Electronic supplementary information

pH-responsive colorimetric, emission and redox switches based on Ru(II)-terpyridine complexes

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Physical measurements

UV-vis absorption spectra were of the complexes were recorded with a Shimadzu UV 1800 spectrometer. Steady state luminescence spectra were obtained by a Horiba Fluoromax-4 spectrometer. Luminescence quantum yields were determined by using literature method taking quinine $[Ru(bpy)_3]^{2+}$ as the standard. Luminescence lifetime measurements were carried out by using time–correlated single photon counting set up from Horiba Jobin-Yvon. The 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 (3:2 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.

Electrochemical measurements were carried out 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. In all the experiments, 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.

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficients, 10%; emission maxima, ±5 nm; excited–state lifetimes, 10%; luminescence quantum yields, 20%; pK_a = ± 0.05.

Table S1 Luminescence quantum yield ($\Phi\times10^3$) of the complexes as a function of pH in 3:2 MeCN-H_2O buffer.

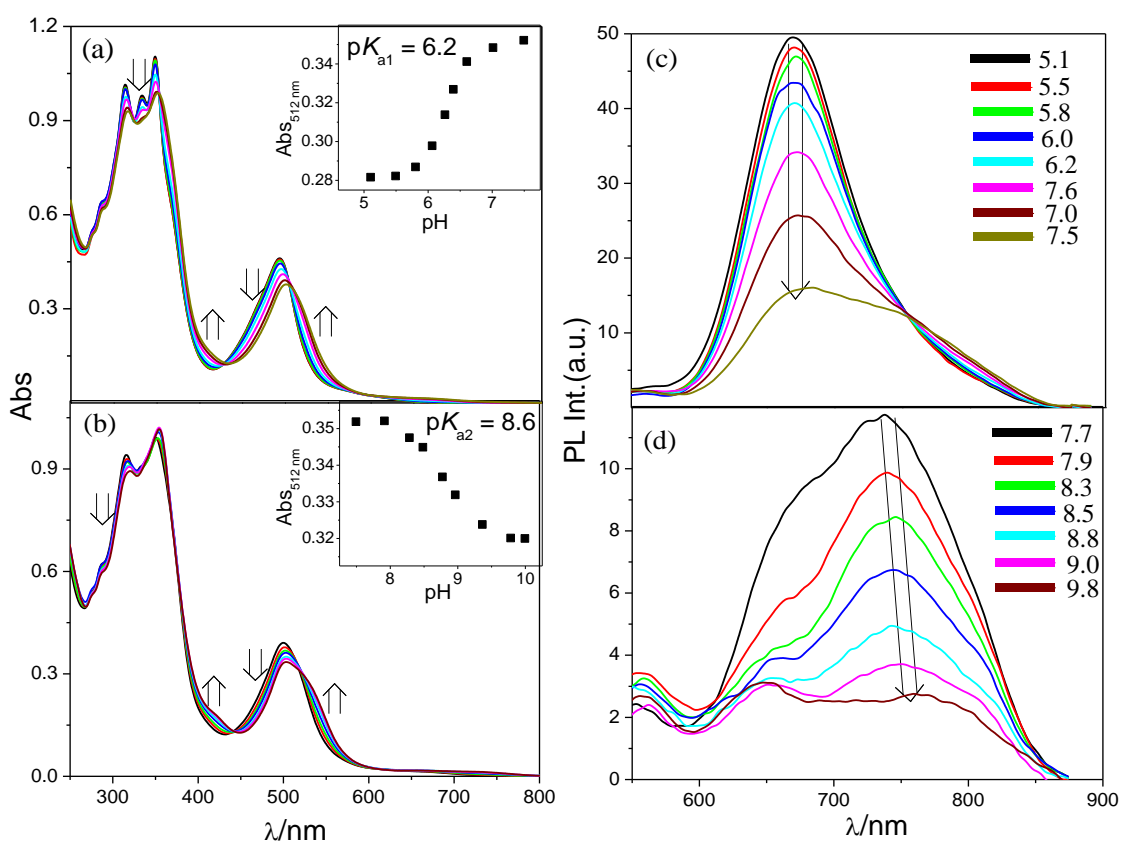| compounds	Luminescence Quantum Yield ($\Phi\times10^3$)		
	Initial	After ^{1st} step change	After ^{2st} step change
1H$_2$	9.72	6.16	1.34
2H$_2$	8.91	4.43	1.25
3H$_2$	10.45	5.45	0.09
4H$_2$	7.36	4.38	0.10
5H$_2$	10.65	8.29	0.09

Fig. S1 Absorption (a,b) and emission (c,d) spectral changes of **2H$_2$** as a function of pH. Inset to figure a and b shows the change of absorbance at 512 nm and corresponding pK_a values, while the inset of figure c and d display pH indication of the curves. Isosbestic points for the first change (a) are at 602, 506, 430, and 353 nm, while for the second step change (b) are 620, 520, 444 and 342 nm. Isoemissive point associated with first step emission spectral change (c) is observed at 754 nm.
