Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Tuning of photo-redox behaviours, and thermodynamic and kinetic aspects of intercomponent energy transfer in trimetallic complexes of Ru(II) and Os(II) by exploiting their second coordination sphere

Animesh Paul, Soumi Das, Manoranjan Bar, and Sujoy Baitalik*

Inorganic Chemistry Section, Department of Chemistry, Jadavpur University

Kolkata 700 032, India

Physical measurements

UV-vis absorption spectra were recorded using a Shimadzu UV 1800 spectrometer. Steady state luminescence spectra were acquired by a Horiba Fluoromax-4 spectrofluorometer. Luminescence quantum yields were determined using literature method taking $[Ru(bpy)_3]^{2+}$ as the standard. Luminescence lifetime measurements in nanosecond were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon. The samples were excited at 490 nm using a nanosecond diode laser. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software. Spectrophotometric titrations were carried out with a series of acetonitrile-water (1:10 v/v) solutions containing the same amount of complex (10^{-5} M) and pH adjusted in the range of 2.0-12. Robinson-Britton buffer was used in the study. The pH measurements were made with a Beckman Research Model pH meter. Steady state emission spectra also carried out at 77K in EtOH-MeOH (4:1, v/v) glass.

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 Ag/AgCl reference electrode were used. Both cyclic voltammetry (CV) and square wave voltammetric (SWV) measurements were carried out in argon purged acetonitrile-water (1:10, v/v) solution of the complexes (*ca.*1 mM) at 25°C and the concentration of the supporting electrolyte (TEAP) was maintained at 0.1 M. The scan rate of acquiring CV was 100 mV/s, while SWV was acquired at a scan rate of 25 mV/s. 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.

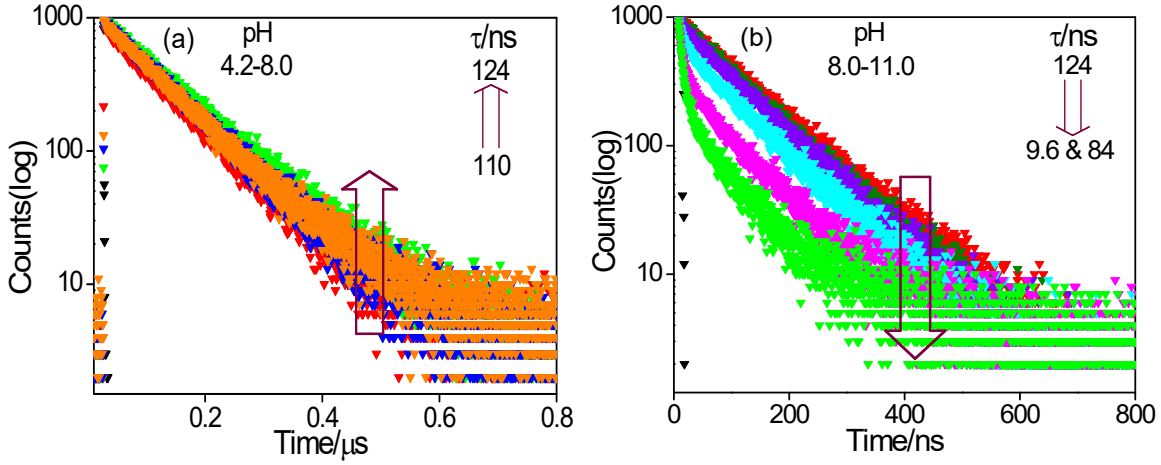

Fig. S1 pH dependent luminescence decays of RuOsRu (**4H$_2$**) in acetonitrile-water (1:10 v/v) buffer. The insets show the extent of lifetime change in the studied pH domain. The solution is excited with 490 nm light using a nanosecond diode laser and emission decay is monitored at 733 nm.

