3.94; N, 10.02. <sup>1</sup>H NMR data {300 MHz, DMSO- $d_6$ ,  $\delta$  (ppm)}: 12.99 (s, 2H, NH imidazole), 9.55 (s, 4H, H3'), 9.14 (d, 4H, J = 7.8 Hz, H6), 8.60 (d, 4H, J = 7.7 Hz, H8), 8.45 (d, 4H, J = 8.2 Hz, H7), 8.08(t, 4H, J = 7.8 Hz, H4), 7.59–7.43 (m, 24H, 4H3 + 20HPh), 7.29 (t, 4H, J = 6.6 Hz, H5). ESI-MS (positive, CH<sub>3</sub>CN) m/z = 577.92 (100%)  $[\text{Ru}(\text{tpy-HImzPh}_3)_2]^{2+}$ . UV-vis  $[\text{CH}_3\text{CN}; \lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1}\text{cm}^{-1})]$ : 498 (53220), 380(sh) (38270), 312 (88460), 282 (71740).

 $[Os(tpy-HImzPh_3)_2](ClO_4)_2 \cdot 3H_2O$  (4). A mixture of tpy-HImzPh<sub>3</sub> (110 mg, 0.21 mmol) and K<sub>2</sub>OsCl<sub>6</sub> (48 mg, 0.10 mmol) in 20 mL degassed ethylene glycol was heated at 200 °C with continuous stirring for 24 h. The resulting black solution was cooled to room temperature and then poured into 5 mL of an aqueous solution of NaClO4·H2O (1.0 g) and stirred for few minutes when a black precipitate appeared. The precipitate was collected by filtration and washed thoroughly with water and then dried under vacuum. The crude product was purified by silica gel column chromatography with CH<sub>3</sub>CN as the eluent. The compound was finally recrystallized from a CH<sub>3</sub>CN-MeOH (1:2) mixture in the presence of a few drops of aqueous  $10^{-4}$ HClO<sub>4</sub> affording shiny black crystals (72 mg, yield: 50%). Anal. calcd. for C<sub>72</sub>H<sub>56</sub>N<sub>10</sub>Cl<sub>2</sub>O<sub>11</sub>Os: C, 57.71; H, 3.76; N, 9.34. Found: C, 57.69; H, 3.79; N, 9.31. <sup>1</sup>H NMR data {300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  (ppm)}: 12.96 (s, 2H, NH imidazole), 9.56 (s, 4H, H3'), 9.11 (d, 4H, J = 8.2 Hz, H6), 8.55 (d, 4H, J = 8.4 Hz, H8), 8.45 (d, 4H, J = 8.4 Hz, H8)4H, J = 8.3 Hz, H7), 7.94 (t, 4H, J = 7.7 Hz, H4), 7.61–7.28 (m, 24H, 4H3 + 20HPh), 7.23 (t, 4H, J = 6.6 Hz, H5). ESI-MS (positive, CH<sub>3</sub>CN) m/z = 623.19 (100%) [Os(tpy-HImzPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>. UV-vis [CH<sub>3</sub>CN;  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>)]: 673 (10400), 645 (9040), 497 (47700), 355 (55450), 313 (93810), 283 (74700)

## Physical measurements

Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400II analyzer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass Qtof YA 263 mass spectrometer. <sup>1</sup>H and  $\{^{1}H-^{1}H\}$  COSY spectra were obtained on a Bruker Avance DPX 300 and 500 spectrometer using DMSO $d_6$  solutions. Electronic absorption spectra were obtained with a Shimadzu UV 1800 spectrophotometer at room temperature. Steady state emission spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. The room temperature spectra were obtained in CH<sub>3</sub>CN solutions, while the spectra at 77 K were recorded in 4:1 EtOH-MeOH glass. Quantum yields were determined by a relative method using  $[Ru(bpy)_3]^{2+}$ in the same solvent as the standard. Time-correlated singlephoton-counting (TCSPC) measurements were carried out for the luminescence decay of complexes 1-4. For TCSPC measurement, the photoexcitation was carried out at 440 nm using a picosecond

diode laser (IBH Nanoled–07) in an IBH Fluorocube apparatus. The fluorescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software.

The electrochemical measurements were carried out with a BAS epsilon electrochemistry system. A three-electrode assembly comprising a Pt (for oxidation) or glassy carbon (for reduction) working electrode, Pt auxiliary electrode, and an aqueous Ag/AgCl reference electrode were used. The cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out at 25 °C in CH<sub>3</sub>CN solution of the complexes (*ca.* 1 mM) and the concentration of the supporting electrolyte tetraethyl ammonium perchlorate (TEAP) was maintained at 0.1 M. All of the potentials reported in this study were referenced against the Ag/AgCl electrode, which under the given experimental conditions gave a value of 0.36 V for the ferrocene/ferrocenium couple.

Experimental uncertainties were as follows: absorption maxima,  $\pm 2$  nm; molar absorption coefficients, 10%; emission maxima,  $\pm 5$  nm; excited-state lifetimes, 10%; luminescence quantum yields, 20%; redox potentials,  $\pm 10$  mV.