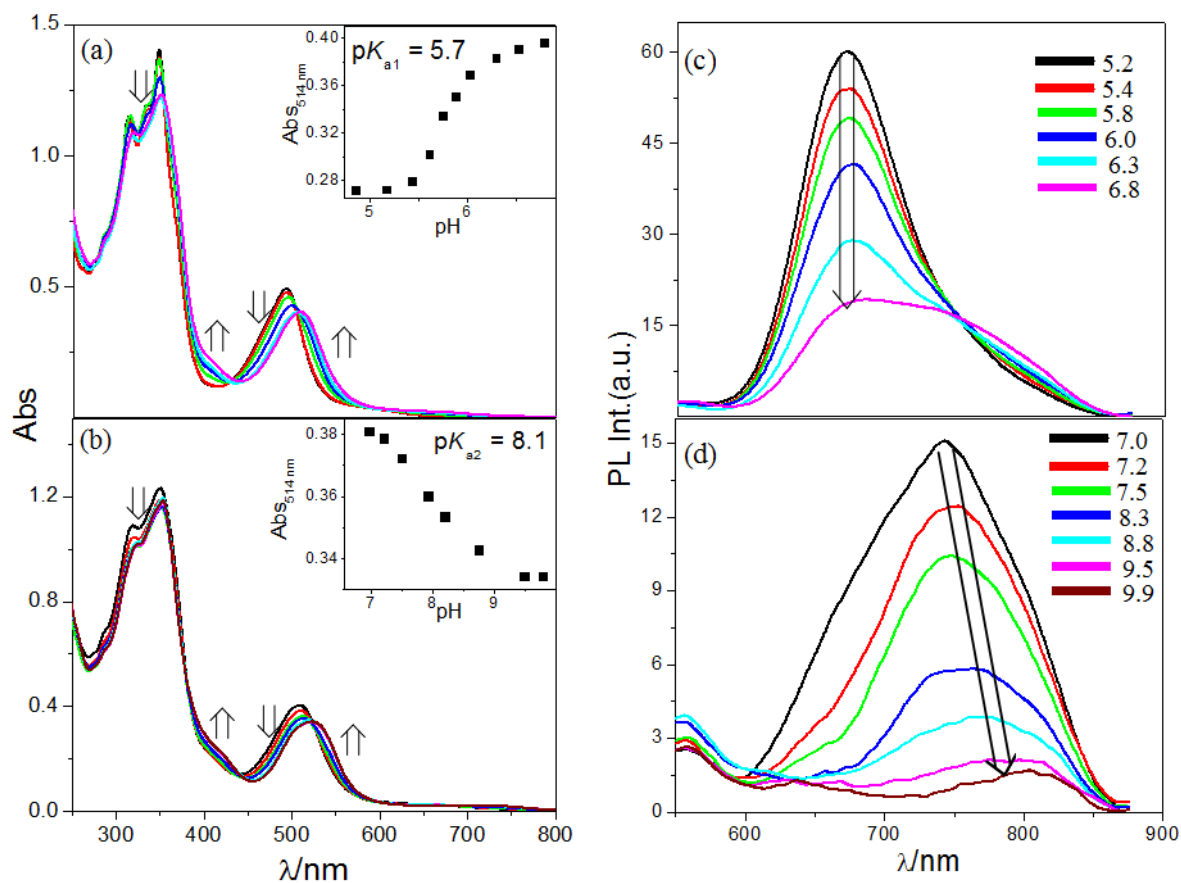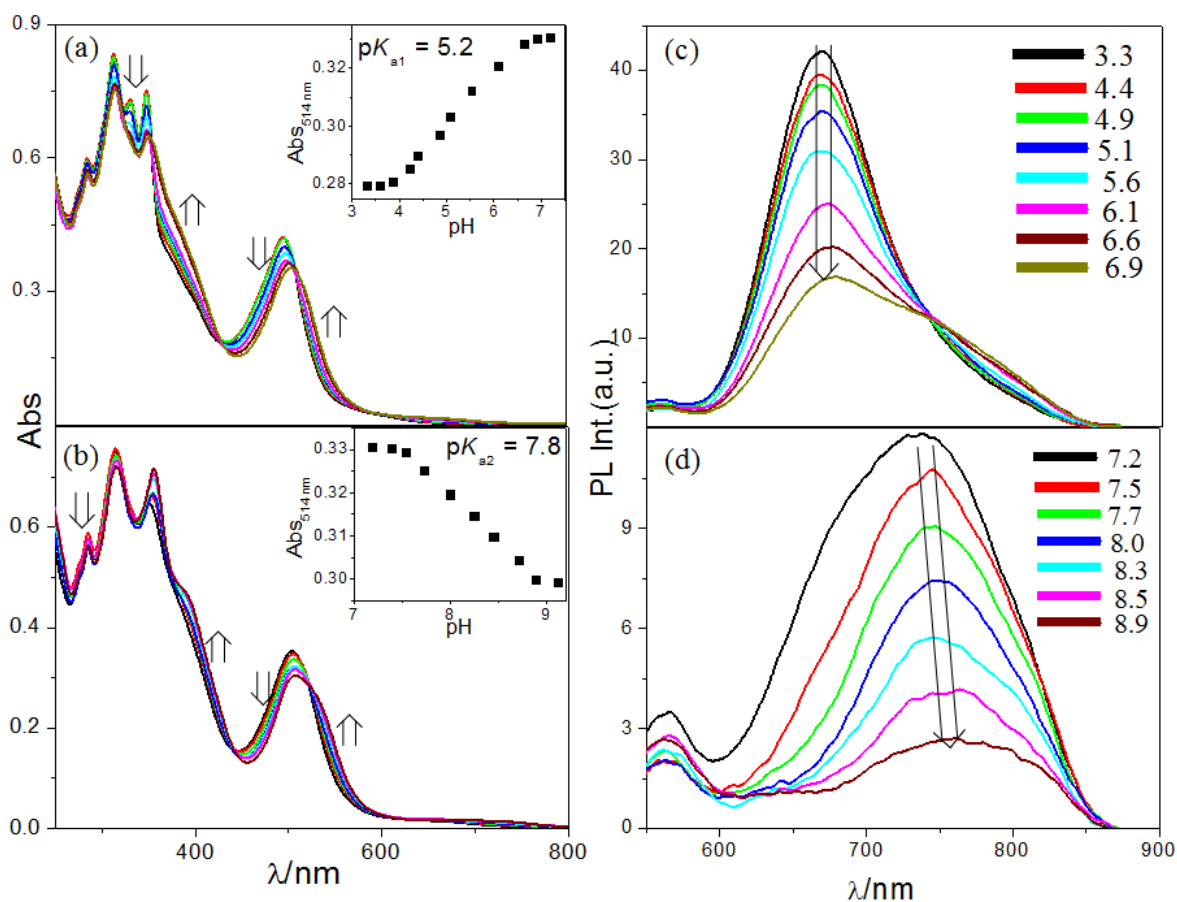
Fig. S2 Absorption (a,b) and emission (c,d) spectral changes of **3H₂** as a function of pH. Inset to figure a and b shows the change of absorbance at 514 nm and corresponding pK_a values, while the inset of figure c and d display pH indication of the curves. Isosbestic points for the first change (a) are at 507, 430 and 355 nm, while for the second step change (b) are 524, 442 and 380 nm. Isoemissive point associated with first step emission spectral change (c) is observed at 753 nm.
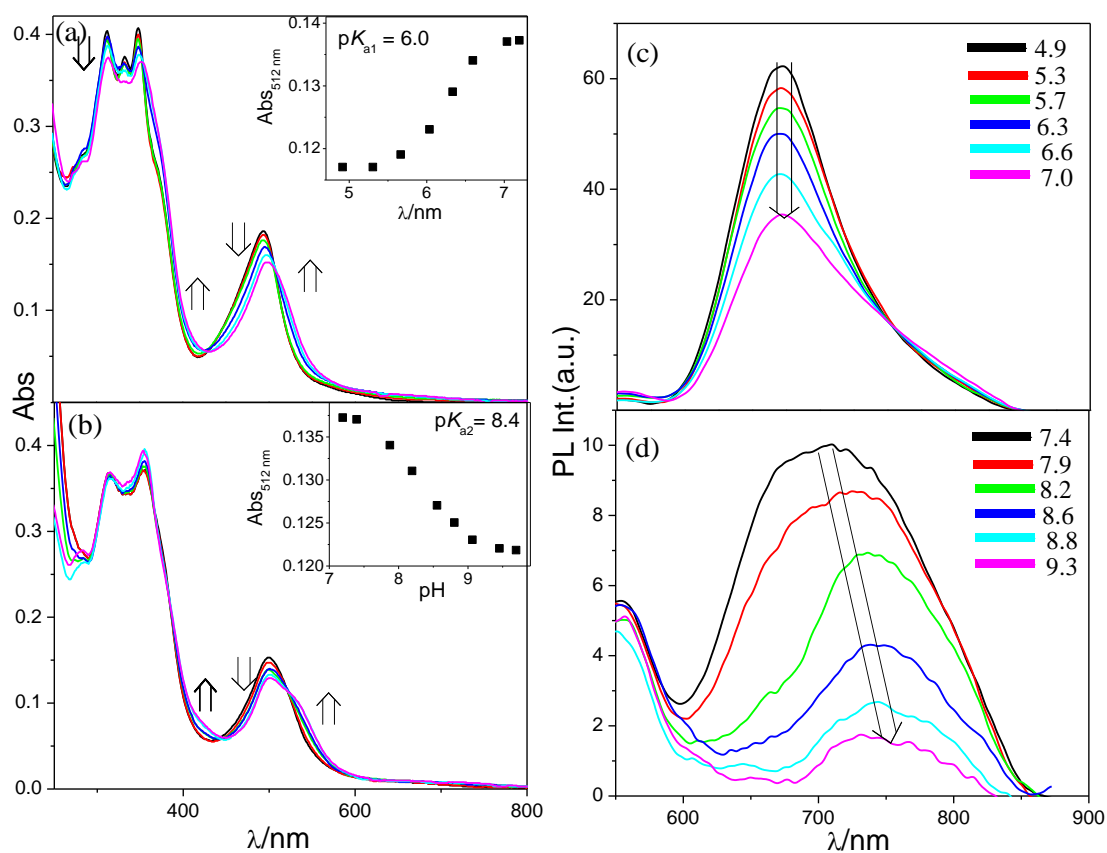
