Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Ru-Os dyads based on a mixed bipyridine-terpyridine bridging ligand: modulation of rate of energy transfer and pH-induced luminescence switching in the infrared domain

Manoranjan Bar, Dinesh Maity, Sourav Deb, Shyamal Das, and Sujoy Baitalik*

Department of Chemistry, Inorganic Chemistry Section, Jadavpur University,

Kolkata – 700032, India

Experimental section

Synthesis of the metal complexes

[(dipy-Hbzim-tpy)Os(tpy-PhCH$_3$)](ClO$_4$)$_2$·2H$_2$O (1a). To a suspension of Os(tpy-PhCH$_3$)Cl$_3$ (100 mg, 0.17 mmol) in 25 mL of Me$_2$CO solid AgBF$_4$ (102 mg, 0.51 mmol) was added and refluxed for 3h with continuous stirring. The resulting mixture was cooled to room temperature and the white precipitate of AgCl was separated out by quick filtration. The filtrate consisting of the solvated complex of the type [(tpy-PhCH$_3$)Os(Me$_2$CO)$_3$]$^{3+}$ was added slowly to an ethanol-chloroform solution of the excess bridging ligand, dipy-Hbzim-tpy (120 mg, 0.23 mmol) and refluxed for 6h under argon protection when the color of the solution gradually changed from violet to orange-red. The reaction mixture was cooled to room temperature and the suspended material was removed by filtration and upon rotary evaporation to a small volume (~10 mL), a red compound deposited. The compound was filtered, washed with chloroform and ether and then dried under vacuum. The compound was dissolved in small acetonitrile and subjected to silica-gel column chromatography (eluent: 1:1 acetonitrile-methanol). The eluent were rotary evaporated to small volume and then anion exchange reaction with NaClO$_4$ give rise to the desired compound. Further purification of the compound was done by recrystallization from acetonitrile-methanol (1:1 v/v) mixture in presence of a few drops of aqueous 10^{-4} M HClO$_4$. Yield: 130 mg, 64%. Anal. Calcd. for C$_{56}$H$_{44}$N$_{10}$Cl$_2$O$_{10}$Os: C, 52.62; H, 3.15; N, 10.96. Found: C, 52.74; H, 3.24; N, 10.62. ^{1}H NMR (300 MHz, DMSO-d_6, δ / ppm): 13.03 (s, 1H, NH imidazole), 9.58 (s, 2H, 2H3$^{'}$), 9.49 (s, 2H, 2H3$^{'}$), 9.19 (d, 2H, J = 5.4 Hz, 2H9), 9.13-9.09 (m, 4H, 4H6), 8.76 (d, 2H, J = 7.8 Hz, 2H12), 8.68-8.60 (m, 4H, 4H8), 8.54 (t, 2H, J = 7.5 Hz, 2H11), 8.33 (d, 2H, J = 7.8 Hz, 2H7), 7.97-7.90 (m, 6H, 4H3+2H10), 7.57 (d, 2H, J = 7.8 Hz, 2H7), 7.44 (t, 4H, J = 7.4 Hz, 4H4), 7.25-7.18 (m, 4H, 4H5), 2.48 (s, 3H, CH$_3$).

[(dipy-Hbzim-tpy)Os(H$_2$pbbzim)](ClO$_4$)$_2$·H$_2$O (1b). A mixture of [(H$_2$pbbzim)OsCl$_3$] (100 mg, 0.16 mmol) and dipy-Hbzim-tpy (90 mg, 0.17 mmol) in 20 mL of ethylene glycol was refluxed for 3h with continuous stirring under argon protection. The resulting solution was then cooled down to room temperature, filtered and poured into an aqueous solution of NaClO$_4$·H$_2$O (1.0 g in 5 mL of water) to precipitate the complex as the perchlorate salt. The red colored precipitate was filtered, washed with water and then dried under vacuum. The complex was then purified by silica gel column chromatography using CH$_3$CN as the eluent. The desired compound

was obtained by rotary evaporation of the eluent and subsequent anion exchange reaction with $NaClO_4 \cdot H_2O$. The compound was finally recrystallized from CH_3CN-H_2O (2:1) mixture in presence of a few drops of 10^{-4} M $HClO_4$ Yield: 30 mg, 65%. Anal. Calcd. for $C_{53}H_{38}N_{12}Cl_2O_9Os$: C, 51.00; H, 3.06; N, 13.47 Found: C, 51.24; H, 3.22; N, 13.32. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 15.05 (s, 2H, NH imidazole, H_2pbbzim), 13.05 (s, 1H, NH imidazole), 9.66 (s, 2H, 2H3′), 9.19 (d, 2H, *J* = 4.8 Hz, 2H6), 9.00 (d, 2H, *J* = 8.1 Hz, 2H9), 8.78 (d, 4H, *J*=8.1 Hz, 2H7+2H8), 8.68 (t, 5H, *J* = 7.8 Hz, 2H3+H17+2H18), 8.54 (t, 1H, *J* = 7.9 Hz, H4), 8.05 (t, 1H, *J* = 7.9 Hz, H4), 7.92 (t, 2H, *J* = 6.0 Hz, 2H5), 7.78 (t, 2H, *J* = 7.6 Hz, 2H10), 7.64 (d, 2H, *J* = 8.1 Hz, 2H19), 7.38-7.30 (m, 4H, 2H12+2H20), 7.17 (t, 2H, *J* = 6.6 Hz, 2H11), 6.96 (t, 2H, *J* = 7.8 Hz, 2H21). 6.03 (d, 2H, *J* = 8.4 Hz, 2H22).

