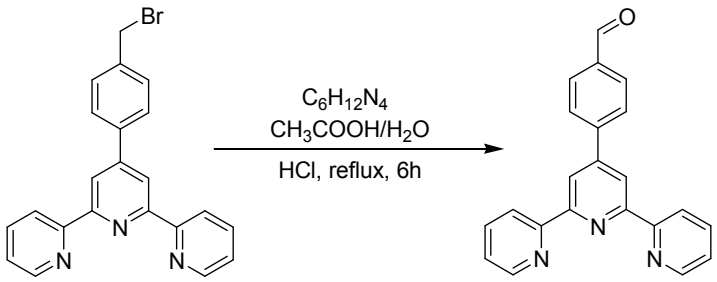
Electronic Supplementary Material (ESI) for RSC Advances.



Scheme S1. Synthesis of 4′-(*p*-formylphenyl)-2,2′:6′,2″-terpyridine.

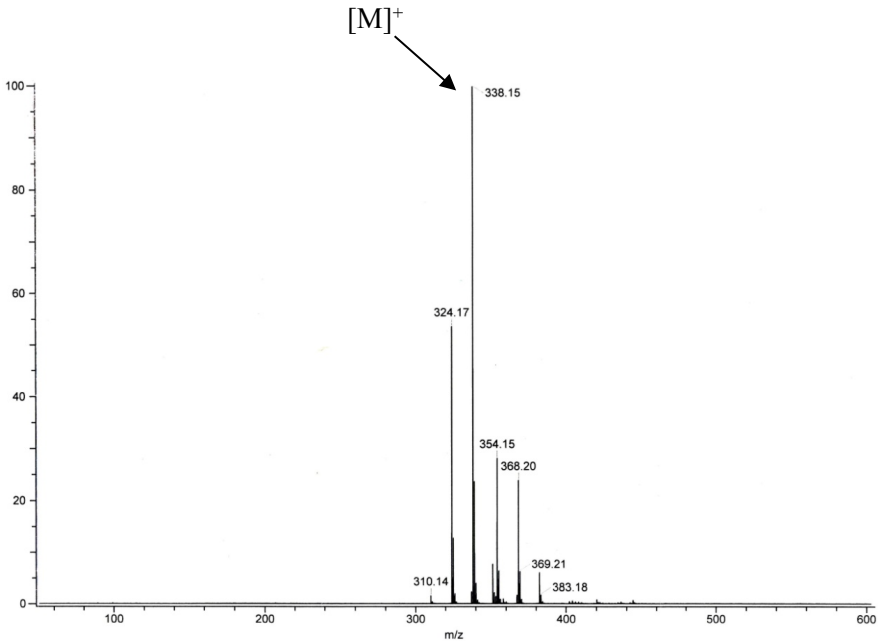


Figure S1. ESI Mass spectrum 4′-(*p*-formylphenyl)-2,2′:6′,2″-terpyridine.

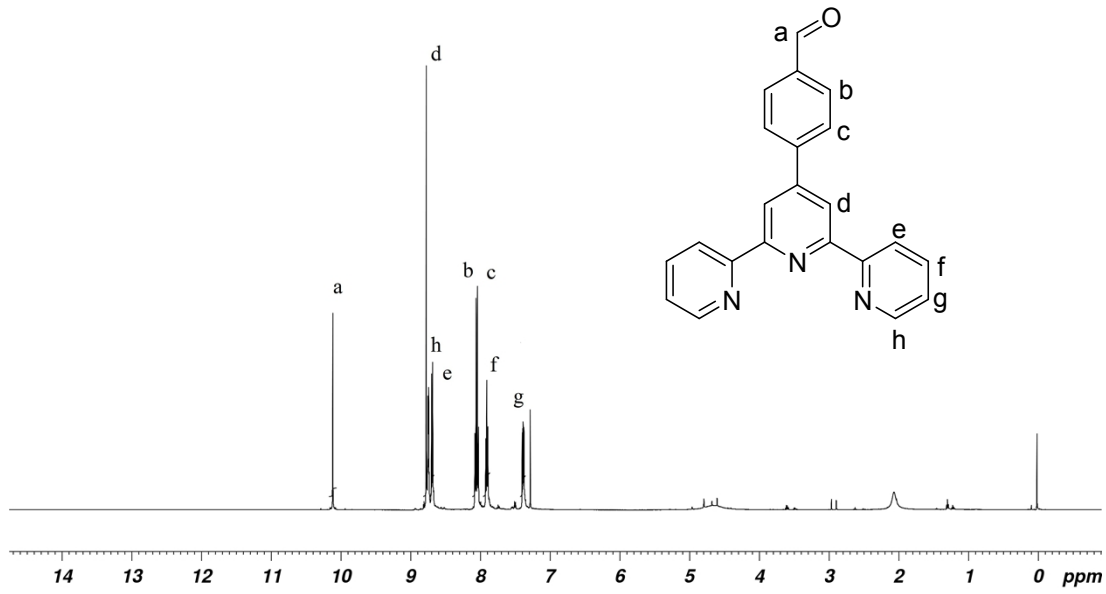
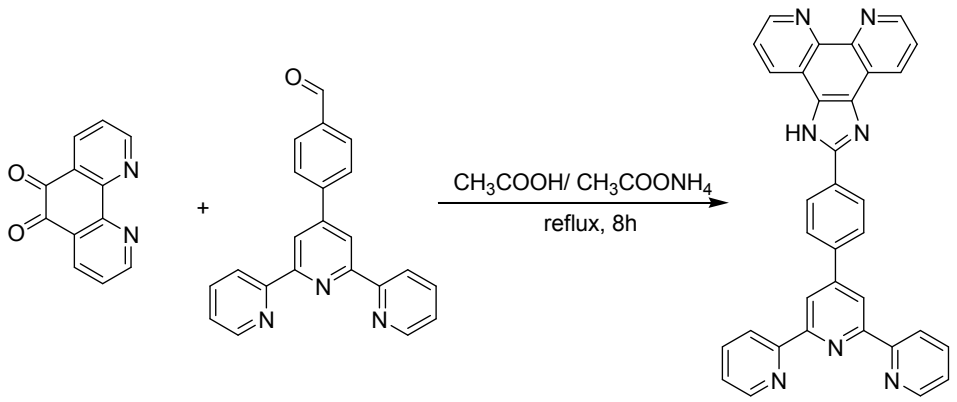