Fig. S3 Absorption (a,b) and emission (c,d) spectral changes of **4H₂** as a function of pH. Inset to figure a and b shows the change of absorbance at 514 nm and corresponding pK_a values, while the inset of figure c and d display pH indication of the curves. Isosbestic points for the first change (a) are at 508, 430 and 354 nm, while for the second step change (b) are 523, 443 and 327 nm. Isoemissive point associated with first step emission spectral change (c) is observed at 744 nm.

Fig. S4 Absorption (a,b) and emission (c,d) spectral changes of **5H$_2$** as a function of pH. Inset to figure a and b shows the change of absorbance at 512 nm and corresponding pK_a values, while the inset of figure c and d display pH indication of the curves. Isosbestic points for the first change (a) are at 507, 430 and 355 nm, while for the second step change (b) are 521, 443 and 384 nm. Isoemissive point associated with first step emission spectral change (c) is observed at 755 nm.
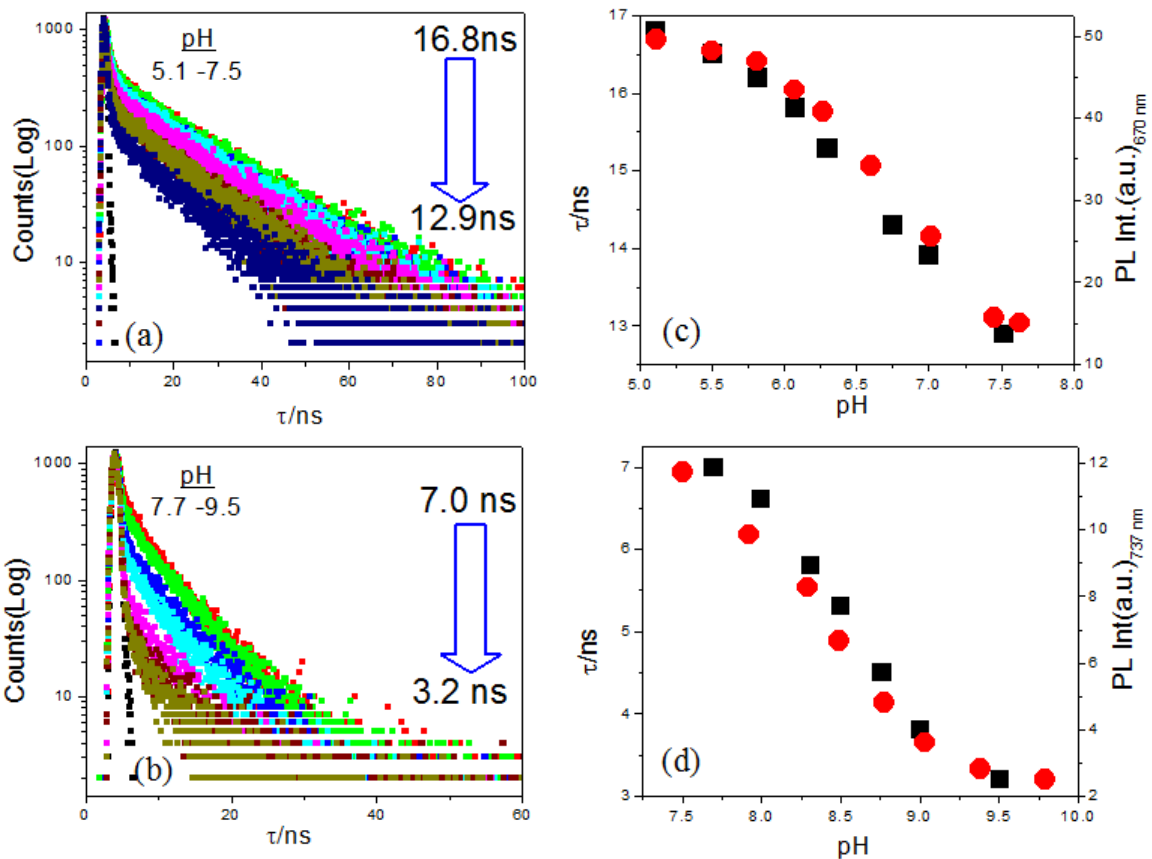
Fig. S5 Parts a and b display the change of luminescence decay profile of **2H₂** with the variation of pH in 3:2 MeCN-H₂O buffer. Parts c and d show the corresponding change in emission intensity (red circle) and excited state lifetimes (black squares) as a function of pH.