[(bpy)$_2$Ru(dipy-Hbzim-tpy)Os(tpy-PhCH$_3$)] (ClO$_4$)$_4$·H$_2$O (3). [Os(tpy-PhCH$_3$)Cl$_3$] (62 mg, 0.1 mmol) and [(bpy)$_2$Ru(dipy-Hbzim-tpy)](ClO$_4$)$_2$ (**1**) (115 mg, 0.1 mmol) was added to ethylene glycol (10 mL) and refluxed with continuous stirring for 6h under argon protection. The resulting solution was cooled to room temperature and then poured into a saturated aqueous solution of $NaClO_4 \cdot H_2O$ (5 mL of water) to precipitate the complex as its perchlorate salt. The compound that deposited was filtered and washed with water and subjected to silica gel column chromatography for purification using a mixture of CH_3CN and toluene as the eluent. The eluent was rotary evaporated and finally recrystallized from acetonitrile-methanol (1:2 v/v) mixture in the presence of a few drops of aqueous 10^{-4} M $HClO_4$ when a black microcrystalline compound was obtained (100 mg, Yield: 61 %). Anal. Calcd. for $C_{76}H_{58}N_{14}Cl_4O_{17}RuOs$: C, 48.76; H, 3.12; N, 10.47. Found: C, 48.82; H, 3.20; N, 10.42. ^{1}H NMR (500 MHz, DMSO-d_6, δ/ppm: 14.28 (s, 1H, NH imidazole), 9.48 (s, 2H, 2H3′), 9.21 (s, 2H, 2H3′), 9.09 (d, 2H, *J* = 8.5 Hz, 2H6), 9.05 (d, 2H, *J* = 8.0 Hz, 2H3′′), 8.99 (d, 1H, *J* = 8.0 Hz, H9), 8.92 (d, 1H, *J* = 5.0 Hz, H16), 8.85 (d, 1H, *J* = 8.5 Hz, H3′′), 8.78 (d, 3H, *J* = 8.5 Hz, 2H8+ H3′′), 8.71-8.69 (m, 2H, 2H6), 8.32 (d, 4H, *J* = 8.0 Hz, 2H7+2H8), 8.24 (d, 2H, *J* = 8.0 Hz, 2H6′), 8.15-8.08 (m, 2H, H11+H4), 7.97-7.93 (m, 5H, H4+H10+ 3H4′), 7.76-7.66 (m, 4H, H4′+2H4+H15), 7.58 (d, 2H, *J* = 7.5 Hz, 2H7), 7.52 (d, 2H, *J* = 8.0 Hz, 2H6′), 7.47-7.44 (m, 2H, 2H3), 7.46 (t, 1H, *J* = 7.0 Hz, H14), 7.37-7.29 (m, 4H, 4H5′), 7.36 (d, 2H, *J* = 5.5 Hz, 2H3), 7.33 (d, 1H, *J* = 8.0 Hz, H12), 7.29-7.27 (m, 4H, 4H5), 7.24-7.19 (m, 1H, H13), 2.49 (s, 3H, CH_3). ESI-MS (positive, CH_3CN) *m/z* = 364.09 (100

%) [(bpy)$_2$Ru(dipy-Hbzim-tpy)Os(tpy-PhCH$_3$)]$^{4+}$ and *m/z* = 485.13 (28 %) [(bpy)$_2$Ru(dipy-bzim-tpy)Os(tpy-PhCH$_3$)]$^{3+}$.

[(phen)$_2$Ru(dipy-Hbzim-tpy)Os(tpy-PhCH$_3$)](ClO$_4$)$_4$·H$_2$O (4). Complex 4 was synthesized by adopting the same procedure as for **3** with the exception that [(phen)$_2$Ru(dipy-Hbzim-tpy)](ClO$_4$)$_2$ (**2**) (120 mg, 0.1 mmol) was used instead of [(bpy)$_2$Ru(dipy-Hbzim-tpy)](ClO$_4$)$_2$**.** Yield: 105 mg, 66%. Anal. Calcd. for $C_{80}H_{58}N_{14}Cl_4O_{17}RuOs$: C, 50.50; H, 3.04; N, 10.21. Found: C, 50.62; H, 3.14; N, 10.12. ^{1}H NMR (500 MHz, DMSO-d_6, δ / ppm): 14.21 (s, 1H, NH imidazole), 9.49 (s, 2H, 2H3′), 9.19 (s, 2H, 2H3′), 9.10 (d, 2H, *J* = 7.5, 2H6), 9.04 (t, 3H, *J* = 8.7 Hz, H9+ 2H3′′), 8.93-8.89 (m, 3H, 2H6+H16), 8.70-8.65 (m, 2H, 2H8), 8.46-8.42 (m, 2H, 2H8), 8.36-8.32 (m, 4H, H4+2H7+H10), 8.19-8.13 (m, 3H, 2H3′′+H15), 8.09-8.06(m, 1H, H5), 8.03-8.01 (d, 1H, *J* = 7.5 Hz, H5′), 8.02 (d, 1H, *J* = 7.5 Hz, H4′), 7.96-7.92 (m, 8H, 2H4+2H5+H11+2H4′+H5′), 7.86 (d, 1H, *J* = 5.0 Hz, H6′), 7.70 (d, 2H, *J* = 8.0 Hz, 2H6′), 7.64-7.60 (m, 2H, H4′+H14), 7.47 (d, 3H, *J* = 5.5 Hz, 2H3+H12), 7.41 (t, 1H, *J* = 5.2 Hz, H4), 7.36 (d, 2H, *J* = 6.0 Hz, H3+ H5′), 7.31-7.28 (m, 1H, H5′), 7.24 (d, 1H, *J* = 5.5 Hz, H13), 7.19-7.15 (m, 1H, 1H5), 6.99 (d, 2H , *J* = 6.0 Hz, H3+ H6′), 7.58 (d, 2H, *J* = 8.5 Hz, 2H7), 2.48 (s, 3H, CH$_3$). ESI-MS (positive, CH$_3$CN) *m/z* = 376.12 (18 %) [(phen)$_2$ Ru(dipy-Hbzim-tpy)Os(tpy-PhCH$_3$)]$^{4+}$ and *m/z* = 501.83 (100 %) [(phen)$_2$Ru(dipy-bzim-tpy)Os(tpy-PhCH$_3$)]$^{3+}$.

(bpy)$_2$Ru^{II}(dipy-Hbzim-tpy)Os^{II}(H$_2$pbbzim)]ClO$_4$)$_4$·H$_2$O (5). [(bpy)$_2$Ru(dipy-Hbzim-tpy)](ClO$_4$)$_2$·4H$_2$O (**1**) (115 mg, 0.1 mmol) and [Os(H$_2$pbbzim)Cl$_3$] (60 mg, 0.1 mmol) was successively added to ethylene glycol (10 mL) and heated under reflux for 8h with continuous magnetic stirring under argon atmosphere. After cooling at room temperature, the resulting solution was poured to an saturated aqueous solution of NaClO$_4$·H$_2$O (5 mL of water) for precipitating the complex as its perchlorate salt. The precipitated compound was collected by filtration, washed with water, and then dried in vacuum. The complex was purified by silica gel column chromatography by eluting with a mixture of acetonitrile and toluene. After removal of the eluent, the compound was further purified by recrstallization from acetonitrile-water (2:1, v/v) mixture in presence of a few drops of aqueous 10^{-4} M HClO$_4$. Yield: 90 mg, 55%. Anal. Calcd. for $C_{73}H_{54}N_{16}Cl_4O_{17}RuOs$: C, 47.15; H, 2.92; N, 12.05. Found: C, 47.24; H, 3.98; N, 11.96. ^{1}H NMR (500 MHz, DMSO-d_6, δ / ppm): 15.12 (s, 2H, NH imidazole, H$_2$pbbzim), 14.32 (s, 1H, NH imidazole),9.32 (s, 2H, 2H3′), 8.91 (t, 4H, *J* = 9.2 Hz, 2H6+2H3′′), 8.78(d, 1H, *J* =