#### X-ray crystal structure determination

Single crystals of the homoleptic compounds (3 and 4), suitable for structure determinations were obtained by diffusing toluene into their CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> (1:4) solutions. X-ray diffraction data for both the crystals mounted on a glass fiber and coated with perfluoropolyether oil were collected at 296 K using a Bruker–AXS SMART APEX II diffractometer equipped with a CCD detector and using graphite-monochromated Mo–K $\alpha$ radiation ( $\lambda = 0.71073$  Å). Crystallographic data and details of structure determination are summarized in Table 1. The data were processed with SAINT<sup>15</sup> and absorption corrections were made with SADABS.<sup>15</sup> The structures were solved by direct and Fourier

Table 1 Crystallographic data for [3]<sup>2+</sup> and [4]<sup>2+</sup>

3	4
$C_{72}H_{50}N_{10}Cl_2O_8Ru$	C <sub>72</sub> H <sub>50</sub> N <sub>10</sub> Cl <sub>2</sub> O <sub>8</sub> Os
1355.19	1444.32
293(2)	296(2)
Orthorhombic	Orthorhombic
Fddd	Fddd
23.6887(17)	36.393(7)
36.416(4)	37.524(12)
38.285(3)	23.564(5)
90	90
90	90
90	90
33027(5)	32179(14)
1.09	1.192
16	16
0.306	1.704
11104	11616
1.16-25.06	1.16-25.02
7302/0/429	7105/0/395
0.757	1.030
0.0603	0.0509
0.2186	0.1351
0.697/-0.280	0.780/-0.788
	$\begin{array}{c} \textbf{3} \\ \hline C_{72}H_{50}N_{10}Cl_2O_8Ru \\ 1355.19 \\ 293(2) \\ Orthorhombic \\ Fddd \\ 23.6887(17) \\ 36.416(4) \\ 38.285(3) \\ 90 \\ 90 \\ 90 \\ 33027(5) \\ 1.09 \\ 16 \\ 0.306 \\ 11104 \\ 1.16-25.06 \\ 7302/0/429 \\ 0.757 \\ 0.0603 \\ 0.2186 \\ 0.697/-0.280 \\ \end{array}$

<sup>*a*</sup>  $R_1(F) = [\sum_{w \in F_0} ||F_0|| - |F_c|| / \sum_{w \in F_0} |F_0|], {}^{b} w R_2(F^2) = [\sum_{w \in F_0} w (F_0^2 - F_c^2)^2 / \sum_{w \in F_0} w (F_0^2)^2]^{1/2}.$ 

methods and refined by the full-matrix least-square method based on  $F^2$  using WINGX software which utilizes SHELX– 97.<sup>16</sup> For the structure solution and refinement the SHELXTL software package<sup>17</sup> was used. The nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were placed with fixed thermal parameters at idealized positions. The electron density map also showed the presence of some unassignable peaks, which were removed by running the program SQUEEZE.<sup>18</sup> In both the cases, the final least-squares refinement ( $I > 2\sigma(I)$ ) converged to reasonably good R values.

CCDC reference numbers: 842087 for 3, and 842088 for 4.†

#### **Results and discussion**

#### Synthesis and characterization

The terpyridyl-imidazole ligand (tpy-HImzPh<sub>3</sub>) was obtained in good yield by condensation of benzil and 4'-(*p*-formylphenyl)-2,2':6',2"-terpyridine (tpy-PhCHO) in 1 : 1 molar ratio in the presence of excess of NH<sub>4</sub>OAc in refluxing acetic acid. The molecular structures of the homo- and heteroleptic metal complexes derived from tpy-HImzPh<sub>3</sub> are presented in Chart 1. For the synthesis of heteroleptic Ru(II) complex, [(tpy-PhCH<sub>3</sub>)Ru(tpy-HImzPh<sub>3</sub>)]<sup>2+</sup> (1), the solvated cation [(tpy-PhCH<sub>3</sub>)Ru(Me<sub>2</sub>CO)<sub>3</sub>]<sup>3+</sup>, generated by reacting stoichiometric amounts of [(tpy-PhCH<sub>3</sub>)RuCl<sub>3</sub>] and AgBF<sub>4</sub>, acts as a better precursor relative to [(tpy-PhCH<sub>3</sub>)RuCl<sub>3</sub>] itself in terms of reaction time and yield. Thus, the reaction between tpy-HImzPh<sub>3</sub> and [(tpy-PhCH<sub>3</sub>)Ru(Me<sub>2</sub>CO)<sub>3</sub>]<sup>3+</sup> in refluxing ethanol solution produces smoothly complex 1. On the other hand, dehalogenation of the Ru(III) precursor, [(H<sub>2</sub>pbbzim)RuCl<sub>3</sub>] with AgBF<sub>4</sub> in Me<sub>2</sub>CO is not clean. Thus, complex **2** was synthesized by reacting  $[(H_2pbbzim)RuCl_3]$  with tpy-HImzPh<sub>3</sub> in ethylene glycol at ~200 °C, followed by anion metathesis with NaClO<sub>4</sub>. The homoleptic complexes **3** and **4** were synthesized directly by reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O and K<sub>2</sub>OsCl<sub>6</sub>, respectively with 2 equiv of ligands in refluxing ethylene glycol solution, followed by chromatography and counteranion exchange with NaClO<sub>4</sub>. All the complexes were obtained in fairly good yields (50–65%) and recrystallized under weakly acidic conditions to keep the imidazole NH protons intact. The complexes were thoroughly characterized by their elemental (C, H and N) analyses, ESI-MS, UV-vis, <sup>1</sup>H NMR spectroscopic measurements and the results are given in the Experimental Section.

The ESI mass spectra of the complexes 1 and 2 in CH<sub>3</sub>CN and their simulated isotopic distribution patters are shown in Fig. 1. Compound 1 shows one peak at m/z = 476.09, while 2 shows two abundant peaks at m/z = 470.06 and 938.08. The isotopic patterns of the original peak at m/z = 476.09 for 1 and 470.06 for 2 separated by 0.5 Da fit very well to the isotope distribution pattern calculated with the Mass Lynx V 4.0 program for [(tpy-PhCH<sub>3</sub>)Ru(tpy-HImzPh<sub>3</sub>]<sup>2+</sup> and [(H<sub>2</sub>pbbzim)Ru(tpy-HImzPh<sub>3</sub>)]<sup>2+</sup>, respectively. The peak at m/z 938.08 in the case of 2 is assigned to the species, [(pbbzim)Ru(tpy-HImzPh<sub>3</sub>)]. For complexes 3 and 4 also the observed peaks in the ESI mass spectra fit very well to that of the corresponding calculated pattern (Fig. S1, ESI<sup>+</sup>).