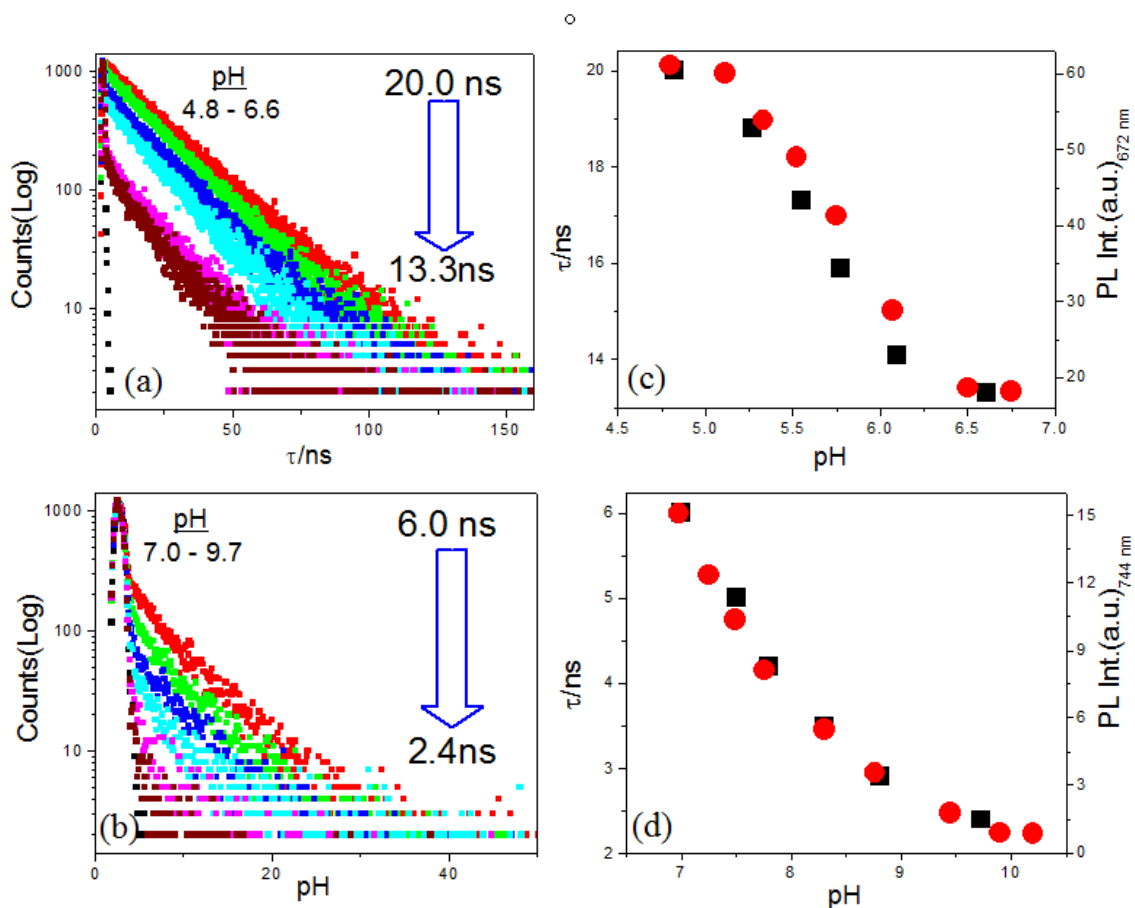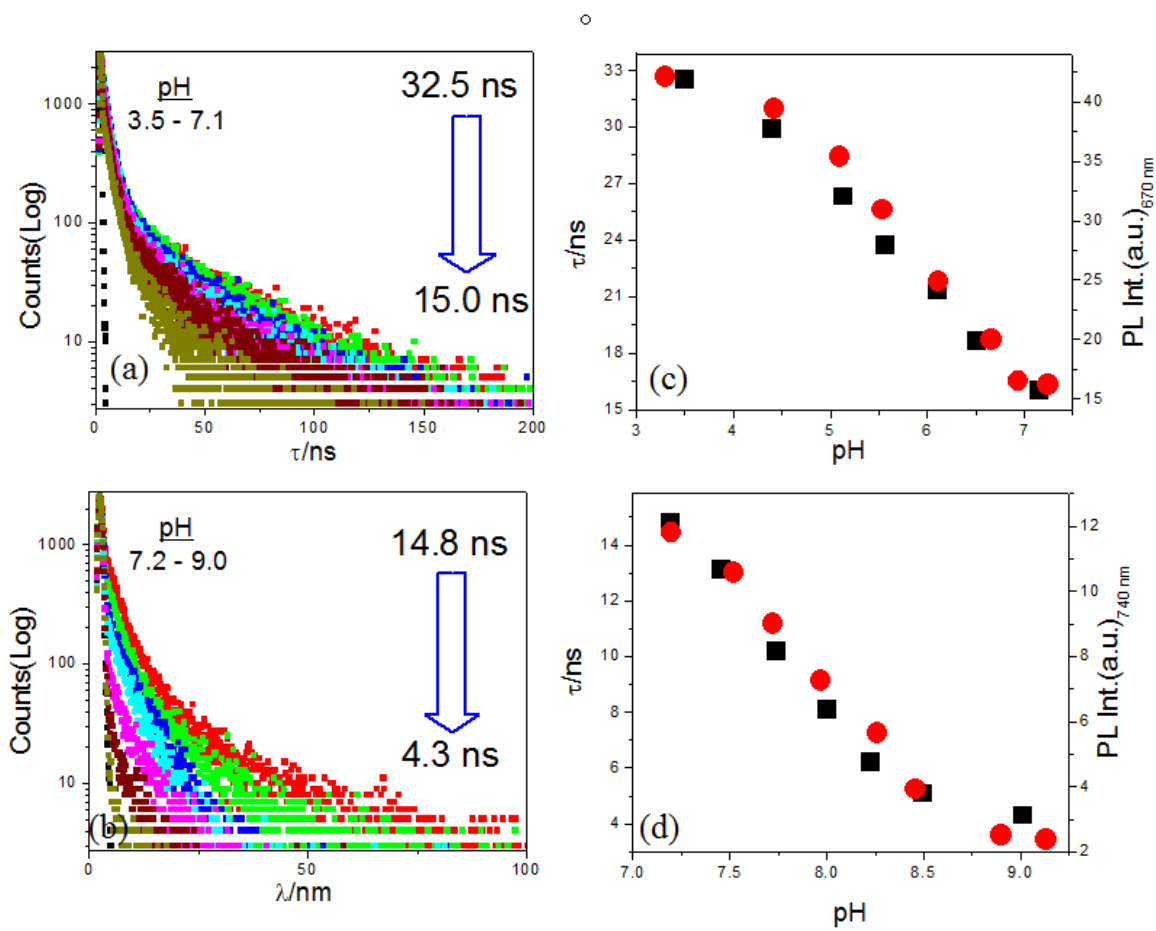
Fig. S6 Parts a and b display the change of luminescence decay profile of **3H₂** with the variation of pH in 3:2 MeCN-H₂O buffer. Parts c and d show the corresponding change in emission intensity (red circle) and excited state lifetimes (black squares) as a function of pH.

Fig. S7 Parts a and b display the change of luminescence decay profile of **4H₂** with the variation of pH in 3:2 MeCN-H₂O buffer. Parts c and d show the corresponding change in emission intensity (red circle) and excited state lifetimes (black squares) as a function of pH.