8.5 Hz, H9), 8.72 (d, 2H, *J* = 8.5 Hz, 2H3′′), 8.67 (d, 3H, *J* = 8.0 Hz, H16+2H18), 8.42 (d, 1H, *J* = 8.0 Hz, H8), 8.26-8.20 (m, 3H, H8+H10+H11), 8.14 (t, 1H, *J* = 8.5 Hz, H17), 8.10 (d, 2H, *J* = 8.0 Hz, 2H6′), 8.06-8.02 (m, 3H, H12+2H6′), 7.99-7.93 (m, 2H, 2H19), 7.76 (t, 2H, *J* = 7.2 Hz, 2H4′), 7.66-7.61 (m, 3H, 2H4′+H15), 7.62 (d, 2H, *J* =8.0 Hz, 2H4),7.51-7.48(m, 2H, 2H7), 7.42(t, 1H, *J* = 6.7 Hz, 2H5′), 7.38 (d, 2H, *J* = 6.0 Hz, 2H3), 7.32-7.31 (m, 4H, H14+2H20+ H5′),7.28-7.26(m, 2H, 2H5), 7.18-7.16 (m, 2H, 2H5′), 7.17(t, 1H, *J* = 4.7 Hz, H13), 6.96(t, 2H, *J* = 7.7 Hz, 2H21), 6.01(d, 2H, *J* = 8.0 Hz, 2H22). ESI-MS (positive, CH_3CN) *m/z* = 481.14 (22 %) $[(bpy)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(Hpbbzim)]^{3+}$ and m/*z* = 721.20 (100 %) $[(bpy)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(pbbzim)]^{2+}$.

$(phen)_2Ru^{II}(dipy\text{-}Hbzim\text{-}tpy)Os^{II}(H_2pbbzim)]ClO_4)_4\cdot H_2O$ (6). The synthetic procedure adopted for **6** is similar to that of **5** except $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)](ClO_4)_2\cdot 4H_2O$ (**2**) (120 mg, 0.1 mmol) was used instead of $[(bpy)_2Ru(dipy\text{-}Hbzim\text{-}tpy)](ClO_4)_2\cdot 4H_2O$ (**1**) .Yield: 95 mg, 60% for **7** Anal. Calcd. for $C_{77}H_{54}N_{16}Cl_4O_{17}RuOs$: C, 48.47; H, 2.85; N, 11.75 Found: C, 48.52; H, 2.90; N, 11.70. ^{1}H NMR (500 MHz, DMSO-d_6, δ / ppm): 15.09 (s, 2H, NH imidazole, H_2pbbzim), 14.30 (s, 1H, NH imidazole), 9.23 (s, 2H, 2H3′), 9.19 (d, 2H, *J* = 5.0 Hz, H9+ H3′′), 8.91(d, 1H, *J* = 4.5 Hz, H16), 8.87 (t, 4H, *J* = 6.5 Hz, 2H6+2H3′′), 8.66 (d, 2H, *J* = 8.0 Hz, 2H18), 8.62 (d, 1H, *J* = 8.0 Hz, H3′′), 8.46 (d, 2H, *J* = 8.5 Hz, 2H8), 8.39 (d, 1H, *J* = 8.5 Hz, H6′), 8.31 (d, 1H, *J* = 9.0 Hz, H7), 8.15-8.09 (m, 4H, H15+H17+2H4′), 8.04-8.01 (m, 3H, H4+H10+H11), 7.92 (t, 1H, *J* = 5.0 Hz, H4), 7.82 (d, 1H, *J* =5.0 Hz, H12),7.78-7.74(m, 2H, 2H6′), 7.76(t, 2H, *J* = 9.2 Hz, 2H5′), 7.69-7.58(m, 4H, H6′+H14+2H19),7.46 (t, 2H, *J* = 5.5 Hz, 2H4′),7.37(d, 2H, *J* = 5.5 Hz, 2H3), 7.32-7.28 (m, 3H, H5+H7+H13), 7.17(t, 3H, *J* = 6.5 Hz, H5+2H20), 6.98-6.93 (m, 4H, 2H21+ 2H5′), 6.02(d, 2H, *J* = 8.0 Hz, H22). ESI-MS (positive, CH_3CN) *m/z* = 497.45 (70 %) $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(Hpbbzim)]^{3+}$ and m/*z* = 746.65 (100 %) $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(pbbzim)]^{2+}$.

Physical measurements. Elemental analyses of the compounds were performed with a Vario-Micro V2.0.11 elemental (CHNSO) analyzer. NMR spectra were collected on either a Bruker 300 or Bruker 500 spectrometer in DMSO-d_6, and high resolution mass spectroscopy was performed on a Waters Xevo G2 QTOf mass spectrometer. UV-vis absorption spectra were recorded using a Shimadzu UV 1800 spectrometer at room temperature. Steady state

luminescence spectra were obtained by either Perkin–Elmer LS55 or Horiba Fluoromax-4C spectrofluorometer. Luminescence quantum yields were determined using literature method taking $[Ru(bpy)_3]^{2+}$ as the standard. Luminescence lifetime measurements were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon. The samples were excited with 450 nm Nanoled. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software. Cyclic and square-wave voltammetric experiments were performed in deaerated acetonitrile with a BAS epsilon electrochemistry system and a three-electrode set up consisting of a platinum or glassy carbon working electrode, a platinum counter electrode, and Ag/AgCl reference electrode. Tetraethylammonium perchlorate (TEAP) was used as background electrolyte. 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 Fc/Fc^+ couple.

To determine the ground state pK_a values of the complexes, spectrophotometric titrations were carried out with a series of acetonitrile-water (3:2 v/v) solutions containing the same amount of complex (10^{-5} M) and pH adjusted in the range of 2.5-12. Robinson-Britton buffer was used in the study. The pH measurements were made with a Beckman Research Model pH meter. The pK_a values were evaluated from the titration data and using eqn (S1).

$$\mathrm{pH} = \mathrm{p}K - \log \frac{A - A_0}{A_f - A_0} \qquad \text{(S1)}$$