#### Description of the crystal structures of complexes (3<sup>2+</sup> and 4<sup>2+</sup>)

ORTEP representations of the cations of complexes are shown in Fig. 2 and selected bond distances and angles are given in



**Fig. 1** ESI mass spectra (positive) for the complex cations (a)  $[(tpy-PhCH_3)Ru(tpy-HImzPh_3)]^{2+}$  (m/z = 476.09) and (b)  $[(H_2pbbzim)Ru(tpy-HImzPh_3)]^{2+}$  (m/z = 470.06) and  $[(pbbzim)Ru(tpy-HImzPh_3)]$  (m/z = 938.08) in acetonitrile showing the observed and simulated isotopic distribution patterns.



Fig. 2 ORTEP representations of the complex cations,  $[Ru(tpy-HImzPh_3)_2]^{2+}$  ( $3^{2+}$ ) and  $[Os(tpy-HImzPh_3)_2]^{2+}$  ( $4^{2+}$ ) showing 30% probability ellipsoid plots. The anions, solvents of crystallization, and the hydrogen atoms are omitted for clarity.

Table 2. The structures display the expected geometry, with both ligands coordinated in the tridentate meridional fashion to the metal center and having a distorted octahedral geometry. Both the complexes crystallized in the orthorhombic form with the space group, Fddd. The bite angles of the chelate rings lie in the range between 78.80 and 101.25° for **3** and between 78.16 and 102.18° for **4**. It is of interest to note that although the inter-ligand *trans* angle made by N3–M–N3 is 179.9° is very close to linearity, the intra-ligand *trans* angles, N1–M–N3 is 156.68°, which deviates largely from linearity. The Ru(II)–N and Os(II)–N bond lengths are very close and lie within the range of 1.968(4) and 2.063(5) Å. Similar Ru–N and Os–N bond distances have also been observed for the reported Ru(II) and Os(II) terpyridine type complexes.<sup>7-14</sup>

Table 2Selected bond distances (Å) and angles (°) for  $[3]^{2+}$  and  $[4]^{2+}$ 

3		4	
Ru–N(1)	2.063(3)	Os–N(1)	2.048(4)
Ru-N(2)	2.056(3)	Os-N(2)	1.968(4)
Ru-N(3)	1.974(3)	Os–N(3)	2.063(5)
N(1)-Ru-N(1)	91.24(18)	N(1)–Os–N(1)	89.8(2)
N(2)-Ru-N(1)	93.88(13)	N(2) - Os - N(1)	78.16(17)
N(2)-Ru-N(1)	157.96(13)	N(2) - Os - N(1)	102.18(17)
N(3)-Ru- $N(1)$	79.18(13)	N(3) - Os - N(1)	94.22(17)
N(3)-Ru-N(1)	100.76(13)	N(3) - Os - N(1)	156.68(18)
N(2)-Ru-N(2)	89.37(18)	N(2) - Os - N(2)	179.5(2)
N(3)-Ru- $N(2)$	101.25(12)	N(3) - Os - N(2)	78.53(18)
N(3)-Ru-N(2)	78.80(12)	N(3)–Os– $N(2)$	101.13(18)
N(3)-Ru- $N(3)$	179.9(2)	N(3)-Os- $N(3)$	91.2(2)

The central M(II)–N bond distance [1.974(3) for **3** and 1.968(4) Å for **4**] is shorter than that of the two outer bonds whose distances lie in the range between 2.048(4) and 2.063(5) Å, probably because of efficient overlap of the metal  $t_{2g}$  orbital with the  $\pi^*$  orbitals of the central pyridyl group. It is to be noted that the dihedral angles between the central pyridine plane and the two lateral ones are 2.93 and 7.36° for **3** and 2.11 and 7.08° for **4**. Again the two phenyl groups twisted heavily from the plane of the imidazole ring as evidenced by the high values of their dihedral angles which lie between 22.48 and 57.51°.

#### Proton NMR spectra

<sup>1</sup>H and {<sup>1</sup>H-<sup>1</sup>H} COSY NMR spectra for complexes 1-4 were recorded in DMSO- $d_6$  at room temperature to confirm the molecular structures of the compounds in solution. The assignments made for the observed chemical shifts are listed in Table S1 (ESI<sup>†</sup>). The <sup>1</sup>H NMR spectra for complexes 1-4 as well as that of the free ligand tpy-HImzPh<sub>3</sub> are shown in Fig. 3. The <sup>1</sup>H NMR spectra of the complexes show the occurrence of a fairly large number of resonances, some of which are overlapped with each other. The COSY spectra (shown in Fig. S2, ESI<sup>†</sup>) have been particularly useful to locate spin couplings in the aromatic protons of tpy-HImzPh<sub>3</sub>, tpy-PhCH<sub>3</sub> and H<sub>2</sub>pbbzim moieties bound to the metal center. The relative simplicity of the <sup>1</sup>H NMR spectra for the homoleptic complexes (3 and 4) reflects the symmetrical environment around the metal center and are consistent with the solid state structures of the complexes as shown by single crystal X-ray crystallography. On the other hand, for the heteroleptic





Fig. 3  $^{1}$ H NMR spectra of tpy-HImzPh<sub>3</sub> and complexes 1–4 in DMSO- $d_6$ . Atom numbering is shown in the top.

complexes (1 and 2) the spectra are more complicated due to the presence of overlapping resonances for different protons arising from both the ligands.