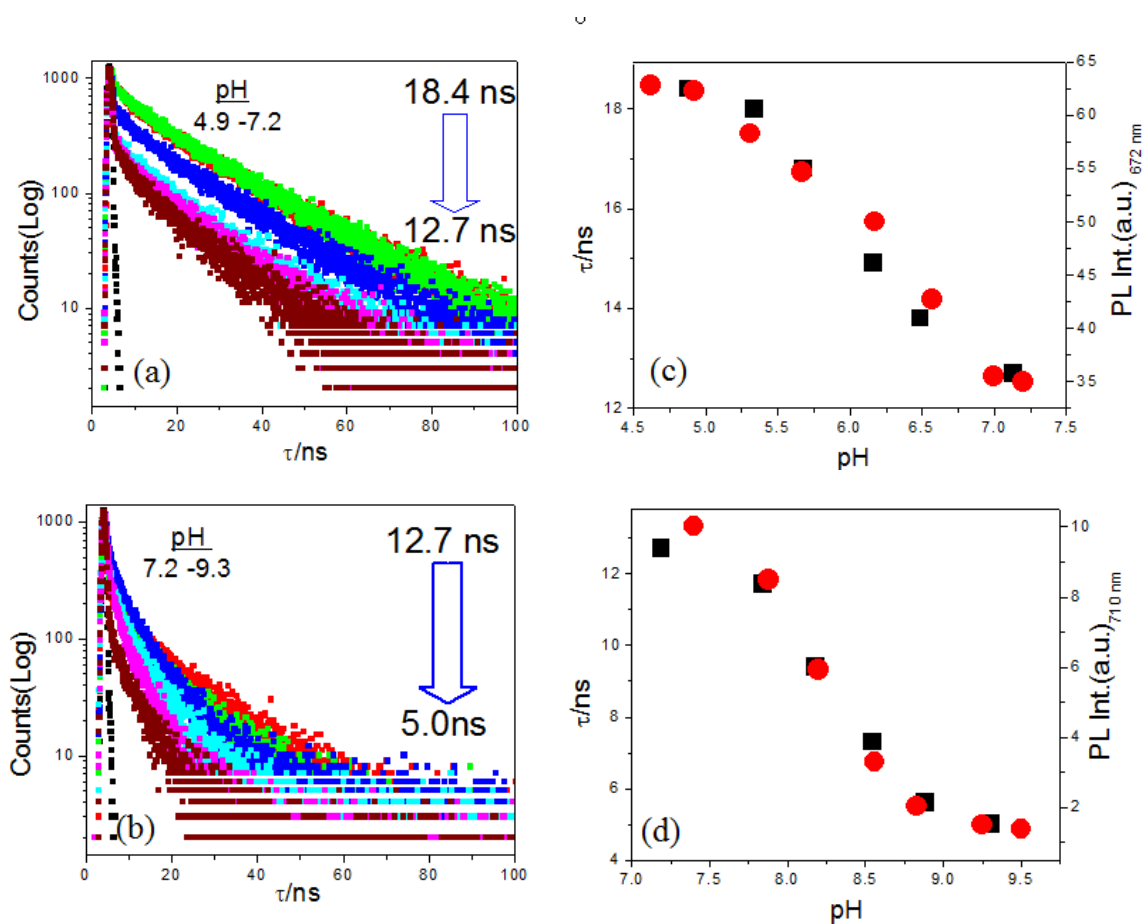
Fig. S8 Parts a and b display the change of luminescence decay profile of **5H₂** with the variation of pH in 3:2 MeCN-H₂O buffer. Parts c and d show the corresponding change in emission intensity (red circle) and excited state lifetimes (black squares) as a function of pH.
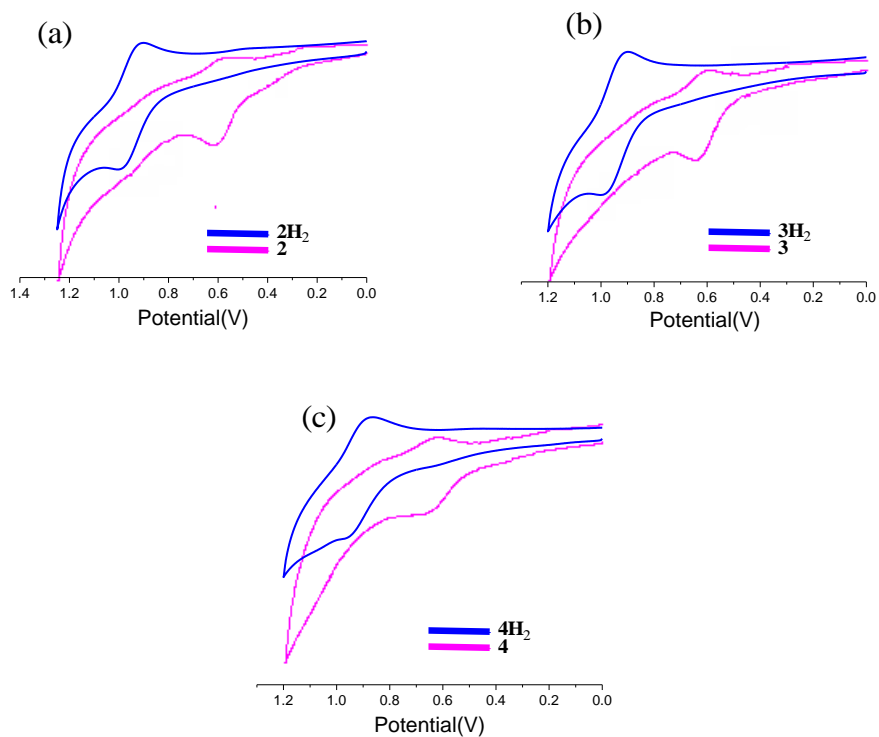
Fig. S9 Cyclic voltammograms of (a) [(H$_2$pbbzim)Ru(tpy-pvp-Me)]$^{2+}$ (blue) and [(pbbzim)Ru(tpy-pvp-Me)](pink), (b) [(H$_2$pbbzim)Ru(tpy-pvp-Cl)]$^{2+}$(blue) and [(pbbzim)Ru(tpy-pvp-Cl)](pink), (c) [(H$_2$pbbzim)Ru(tpy-pvp-NO$_2$)]$^{2+}$ (blue) and [(pbbzim)Ru(tpy-pvp-NO$_2$)] (pink), showing the oxidation in acetonitrile-water (3:2) at room temperature using platinum as the working electrode and Ag/AgCl as the reference electrode.