Figure S2. ^{1}H NMR spectrum of 4′-(*p*-formylphenyl)-2,2′:6′,2″-terpyridine in $CDCl_3$.



Scheme S2. Synthesis of 2-(4-(2,6-di(pyridin-2-yl)pyridin-4-yl)phenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (ttpy-Izphen).

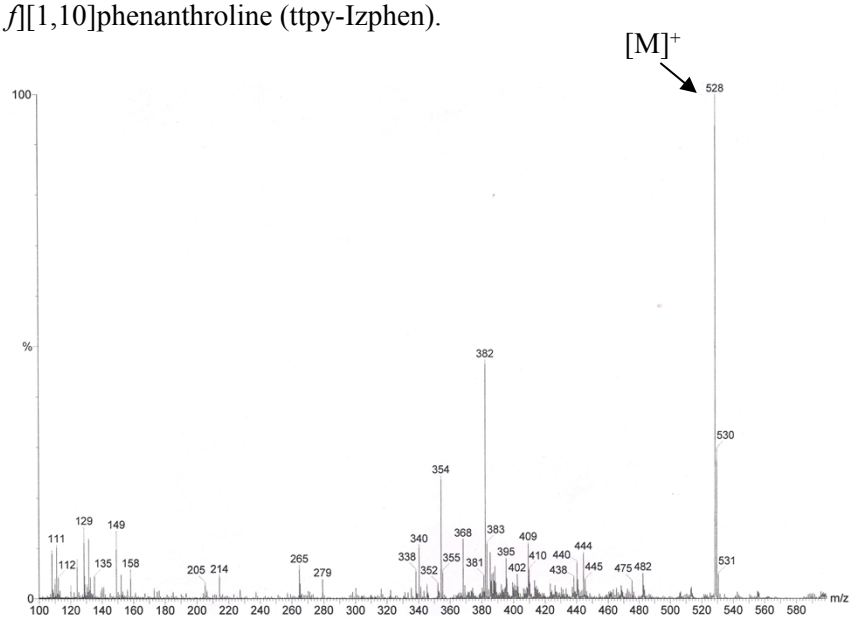


Figure S3. ESI Mass spectrum of ttpy-Izphen.