As may be seen in Fig. 3, all the resonances in the complexes, barring three, occur in the range of 7.03–9.65 ppm. Of the three disparate signals, the one which appears as a singlet at 2.53 ppm (not shown in Fig. 3) accounting for three protons in 1, is clearly due to -CH<sub>3</sub> protons of the coordinated tpy-PhCH<sub>3</sub> moiety. The second highest field resonance which appears as a doublet at 6.09 ppm for 2 is attributable to H(14) of the  $H_2$  pbbzim moiety, because this proton experiences maximum shielding due to the anisotropic ring current effect of the adjacent pyridine rings. The third distinct signal, which is most downfield-shifted, is observed either as a singlet or as a broad feature in the region 12.96-15.02 ppm due to the imidazole NH proton(s) of the coordinated tpy-HImzPh<sub>3</sub> and H<sub>2</sub>pbbzim ligands. The imidazole NH protons are profoundly downfield shifted in all the complexes (1-4) due to H-bonding with DMSO- $d_6$ . In the case of  $[(H_2 pbbzim)Ru(tpy HImzPh_3$ ](ClO<sub>4</sub>)<sub>2</sub> (2), the occurrence of two distinct NH signals at 13.03 and 15.02 ppm are observed as it has two different kinds of imidazole NH protons with different chemical environments. By comparing the chemical shifts of the NH proton of 1, 3, and 4 with 2, the peak at 13.03 ppm can be attributed to the NH

of tpy-HImzPh<sub>3</sub>, while the peak observed at 15.02 ppm is due to the NH of H<sub>2</sub>pbbzim. The chemical shifts of two phenyl ring protons attached to the imidazole moiety are characterized by a bunch of signals in the region 7.28–7.68 ppm, assigned on the basis of coupling constants and chemical shifts. As can be seen, the chemical shifts of H3', H6, H7 and H8 protons shifted to the down-field region while the phenyl protons and H4 of the terpyridine moiety are almost unaffected by coordination. Proton H3 of the tpy moiety is affected the most and shifts significantly to the upfield region because this proton lies above the shielding region of a pyridine ring of the other tpy ligand (Fig. 2).

## Electronic absorption spectroscopic studies

The UV-vis spectra of the complexes 1–4 are shown in Fig. 4, and their absorption maxima and molar extinction coefficients ( $\varepsilon$ ) are given in Table 3, which also contains data for reference mononuclear model complexes. The absorption spectra of the complexes are of a similar type showing a number of bands in the UV-vis region. Assignments were made by comparing with the spectra of [M(tpy)<sub>2</sub>]<sup>2+</sup> and related bis-tridentate M(II) (M = Ru<sup>II</sup> and Os<sup>II</sup>) type complexes.<sup>1,2,5</sup> Thus, the two most intense bands observed around 280 and 315 nm ( $\varepsilon$  = 42000–94000 M<sup>-1</sup> cm<sup>-1</sup>)

Table 3	Spectroscopic and	photophysical data for 1-4 in acetonitrile solutions	
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Absorption		Luminescence						
		At 298 K <sup>a</sup>				At 77 K <sup>b</sup>		
Compounds	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm M}^{-1}~{\rm cm}^{-1})$	$\lambda_{\max nm}$	τ∕ ns	$\Phi$ (×10 <sup>-3</sup> )	$k_{\rm r}/{\rm s}^{-1}~( imes 10^5)$	$k_{\rm nr}/{\rm s}^{-1}~( imes 10^7)$	$\lambda_{ m max\ nm}$	Φ
1	494(43970)							
	382(sh)(22130)	658	6.8	0.03	0.04	14.70	641	0.16
	310 (89910)							
	283(77770)							
2	491(24700)							
	347(54800)							
	332(53220)	690	35.0	5.82	1.66	2.84	674	0.21
	314(57720)							
	283(42450)							
3	498(53220)							
	380(sh)(38270)	660	8.5	0.65	0.76	11.74	644	0.24
	312(88460)							
	282(71740)							
4	673(10400)							
	645(9040)							
	497(47700)	749	29.5	49.10	16.64	3.22	733	0.22
	355(55450)							
	313(93810)							
	283(74700)							
5°	474(10400)	629	0.25	≤0.05	0.04	90.9	598	
<b>6</b> <sup><i>a</i></sup>	490(28000)	640	< 5.0	≤0.03			628, 681(sh)	—
7 <sup>e</sup>	475(17400)							—
8′	657(3650)	718	269	14.0			689	0.124
	477(13750)							
9 <sup>g</sup>	667(6600)	734	220	21.0		—	740	0.049
	490(26000)							

 $\label{eq:alpha} {}^{a} \ In \ CH_3 CN, \ {}^{b} \ MeOH-EtOH(1:4) \ glass, \ {}^{c} \ [Ru(tpy)_2]^{2+, 5c}, \ {}^{d} \ [Ru(tpy-PhCH_3)_2]^{2+, 5c}, \ {}^{e} \ [Ru(H_2 pbbzim)_2]^{2+, 20a}, \ {}^{f} \ [Os(tpy)_2]^{2+, ref5c}, \ {}^{g} \ [Os(tpy-PhCH_3)_2]^{2+, 5c}, \ {}^{e} \ [Os(tpy)_2]^{2+, ref5c}, \ {}^{g} \ [Os(tpy)_2]^{2+, 5c}, \ {}^{f} \ [Os(tpy)_2]^{2+,$ 



Fig. 4 UV-vis spectra of 1-4 in acetonitrile at room temperature.