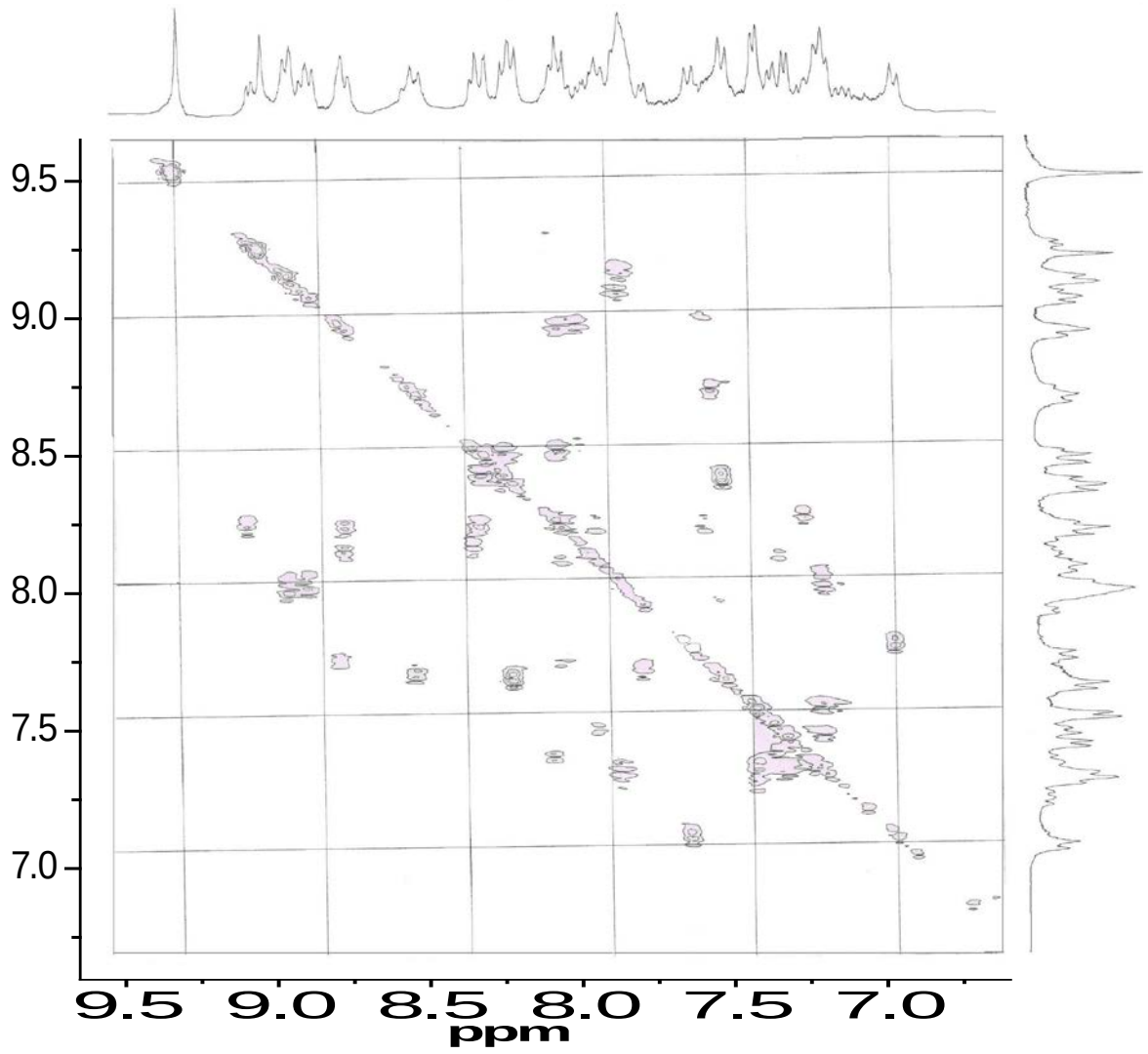

Fig. S1 (^{1}H-^{1}H) COSY NMR spectrum of complex [(phen)$_2$Ru(tpy-Hbzim-dipy)Os(tpy-PhCH$_3$)](ClO$_4$)$_4$ (**4**) in DMSO-d_6.

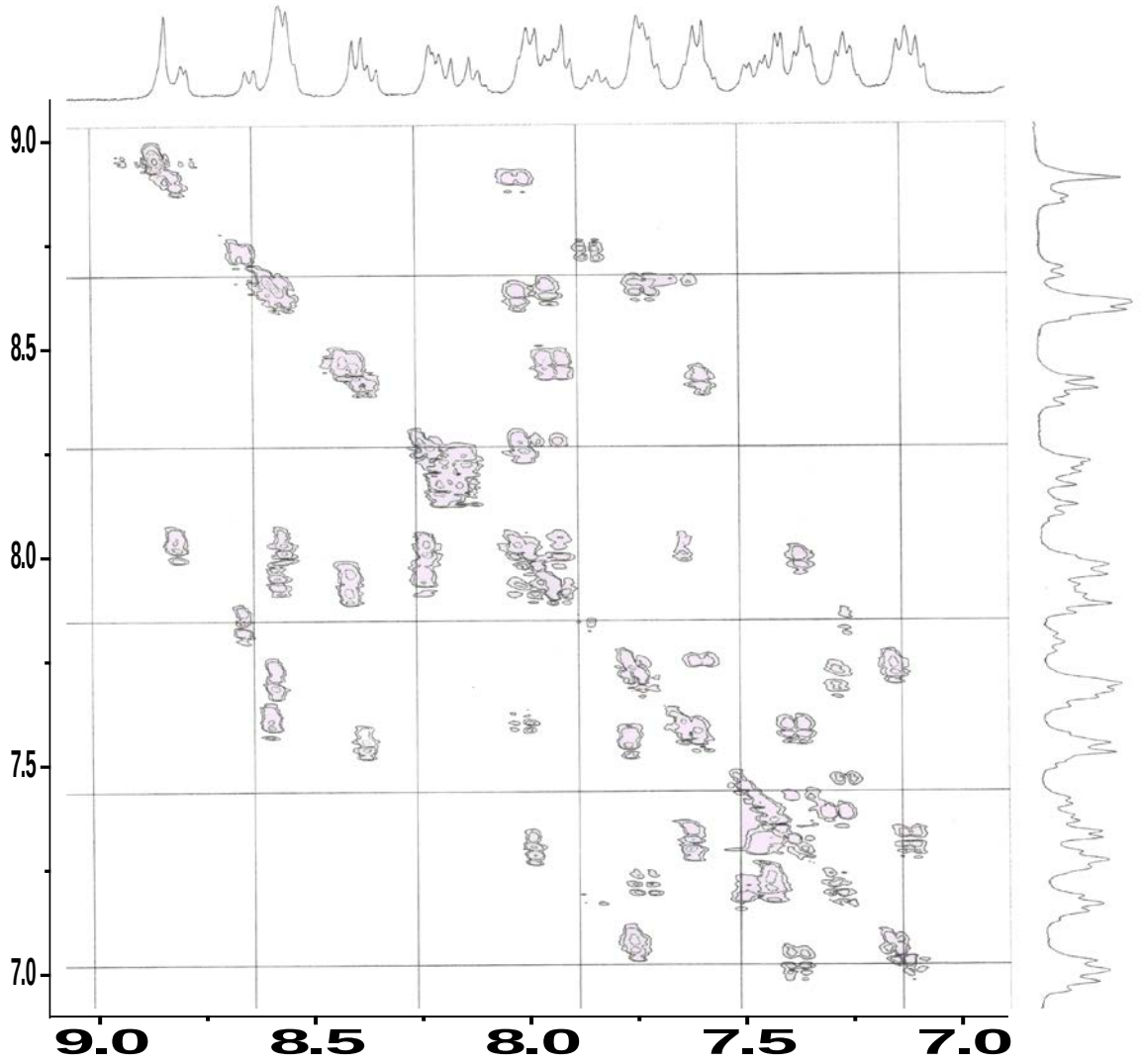

Fig. S2 (^{1}H-^{1}H) COSY NMR spectrum of complex [(phen)$_2$Ru(tpy-Hbzim-dipy)Os(H$_2$pbbzim)] (ClO$_4$)$_4$ (**6**) in DMSO-d_6.