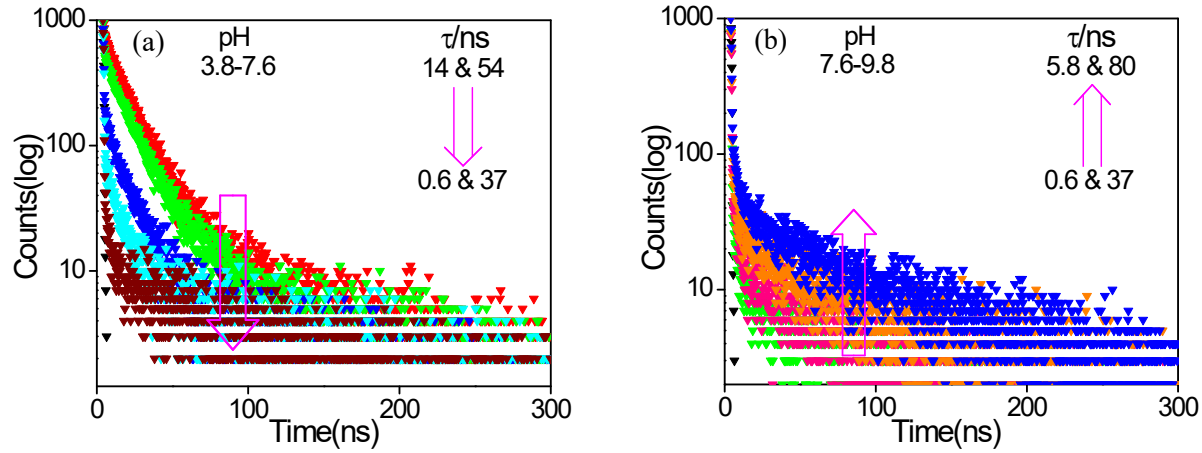

Fig. S2 pH dependent luminescence decays of OsOsOs (**5H$_2$**) in acetonitrile-water (1:10 v/v) buffer. The insets show the extent of lifetime change in the studied pH domain. The solution is excited with 490 nm light using a nanosecond diode laser and emission decay is monitored at 743 nm.

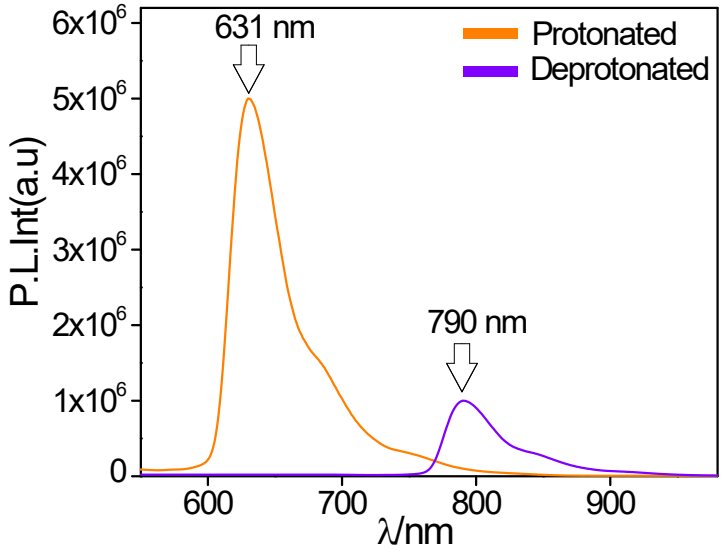

Fig. S3 Luminescence spectrum (λ_{ex}=490 nm) of RuRuRu (**3H$_2$**) in its protonated and deprotonated form at 77 K in EtOH-MeOH (1:4, v/v).

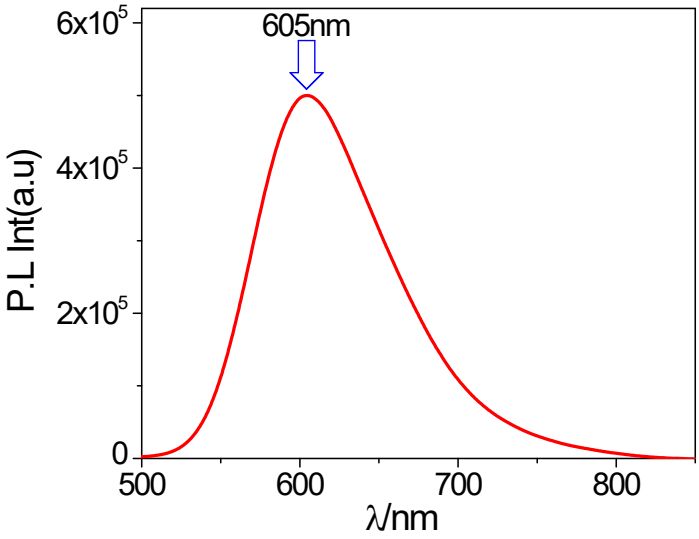

Fig. S4 Luminescence spectrum (λ_{ex}=490 nm) of $[(bpy)_2Ru(d\text{-}HIm\text{-}t)]^{2+}$(**1H**) at 77 K in EtOH-MeOH (1:4, v/v).