are due to  $\pi$ - $\pi^*$  ligand centered transitions, while the next higher wavelength absorptions occurring between 332 and 355 nm are due to internal transitions of the ligands. All the complexes exhibit a fairly strong absorption peak in the range of 490– 500 nm ( $\varepsilon = 24700-53220 \text{ M}^{-1} \text{ cm}^{-1}$ ) which can be assigned as  ${}^{1}[\text{M}^{II}(d\pi)^{6}] \rightarrow {}^{1}[\text{M}^{II}(d\pi)^{5}\text{tpy}\text{-HImzPh}_{3}(\pi^{*})^{1}]$ . The Os(II) compound 4, additionally shows moderately intense broad bands around 645 and 673 nm ( $\varepsilon = 10400 \text{ M}^{-1}\text{cm}^{-1}$ ) which seems to be due to the spin forbidden MLCT transition  ${}^{1}[\text{Os}^{II}(d\pi)^{6}] \rightarrow {}^{3}[\text{Os}^{II}(d\pi)^{5}\text{tpy}-$ HImzPh<sub>3</sub>( $\pi^*$ ) ${}^{1}$ ] that directly populates the triplet MLCT state.<sup>1,5</sup> It is to be noted that the absorption spectrum of 2 also contains a low-energy shoulder at ~600 nm. This band may also arise from  ${}^{1}[\text{Ru}^{II}(d\pi)^{6}] \rightarrow {}^{3}[\text{Ru}^{II}(d\pi)^{5}\text{tpy}\text{-HImzPh}_{3}(\pi^*)^{1}]$  transitions.<sup>19</sup> Analysis of the spectrum of 2 shows that the energy difference between the lowest, intense singlet,  ${}^{1}[\text{Ru}^{II}(d\pi)^{6}] \rightarrow {}^{1}[\text{Ru}^{II}(d\pi)^{5}\text{tpy}$ - HImzPh<sub>3</sub>( $\pi^*$ )<sup>1</sup>] band at 491 nm (20366 cm<sup>-1</sup>,  $\varepsilon$  = 24700 M<sup>-1</sup> cm<sup>-1</sup>) and the triplet  ${}^{1}[Ru^{II}(d\pi)^{6}] \rightarrow {}^{3}[Ru^{II}(d\pi)^{5}tpy-HImzPh_{3}(\pi^{*})^{1}]$  band at ~600 nm (~16666 cm<sup>-1</sup>,  $\varepsilon = 1460 \text{ M}^{-1}\text{cm}^{-1}$ ) is 3700 cm<sup>-1</sup>, which is of similar magnitude to the singlet-triplet splitting energy for  $[Ru(tpy)_2]^{2+}$  and the other mono-tpy complexes.<sup>1,2,19</sup> The magnitude of the molar extinction coefficient ( $\varepsilon$ ) of the spin forbidden <sup>3</sup>MLCT transition is much greater in 4 compared to 2 because the extent of spin-orbit coupling is greater in Os<sup>II</sup> than that in Ru<sup>II</sup>. It is of interest to note that the lowest energy <sup>1</sup>MLCT absorption band for 1-4 is shifted to longer wavelength compared to the parent  $[Ru(tpy)_2]^{2+}$  (474 nm) and  $[Os(tpy)_2]^{2+}$  (477 nm) complexes.<sup>5c</sup> Again, the MLCT absorption of [Ru(H<sub>2</sub>pbbzim)<sub>2</sub>]<sup>2+</sup> was observed at 475 nm, which is almost comparable in energy to that of [Ru(tpy)<sub>2</sub>]<sup>2+</sup>.<sup>20</sup> The differences in the MLCT band energies between the parent  $[M(tpy)_2]^{2+}$  (M = Ru<sup>II</sup> and Os<sup>II</sup>) and the complexes 1–4 are due to the energy differences of the  $\pi^*$  orbitals of the individual ligands. It is interesting to note that the complexes under investigation have very high molar extinction coefficients ( $\varepsilon$ ) in the visible region compared to the parent  $[M(tpy)_2]^{2+}$  (M = Ru<sup>II</sup> and Os<sup>II</sup>) complexes, which make them good candidates for light-harvesting materials. It may also be noted that the MLCT band in the homoleptic Ru(II) complex (3) is much more intense than those for the heteroleptic analogues (1 and 2), which probably arises due to extensive delocalization of tpy-HImzPh<sub>3</sub>.

#### Emission spectroscopic studies

The steady-state luminescence spectra of the four compounds in CH<sub>3</sub>CN solution at room temperature and in EtOH–MeOH

(4:1) glass at 77 K are displayed in Fig. 5. A summary of the photophysical data (emission maxima, quantum yield ( $\Phi$ ), and lifetime ( $\tau$ ) *etc.*) of the complexes together with the data available for the reference mononuclear compounds is given in Table 3. All the three Ru(II) complexes on excitation at their MLCT band, exhibit one broad luminescent band, which lies between 658 (1) and 690 nm (2) at 300 K and between 641 (1) and 674 nm (2) at 77 K (Fig. 5). Excitation at the MLCT peak at 500 nm of 4 also resulted in the appearance of a luminescence band centered at 749 nm at 300 K and 733 nm at 77 K. On the basis of extensive investigations performed on  $[M(tpy)_2]^{2+}$  (M = Ru<sup>II</sup> and Os<sup>II</sup>) and related complexes, it can be concluded that these bands have the characteristics of emission from the <sup>3</sup>MLCT excited state, which corresponds to a spin-forbidden  $M^{II}(d\pi) \rightarrow tpy-HImzPh_3$  $(\pi^*)$  transition.<sup>2,5</sup> The most striking feature of this class of Ru(II) compounds is that they are luminescent at room temperature in fluid solutions though the parent  $[Ru(tpy/tpy-PhCH_3)_2]^{2+6}$  or  $[Ru(H_2pbbzim)_2]^{2+20}$  are practically non-luminescent. The roomtemperature lifetimes of the complexes (shown in Fig. 6) which lie between 6.8 (1) and 35 ns (2), are significantly greater than that of the parent  $[Ru(tpy)_2]^{2+}$  (0.25 ns). It is interesting to note that the enhanced luminescence properties of the complexes have been achieved without lowering the excited-state energy significantly. On going from fluid solution to frozen glass, the emission maxima gets blue-shifted with a significant increase in emission intensity and quantum yield, typical of the <sup>3</sup>MLCT emitters. It is to be noted that the emission maximum of the complexes is also shifted to a longer wavelength compared to that of the parent  $[Ru(tpy)_2]^{2+}$ and  $[Os(tpy)_2]^{2+}$  complexes at both room temperature and 77 K.<sup>5c</sup> Thus, the luminescence behavior of the complexes are similiar to their absorption behavior.