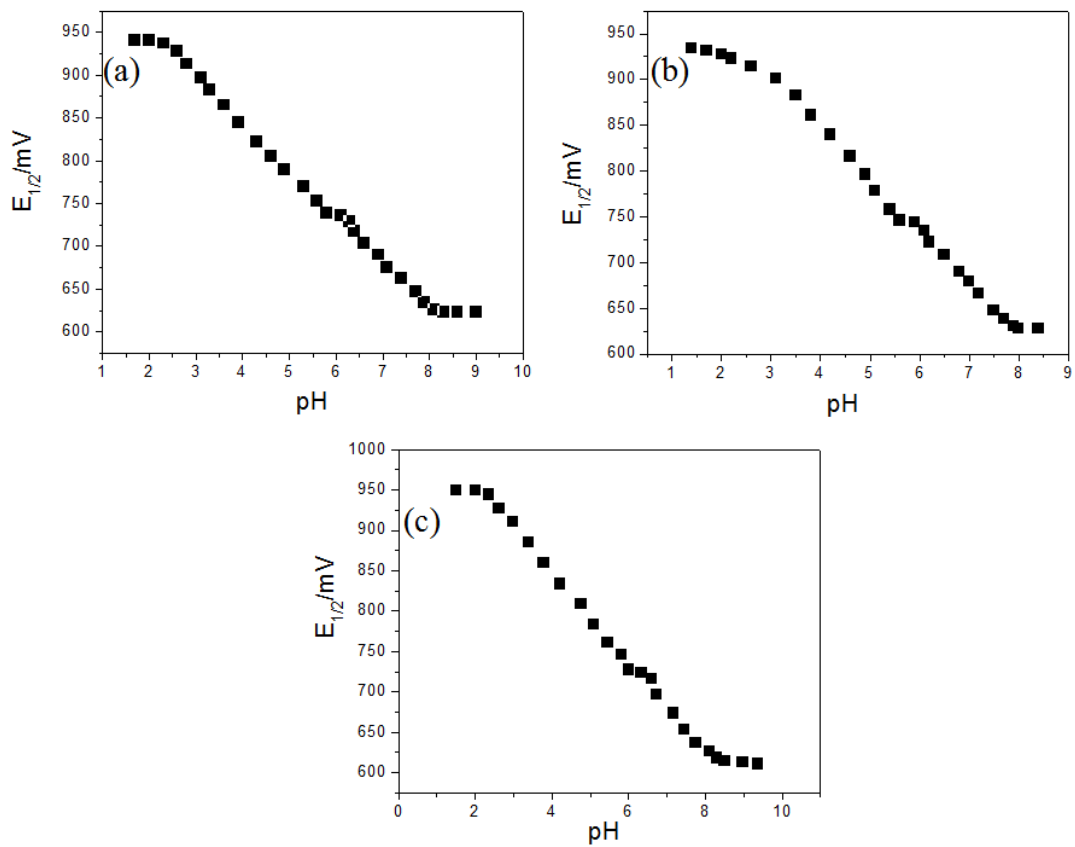
Fig. S10 $E_{1/2}$ vs. pH plot for (a)$[(H_2pbbzim)Ru(tpy\text{-}pvp\text{-}H)]^{2+}$, (b) $[(H_2pbbzim)Ru(tpy\text{-}pvp\text{-}Cl)]^{2+}$ and $[(H_2pbbzim)Ru(tpy\text{-}pvp\text{-}Ph)]^{2+}$ in MeCN-H_2O (3 : 2 v/v).