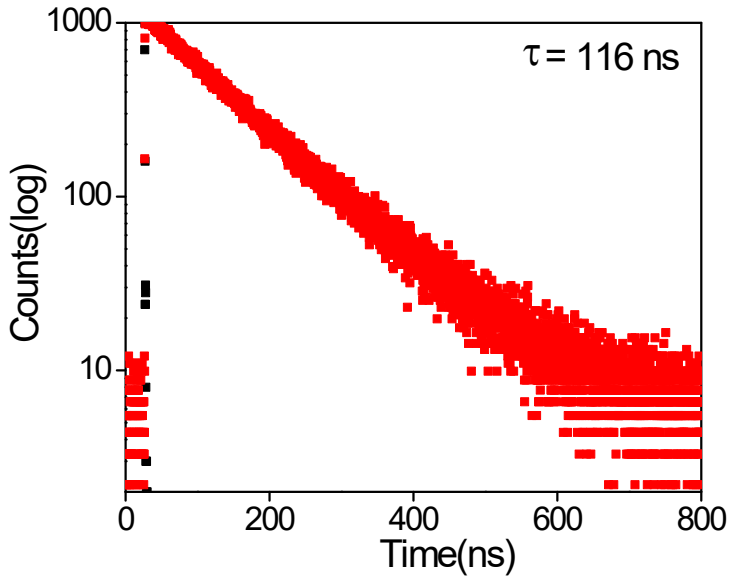

Fig. S5 Luminescence decay of $[(bpy)_2Ru(d\text{-}HIm\text{-}t)]^{2+}$(**1H**) in acetonitrile-water (1:10 v/v) buffer. The solution is excited with 450 nm light using a nanosecond diode laser and emission decay is monitored at 637 nm.

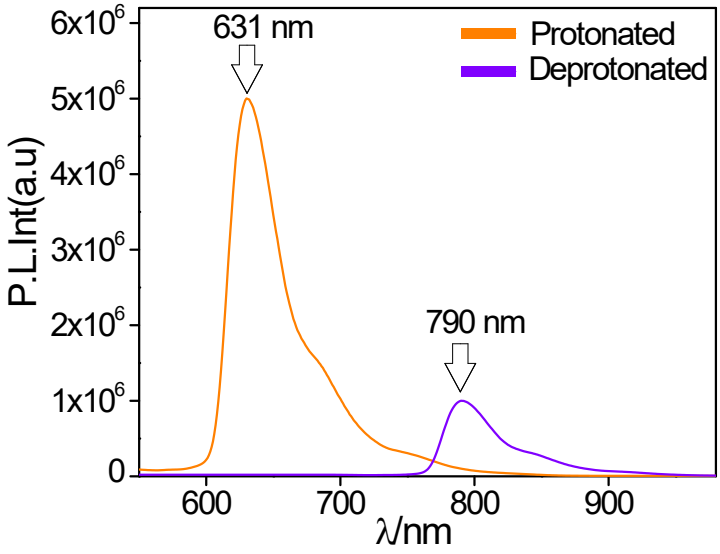

Fig. S6 Luminescence spectrum (λ_{ex}=490 nm) of RuOsRu in its protonated (**4H$_2$**) and doubly deprotonated (**4**) form at 77 K in EtOH-MeOH (1:4, v/v).

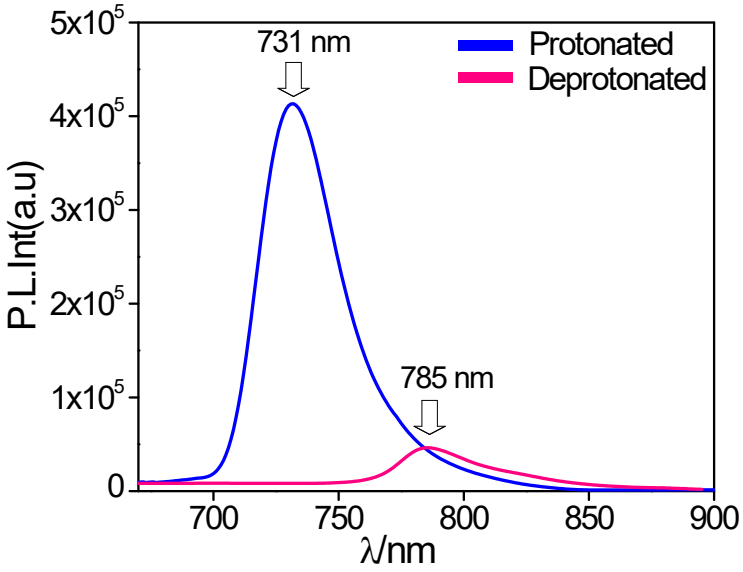

Fig. S7 Luminescence spectrum (λ_{ex}=490 nm) of OsRuOs in its protonated (**6H$_2$**) and deprotonated (**6**) form at 77 K in EtOH-MeOH (1:4, v/v).