**Fig. 5** Luminescence spectra of **1–4** at room temperature in acetonitrile (a) and at 77 K in ethanol–methanol (4:1) glass (b).

The zero-zero excitation energy  $(E_{00})$  values of the <sup>3</sup>MLCT excited states of the complexes (1-4) were estimated from the



**Fig. 6** Time-resolved photoluminescence decays of **1–4** in acetonitrile at room temperature obtained with 440 nm excitation.

energy of the emission maximum at 77 K. The  $E_{00}$  values thus estimated are 1.93 eV for [(tpy-PhCH<sub>3</sub>)Ru(tpy-HImzPh<sub>3</sub>)]<sup>2+</sup> (1), 1.84 eV for [(H<sub>2</sub>pbbzim)Ru(tpy-HImzPh<sub>3</sub>)]<sup>2+</sup> (2), 1.92 eV for [Ru(tpy-HImzPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (3), and 1.69 eV for [Os(tpy-HImzPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> (4). At 77 K, each spectrum displays a well-defined vibronic progression in the lower energy region with spacing of ~1108 cm<sup>-1</sup> for 1, ~1249 cm<sup>-1</sup> for 2, ~1243 cm<sup>-1</sup> for 3 and ~1327 cm<sup>-1</sup> for 4, which are similar to those reported for [M(tpy)<sub>2</sub>]<sup>2+</sup> (M = Ru<sup>II</sup> and Os<sup>II</sup>) and the other mono-tpy complexes of Ru(II) and Os(II) and can be attributed to aromatic stretching vibrations of the ligands.<sup>19,21</sup>

It has been observed from the reported literature data that the majority of the polypyridyl complexes of Ru(II) and Os(II) are sufficiently weak emitters so that their lifetimes are dominated by nonradiative decay. In this limit, the excited-state lifetimes of these complexes are governed by the following relationships.<sup>1,5,13</sup>

$$k_{\rm nr} = k_{\rm nr}^{0} + k'_{\rm nr} \tag{1}$$

The overall radiationless decay is the sum of two terms. The first one,  $k_{nr}^{0}$ , leads directly from the MLCT state to the ground state, whereas the second term,  $k'_{nr}$ , is related to the thermally activated process that takes into account a surfacecrossing from the lowest-lying MLCT state to a closely lying metal-centered (MC) level, so it depends on the energy gap  $\Delta E$ between the MLCT and MC states (when coupling between these two states is relatively high).<sup>1,2,5,8a</sup> For Ru(II) complexes with tridentate ligands, the second term normally dominates the equation. The small energy difference between MLCT and MC states in Ru(II) tridentate polypyridine complexes is due to an illfitted octahedral arrangement, which in turn is responsible for the poor room-temperature luminescence properties of Ru(tpy)2type complexes.<sup>5,8-13</sup> By contrast, for the analogous osmium(II) complex this deactivation channel is unimportant because Os(II) exhibits a considerably stronger ligand field than Ru(II), so that  ${}^{3}MLCT \rightarrow {}^{3}LF$  crossing should remain inaccessible even in room temperature. Moreover, as the osmium system 4 does not possess this low-lying LF state, hence deactivation is only from the <sup>3</sup>MLCT state leading to the observed longer excited state lifetime compared to its analogous Ru(II) compound. In the present systems, the energy of the MC level being considered to be constant, the MLCT emitting level is decreased in energy by modulating the electronic influence of the terpyridine moiety by extensive delocalization due to the triphenyl-imidazole group, thereby reducing the efficiency of the MLCT-to-MC surface-crossing pathway. However, the larger energy gap between MLCT and MC states may not be the only reason to fully justify the relatively long luminescence lifetimes of the complexes.

## Solvent dependence

The influences of different solvents on the absorption and emission spectral behavior of the complexes have also been studied and the relevant photophysical data are summarized in Table 4. Fig. 7 shows the UV-vis spectra of **2** (a) and **4** (c) in different solvents. It is of interest to note that the lowest energy absorption maxima of the complexes are influenced by the solvents and in general the MLCT band maxima shifted to a lower energy region with an increase in polarity as well as with the extent of hydrogen bonding ability of the solvent. The solvent effect is particularly dramatic for the complex **2** compared to the other three complexes (**1**, **3**, and **4**). In case of **2**, the lowest energy band maximum shifted from 491 nm in CH<sub>3</sub>CN to 535 nm in DMF ( $\Delta \lambda_{max} = 44$  nm) with a concomitant change of color from yellow–orange to violet (shown in Fig. 8). For the complexes **1**, **3**, and **4** the corresponding change is small and varies within 10 nm (Fig. 7 and Fig. S3, ESI†).



Fig. 7 UV-vis and luminescence spectra of complex 2 (a and b, respectively) and complex 4 (c and d, respectively) in different solvents.

Fig. 7b and 7d show the emission spectra of **2** and **4**, respectively in different solvents. In line with the absorption spectral behavior, the emission band of the complexes is also red-shifted with the increase in polarity of the solvent As compared with **1**, **3**, and **4**, the emission spectral behavior of **2** shows significantly larger solvatochromism. By changing the solvents, the lowest energy emission maximum get red-shifted from 682 (C<sub>2</sub>H<sub>5</sub>OH) to 776 nm (DMSO) ( $\Delta \lambda_{em} = 94$  nm). In the case of **1**, **3**, and **4**, the corresponding change in the emission maxima are small (Table 4).