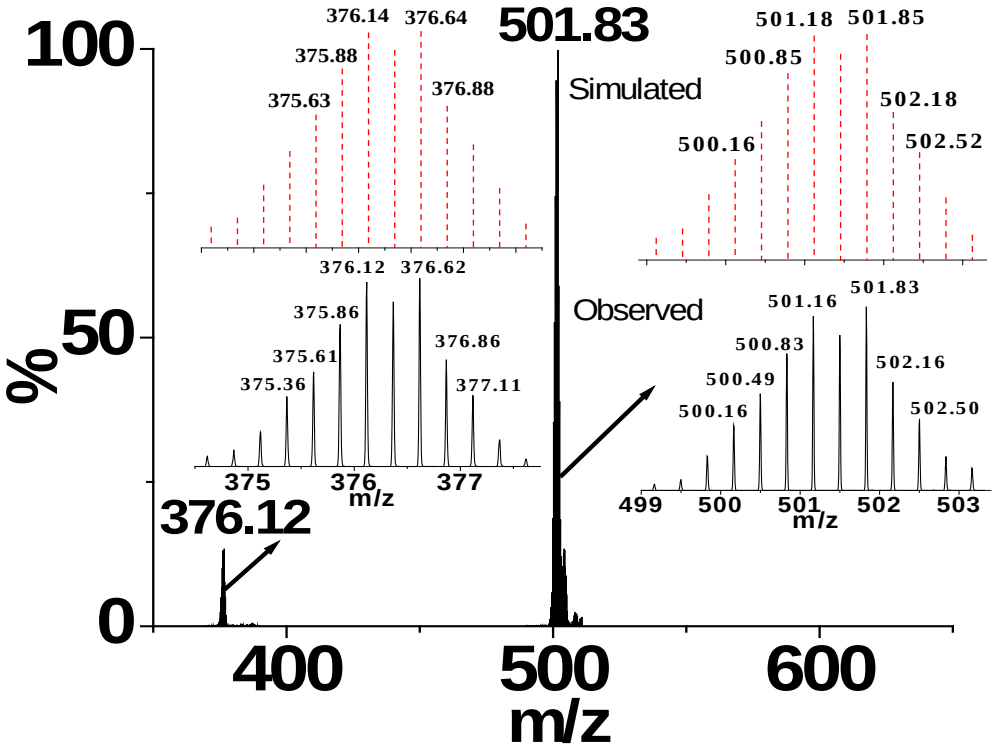

Fig. S3 ESI-MS (positive) for the complex cation of **4**, $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(tpy\text{-}PhCH_3)]^{4+}$ (*m/z* = 376.12) and $[(phen)_2Ru(dipy\text{-}bzim\text{-}tpy)Os(tpy\text{-}PhCH_3)]^{3+}$ (*m/z* = 501.83) in acetonitrile showing the observed and simulated isotopic distribution patterns.

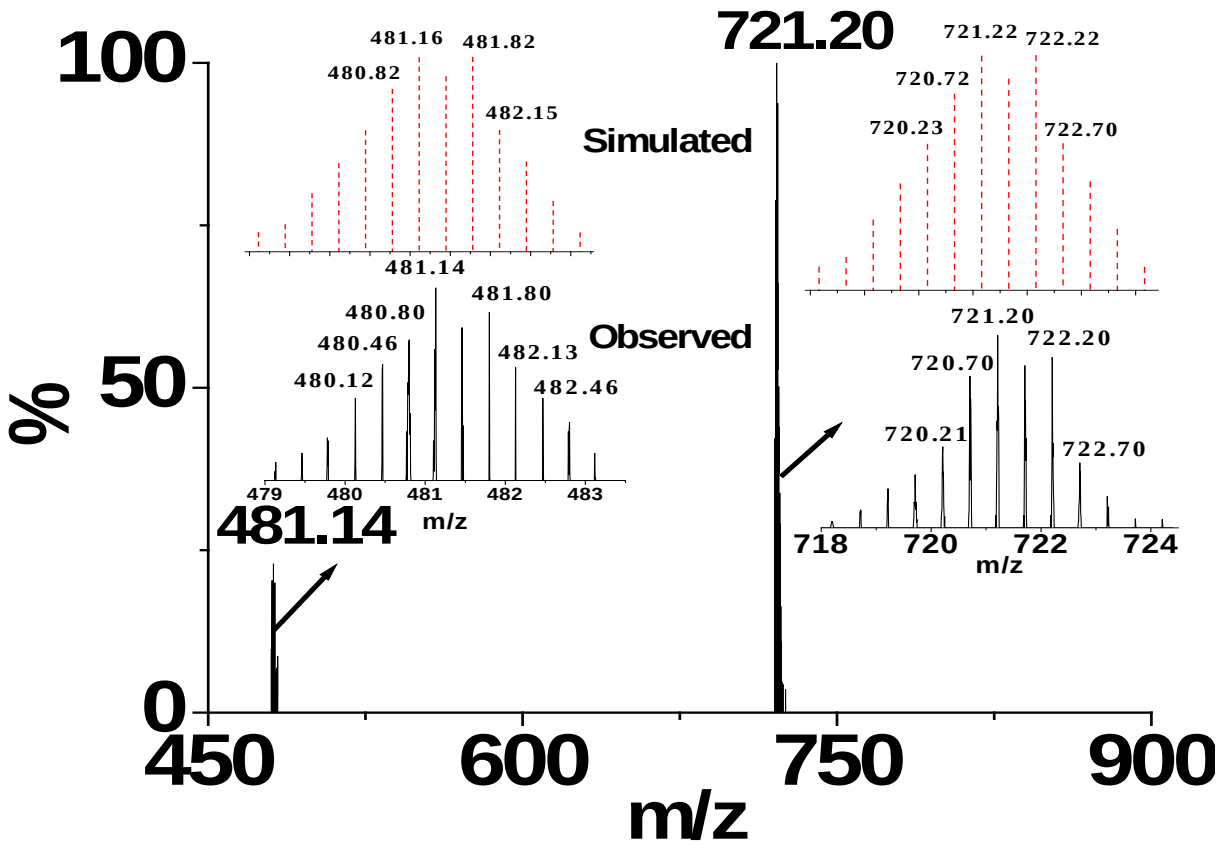

Fig. S4 ESI-MS (positive) for the complex cation of **5,** $[(bpy)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(Hpbbzim)]^{3+}$ (*m/z* = 481.14) and $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(pbbzim)]^{2+}$ (*m/z* = 721.20) in acetonitrile showing the observed and simulated isotopic distribution patterns.