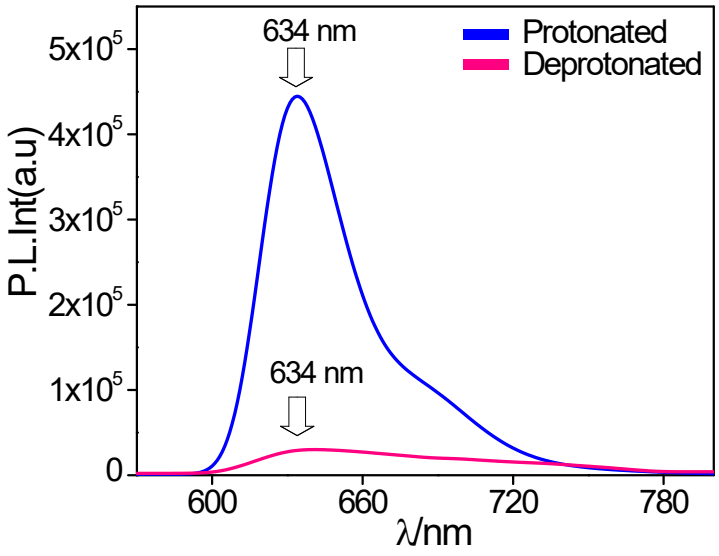

Fig. S8 Luminescence spectrum (λ_{ex}=490 nm) of $[Ru(t\text{-}Him\text{-}d)_2]^{2+}$ in protonated and deprotonated form at 77 K in EtOH-MeOH (1:4, v/v).

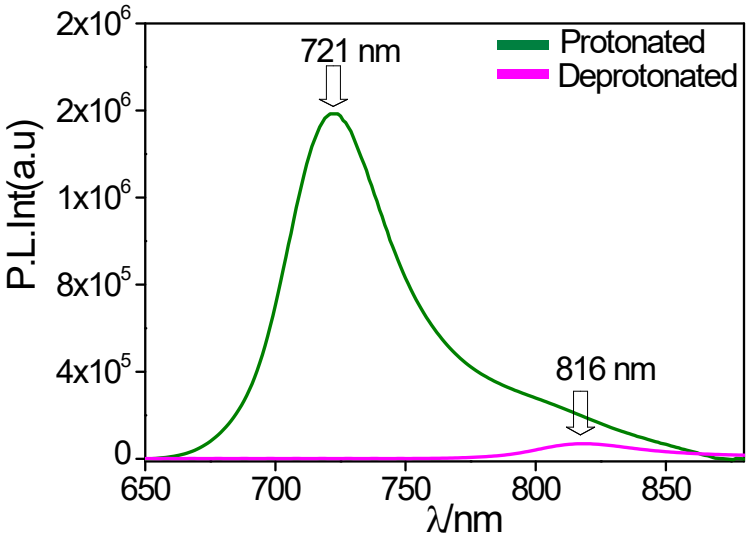

Fig. S9 Luminescence spectra (λ_{ex}=490 nm) of OsOsOs in protonated (**5H$_2$**) and deprotonated (**5**) form at 77 K in EtOH-MeOH (1:4, v/v).

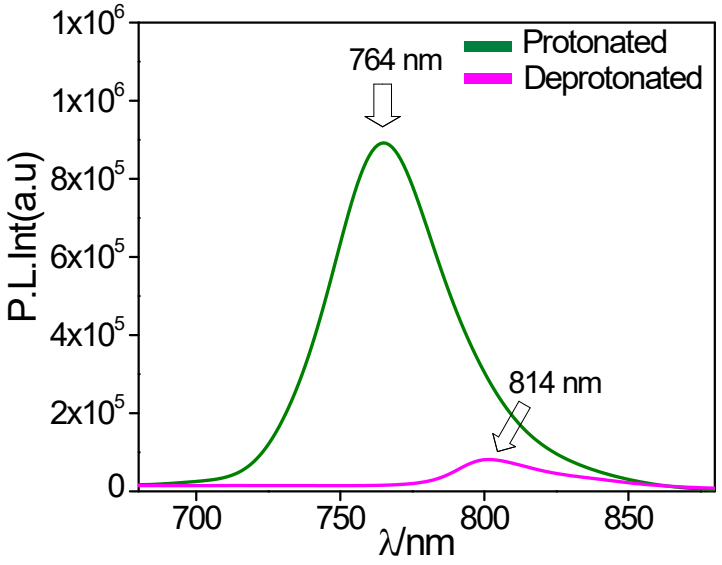

Fig. S10 Luminescence spectrum (λ_{ex}=490 nm) of $[(bpy)_2Os(d\text{-}HIm\text{-}t)]^{2+}$ in its protonated (**2H**) and deprotonated (**2**) form at 77 K in EtOH-MeOH (1:4, v/v).