663, 0.78 1.88 657, 0.68 657, 0.57 657, 0.65 660, 0.65 566, 1.38 569, ŝ 692, 8.65 690, 5.88 750, 3.16 582, 5.36 588, 5.26 776, 2.90  $\sim$  $\lambda_{\rm emi}/\,{
m nm},\, \Phi~( imes 10^{-3})$ Compounds 652, 0.07 552, 0.17 548, 0.09 652, 0.21 558, 0.03 564, 0.06 568, 0.34 357(sh)(55260), 313(115550) 675(9080), 500(41820), 390(sh)(38340), 357(45790)680(14300), 507(60110), 365(66220), 322(108330), 400(sh)(43100), 357(sh) 571(11700), 496(52910). 578(12930), 505(47270) 387(sh)(30840), 355(sh) 673(10400), 497(47700) 355(55450), 313(93810) 577(11870), 500(52220) 863(57910), 320(95750) 674(9760), 498(42800), (62930), 318(99730) (43830), 316(92200) 4 36970), 312(89800) 500(52380), 389(sh) 38270), 312(88460) 505(57900), 387(sh) 38910), 315(91260) 507(54540), 387(sh) (37370), 317(85500) 502(45580), 402(sh) 21030), 312(81220) 197(53480), 380(sh) 30480), 312(86280 498(53220), 380(sh) 387(sh)(32560) 501(50530) ŝ 497(14270), 403(sh) (8940) 354(28520), 336(27940), 519(24060), 352(47410), 320(59610) 506(21200), 350(46500) 333(53270), 315(64200) 491(26630), 348(59140) 332(57500), 315(62220) 535(18260), 362(50660)494(24140), 400(sh) (13150), 349(50000) 494(28300), 398(sh) (15640), 351(55160) 315(55480) 316(34990) 319(50560)  $\sim$  $\lambda_{
m max}/
m nm~(\epsilon/M^{-1}~
m cm^{-1})$ 24040), 316(103910) 494(42970), 383(sh) 20250), 310(87580) 494(43970), 382(sh) (22130), 310(89910) 500(52550), 394(sh) 196(41900), 400(sh) 14140), 311(89350) 496(37240), 390(sh) 15570), 311(75140) (90(sh)(17690) 92(sh)(27500) Compounds (119170) 196(38760) 600(61110) (CH<sub>3</sub>)<sub>2</sub>CO CH<sub>3</sub>OH C<sub>2</sub>H<sub>5</sub>OH Solvents  $CH_2CI_2$ CH<sub>s</sub>CN DMSO DMF

Absorption and luminescence spectral data of 1-4 in different solvents

Table 4

746, 59.6

748, 47.7

4

745, 50.3 752, 56.7 62.7

760,

757, 54.4

749, 49.1



Fig. 8 Color changes exhibited by solutions of complex 2 in different solvents.

It may be noted that the intensity of the emission band of **2** quenched to a significant extent with DMF indicating a strong hydrogen bonding interaction with the solvent.

It is of interest to note that compared to 1, 3, and 4, complex 2 shows a marked difference in behavior towards different solvents. The reason probably arises due to the presence of two different types of imidazole NH protons with different chemical environments in 2 compared to other complexes under investigation. The two imidazole NH protons associated to 2,6-bis(benzimidazole-2-yl)pyridine (H<sub>2</sub>pbbzim) moiety are more acidic compared with the NH proton associated to the tpy-HImzPh<sub>3</sub> ligand in all the complexes as evidenced by the <sup>1</sup>H NMR spectra of the complexes. So the extent of hydrogen bonding between the NH protons of the H<sub>2</sub>pbbzim moiety and solvents like DMF and DMSO will be much more compared with that of the NH proton of tpy-HImzPh<sub>3</sub>. The red-shift of the MLCT bands can be attributed to the secondsphere hydrogen bonding interactions between metal coordinated imidazole NH protons and the solvents.

In binary solvent systems, the incremental addition of a high polar solvent to a solution of **2** in a lower polarity solvent causes a large red shift in both the UV-vis and emission spectra. For example, when DMF was added gradually to a  $CH_2Cl_2$  solution of **2**, the MLCT peak at 497 nm in successive absorption curves undergo gradual red shifts, till it reached 535 nm (Fig. 9a). With an increase of the ratio of DMF/CH<sub>2</sub>Cl<sub>2</sub>, the emission maxima of **2** also shifted steadily from 692 to 790 nm with a significant decrease in the intensity (Fig. 9b). The changes in the spectral profiles are due to the formation of hydrogen bonding between the NH protons of the coordinated imidazole ligands (H<sub>2</sub>pbbzim and tpy-HImzPh<sub>3</sub>) and highly polar DMF.



**Fig. 9** Changes in UV-vis (a) and photoluminescence (b) spectra of 2 (3D views) in CH<sub>2</sub>Cl<sub>2</sub> upon incremental addition of DMF.