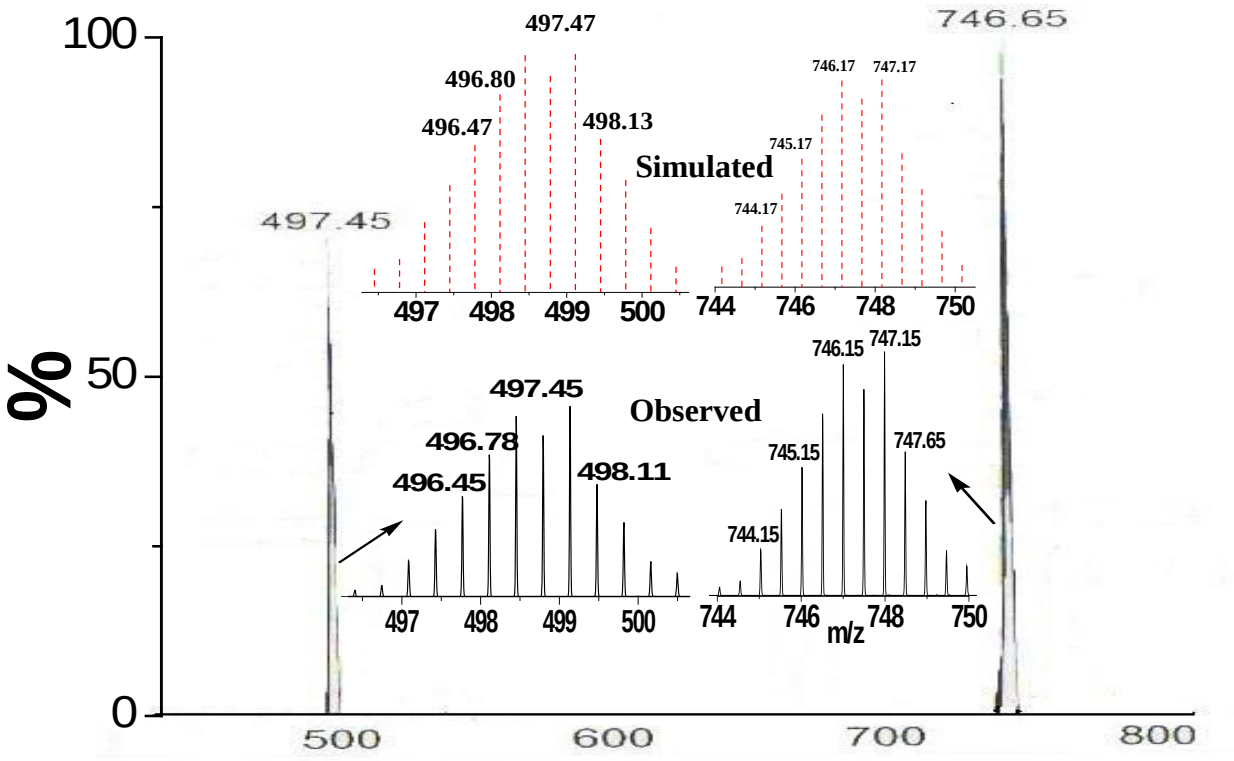

Fig. S5 ESI-MS (positive) for the complex cation of **6,** $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(Hpbbzim)]^{3+}$ (*m/z* = 497.45) and $[(phen)_2Ru(dipy\text{-}Hbzim\text{-}tpy)Os(pbbzim)]^{2+}$ (*m/z* = 746.65) in acetonitrile showing the observed and simulated isotopic distribution patterns.

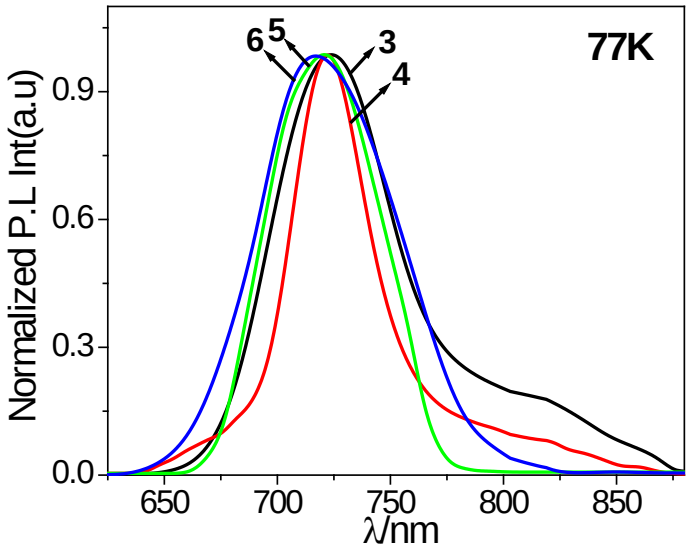

Fig. S6 Normalized photoluminescence spectra of **3-6** at 77 K in methanol-ethanol (1:4, v/v) glass.

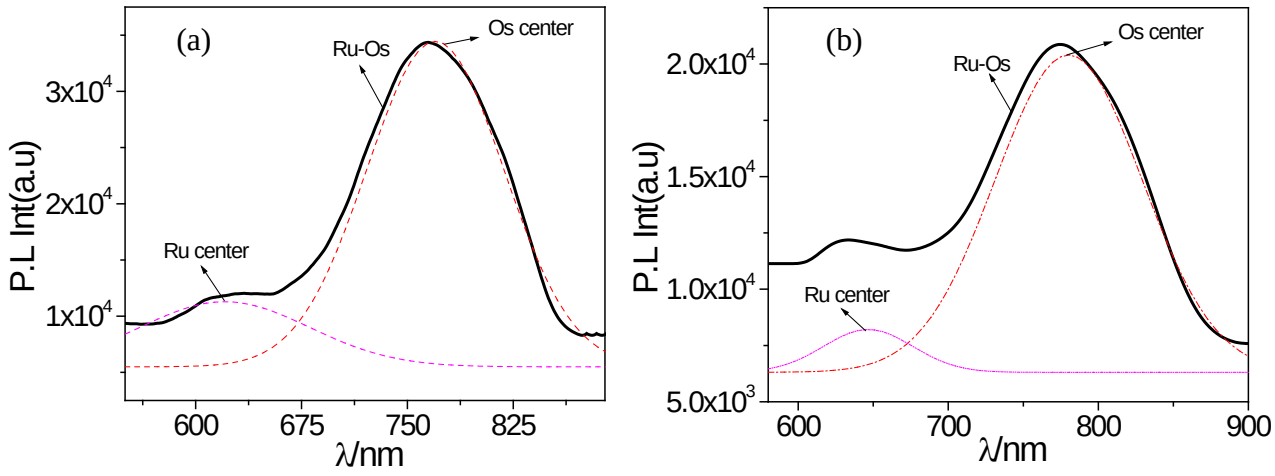

Fig. S7 The emission and deconvoluted spectra of Ru-Os in complex **5** (a) and complex **6** (b).