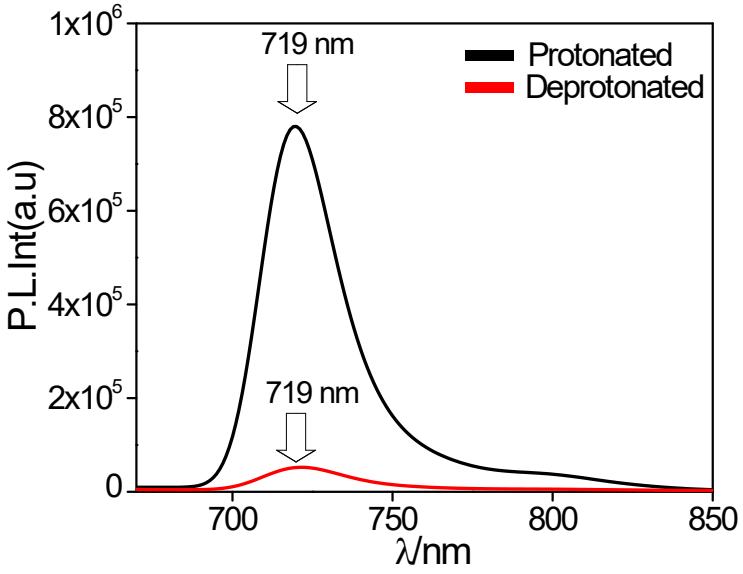

Fig. S11 Luminescence spectrum (λ_{ex}=490 nm) of $[Os(t\text{-}Him\text{-}d)_2]^{2+}$ in its protonated and deprotonated form at 77 K in EtOH-MeOH (1:4, v/v).

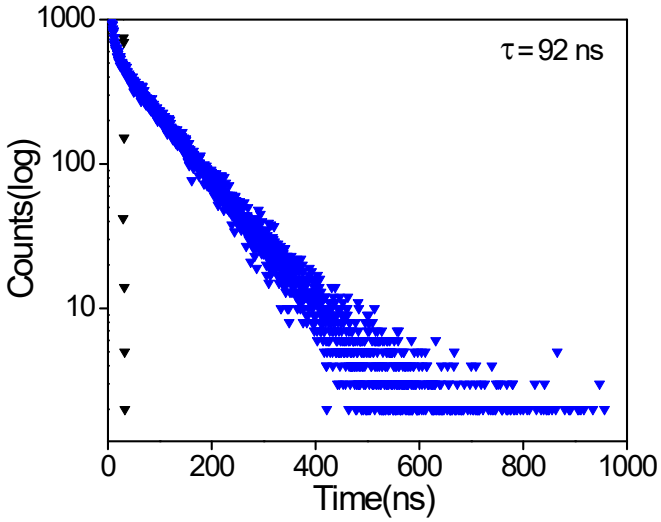

Fig. S12 Luminescence decay of $[Os(t\text{-}Im\text{-}d)_2]$ in acetonitrile-water (1:10 v/v) buffer. The solution is excited with 490 nm light using a nanosecond diode laser and emission decay is monitored at 738 nm.

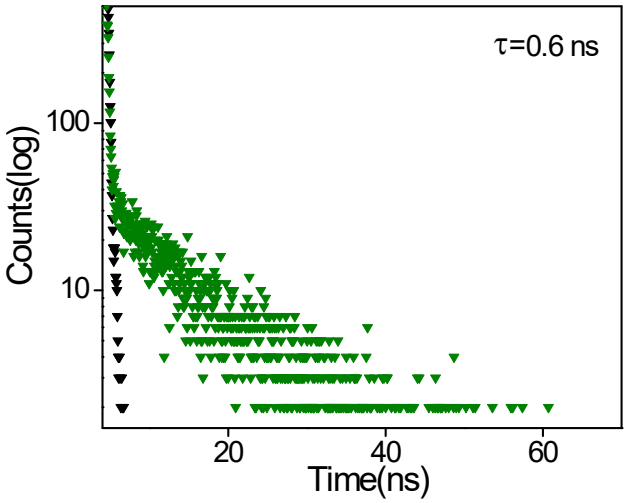

Fig. S13 Luminescence decay of $[(bpy)_2Os(d\text{-}HIm\text{-}t)]$ in acetonitrile-water (1:10 v/v) buffer. The solution is excited with 490 nm light using a nanosecond diode laser and emission decay was monitored at 774 nm.