The electrochemical characteristics of the homo- and heteroleptic Ru(II) and Os(II) complexes (1-4) along with free tpy-HImzPh<sub>3</sub> have been examined by cyclic voltammetry (CV) and square wave voltammetry (SWV) in CH<sub>3</sub>CN solutions and the relevant electrochemical data are given in Table 5, together with the results available for the reference mononuclear species. The  $E_{1/2}$  values for the reversible couple were determined from CV using the relation  $E_{1/2} = 0.5(E_{pc} + E_{pa})$ , where  $E_{pc}$  and  $E_{pa}$  are cathodic and anodic peak potentials, respectively, while for quasi-reversible and irreversible processes the  $E_{1/2}$  values are obtained from the peak potential of SWV. The  $E_{1/2}$  values for reversible and quasireversible processes obtained by using the two methods agree within ±10 mV. The complexes are found to undergo one reversible oxidation in the positive potential window (0 to +1.6 V) and one irreversible and two successive quasi-reversible reductions in the negative potential window (0 to -2.0 V) (Fig. 10, Fig. S4 and Fig. S5, ESI<sup>†</sup>). In ruthenium(II) and osmium(II) polypyridyl complexes the highest occupied molecular orbital (HOMO), are normally localized on the metal center and oxidative processes are therefore metal based, whereas the lowest unoccupied molecular orbital (LUMO) are usually ligand based and the reduction processes are therefore ligand centered, in agreement with literature data and the reversibility of most of the processes.<sup>1,5,22</sup> Thus, the oxidation in the range of 1.11–1.32 for the Ru(II) complexes (1, 2, and 3) and at 0.98 V for Os(II) compound (4) has been assigned as a  $M^{II}/M^{III}$ (M = Ru and Os) oxidation processes. In all the complexes an irreversible weak oxidation peak is also seen at around 0.98 V, which can be assigned as the tpy-HImzPh<sub>3</sub>-centered oxidation process by comparing with the oxidation potential (0.98 V) of free tpy-HImzPh<sub>3</sub>. It may be noted that the oxidation potential of the Os<sup>II</sup>/Os<sup>III</sup> couple in 4 is less compared to the Ru<sup>II</sup>/Ru<sup>III</sup> couple in 3, consistent with the greater stability of a third-row transition metal ion vis-à-vis a second row metal ion in higher oxidation states. The first reduction process of all the complexes was observed between -0.60 and -0.75 V, which can be assigned as being metal-coordinated tpy-HImzPh3 centered by comparing with the reduction potential (-0.82 V) of free tpy-HImzPh<sub>3</sub>. In the heteroleptic complex  $[(H_2pbbzim)Ru(tpy-HImzPh_3)]^{2+}$  (2),

Table 5 Electrochemical data<sup>a</sup> for tpy-HImzPh<sub>3</sub> and complexes 1–4 in acetonitrile

Compounds	Oxidation <sup>b</sup> $E_{1/2}(ox)/V$	Reduction <sup>c</sup> $E_{1/2}$ (red)/V
tpy-HImzPh	$0.98^{d}$	-0.82
1	1.29	-0.60, -1.20, -1.44
2	1.11	-0.75, -1.50
3	1.32	-0.74, -1.19, -1.44
4	0.98	-0.71, -1.19, -1.44
$5^e$	1.30	-1.29, -1.54
61	1.25	-1.24, -1.46
<b>7</b> <sup>g</sup>	0.76	-1.40, -1.70
<b>8</b> <sup>h</sup>	0.97	-1.25, -1.57
9 <sup>i</sup>	0.93	-1.23, -1.54

<sup>*a*</sup> All potentials are referenced against the Ag/AgCl electrode with  $E_{1/2} = 0.36$  V for Fc/Fc<sup>+</sup>. <sup>*b*</sup> All metal-centered oxidation processes fulfil the criteria of reversibility. <sup>*c*</sup> The potentials reported are the values obtained from OSW. <sup>*d*</sup> Irreversible, the value obtained from OSW. <sup>*e*</sup> [Ru(tpy)<sub>2</sub>]<sup>2+, 5c</sup>, <sup>*f*</sup> [Ru(tpy-PhCH<sub>3</sub>)<sub>2</sub>]<sup>2+, 5c</sup>, <sup>*s*</sup> [Ru(H<sub>2</sub>pbbzim)<sub>2</sub>]<sup>2+, 20a</sup>, <sup>*h*</sup> [Os(tpy)<sub>2</sub>]<sup>2+, 5c</sup>, <sup>*i*</sup> [Os(tpy-PhCH<sub>3</sub>)<sub>2</sub>]<sup>2+, 5c</sup>



Fig. 10 Cyclic voltammograms (oxidation $\rightarrow$  red line and reduction $\rightarrow$  blue line) of tpy-HImzPh<sub>3</sub> and complexes 1–4 in acetonitrile.

the second reduction occurs at -1.50 V and being assigned as  $H_2pbbzim/H_2pbbzim^-$  ligand-centered processes by comparing the reduction potential of  $[Ru(H_2pbbzim)_2]^{2+}$  (-1.40 V).

# Conclusions

In conclusion, we have developed a new series of homo- and heteroleptic bis-tridentate ruthenium(II) and osmium(II) complexes by using the tridentate ligand, 4'-[4-(4,5-diphenyl-1H-imidazol-2-yl)-phenyl]-[2,2':6',2"]terpyridine (tpy-HImzPh<sub>3</sub>) in combination with 2,6-bis(benzimidazole-2-yl)pyridine (H<sub>2</sub>pbbzim) and pmethyl phenyl terpyridine (tpy-PhCH<sub>3</sub>). These compounds were designed to increase the room temperature excited-state lifetime of bisterpyridine-type complexes of ruthenium(II) and osmium(II). To allow fine-tuning of the electronic properties, several homoand heteroleptic complexes have been synthesized. The most striking feature of this class of complexes is their fairly strong room temperature luminescence and appreciably long excited state lifetimes which lie in the range of 6-35 ns. The sub-nanosecond excited-state lifetime of tpy-type complexes at room temperature is widely accepted as being due to the small energy gap between the emitting <sup>3</sup>MLCT state and the deactivating <sup>3</sup>MC level. The important outcome of this study is to increase the energy level separation of the two states by modulating the <sup>3</sup>MLCT energy level of the complexes by introducing an extensively delocalized triphenyl-imidazole group in the 4'-position of the tpy unit, while keeping the energy of the <sup>3</sup>MC state essentially unchanged.

Another point of interest is that the absorption and emission properties of the compounds are strongly influenced by the polarity as well as with the extent of hydrogen bonding ability of the solvents. This opens the possibility of the application of such compounds as solvatochromic probes.

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