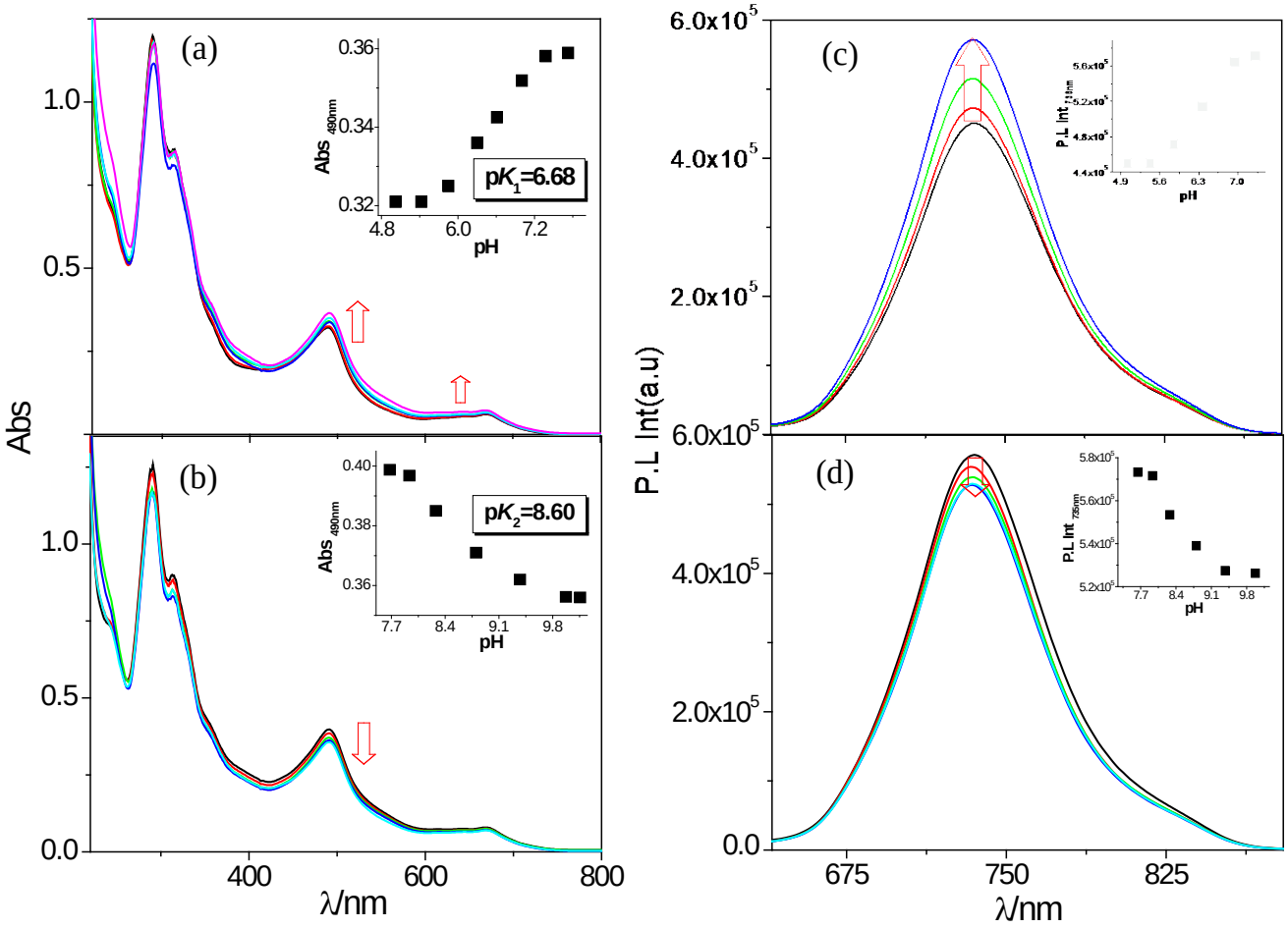

Fig. S8 Changes in the absorption (a and b) and photoluminescence spectra (c and d) of **3** with variation of pH of the solution. The insets show the change of absorbance (a and b) and luminescence (c and d) with pH, the calculated pK_1 and pK_2 of **3** are 6.68 and 8.60 respectively. Excitation wavelength for recording the luminescence spectra was 490 nm.

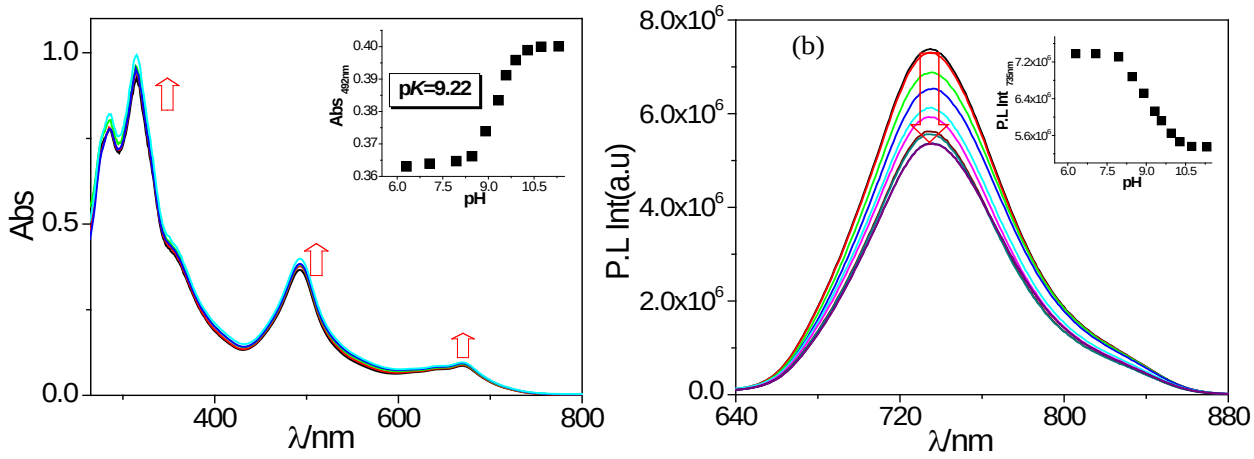

Fig. S9 Changes in the absorption (a) and photoluminescence spectra (b) of **1a** with variation of pH of the solution. The insets show the change of absorbance (a) and luminescence (b) with pH: the calculated p*K* value for **1a** is 9.22 respectively. Excitation wavelength for recording the luminescence spectrum was 490 nm.