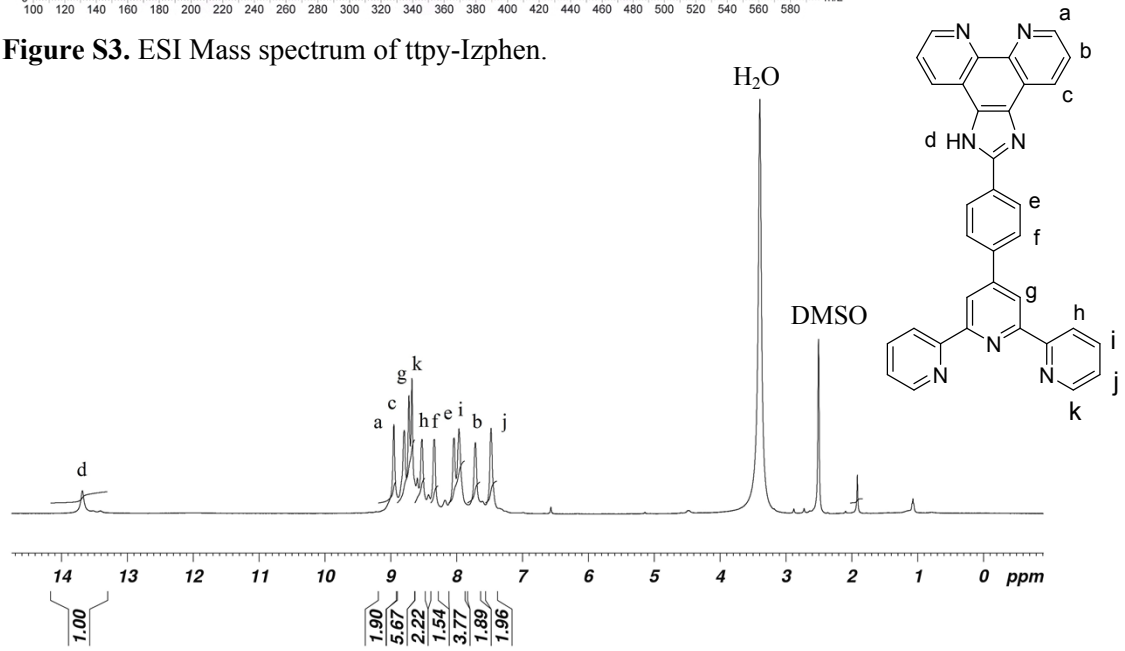


Figure S4. ^{1}H NMR spectrum of ttpy-Izphen in DMSO-d_6.

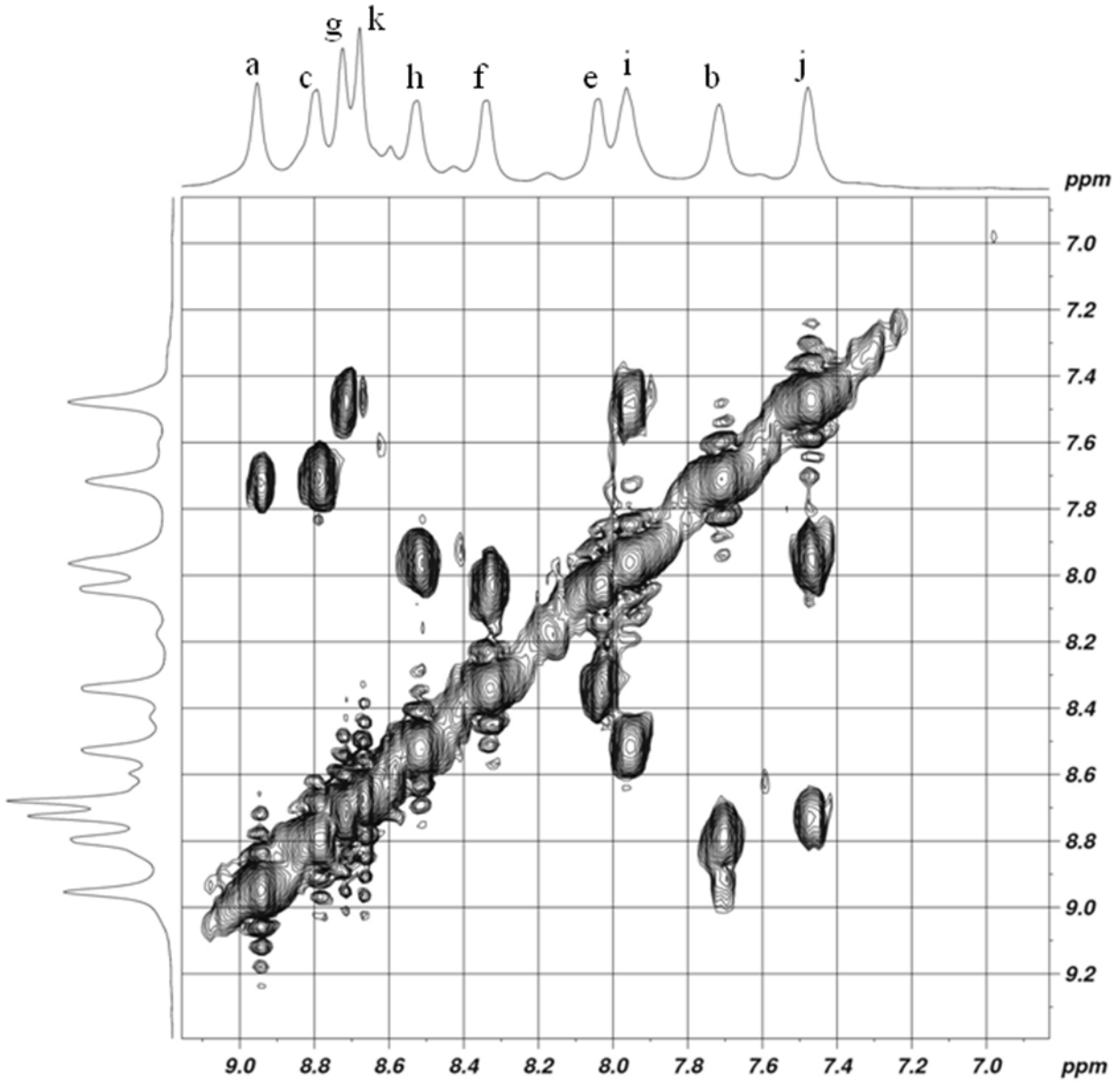
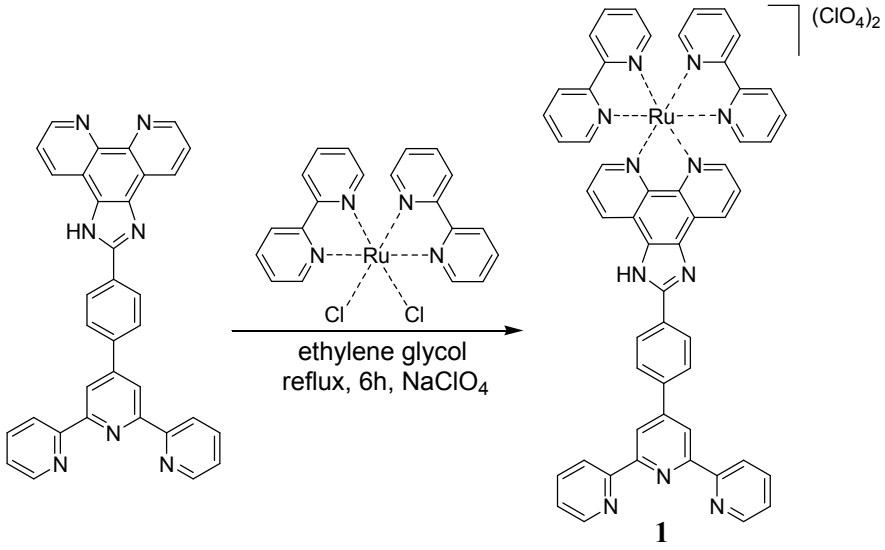