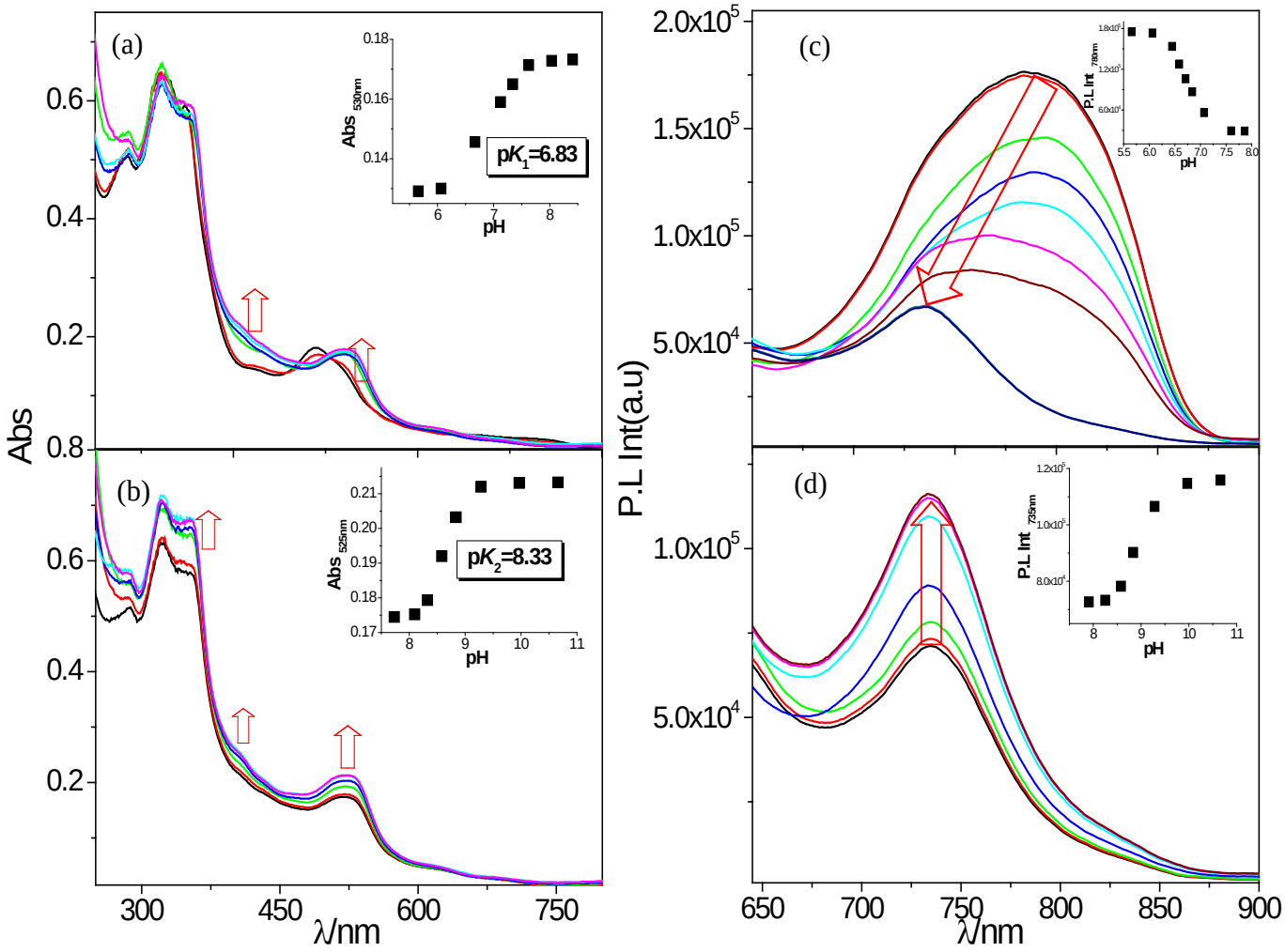

Fig. S10 Changes in the absorption (a and b) and photoluminescence spectra (c and d) of **1b** with variation of pH of the solution. The insets show the change of absorbance (a and b) and luminescence (c and d) with pH. Calculated pK_1 and pK_2 of **1b** are 6.83 and 8.33, respectively. Excitation wavelength for recording the luminescence spectra was 490 nm.

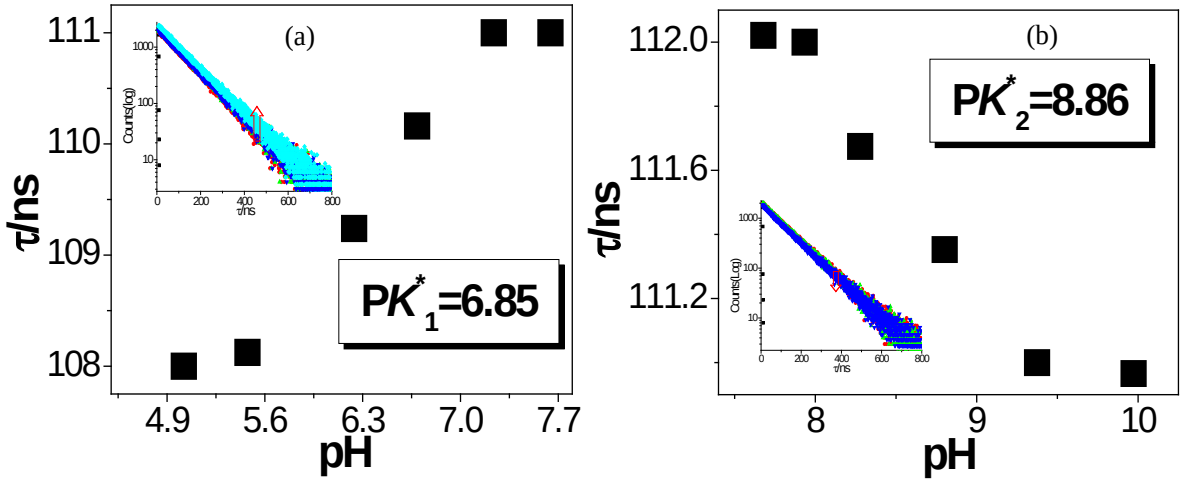

Fig. S11 Two-step changes in the excited state lifetimes of **3** (a and b, respectively) with variation of pH of the solution. Inset shows the decay profiles of **3** as a function of pH. pK_a^* values are also given in the figure.

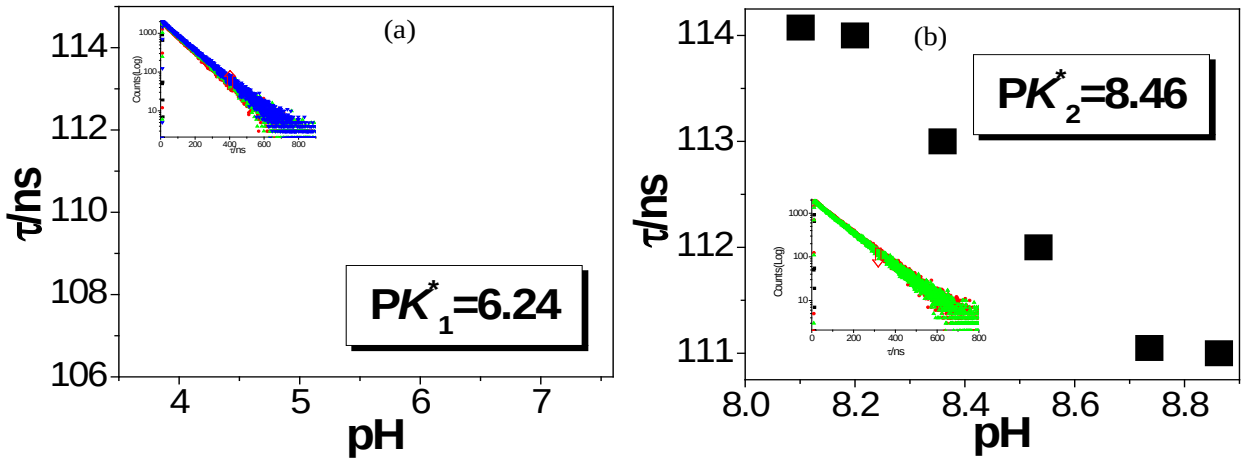

Fig. S12 Two-step changes in the excited state lifetimes of **4** (a and b, respectively) with variation of pH of the solution. Inset shows the decay profiles of **4** as a function of pH. pK_a^* values are also given in the figure.

References

S1 D. D. Perrin and B. Dempsey, *Buffers for pH and metal ion control*. Chapman and Hall, London, 1974.