Figure S5. ^{1}H-^{1}H COSY spectrum of ttpy-Izphen.

[(ttpy-Izphen)Ru(bpy)$_2$](ClO$_4$)$_2$ (1). A solution of the ttpy-Izphen (0.92 g, 1.76 mmol) and [Ru(bpy)$_2$Cl$_2$] (0.84 g, 1.76 mmol) in ethylene glycol (50 mL) was refluxed with stirring for 6 h. The dark red solution was cooled to room temperature, water (500 mL) was added, and filtered. An aqueous solution of sodium perchlorate was added to the filtrate with stirring whereupon a black solid separated out. The compound was filtered, washed with water, dried in vacuo and recrystallised in hot acetonitrile. Black crystalline solid (0.90 g, 44%). IR (KBr, ν_{max}/cm^{-1}): 3391 ν_s(N-H), 3067 ν_s(C-H) (aromatic), 1601 ν_s(C=N), 1443 ν_s(C-H) (pyridine), 1087 ν(ClO$_4$), 794 (β-ring) (pyridine). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 8.88 (dd, 4H, J = 8.5, 8.5, H_4, $H_{4'}$), 8.76 (d, 2H, H_c), 8.70 (d, 2H, H_g), 8.51 (d, 2H, J = 7.5, H_h), 8.38 (d, J = 7, 2H, H_f), 8.23 (t, J = 8, 7, 4H, H_3), 8.14 (t, J = 7.5, 8, 2H, $H_{3'}$), 8.10 (d, 2H, H_a), 8.07 (d, 2H, H_e), 7.88 (m, 6H, H_i, H_k, H_1), 7.62 (t, 4H, $H_{1'}$, H_2), 7.46 (m, 6H, H_b, H_j, $H_{2'}$). ESI MS: *m/z* 470 [M-2ClO$_4$]$^{2+}$ ($C_{54}H_{37}N_{11}Ru$)$^{2+}$.



Scheme S3. Synthesis of [(ttpy-Izphen)Ru(bpy)$_2$](ClO$_4$)$_2$ (**1**).

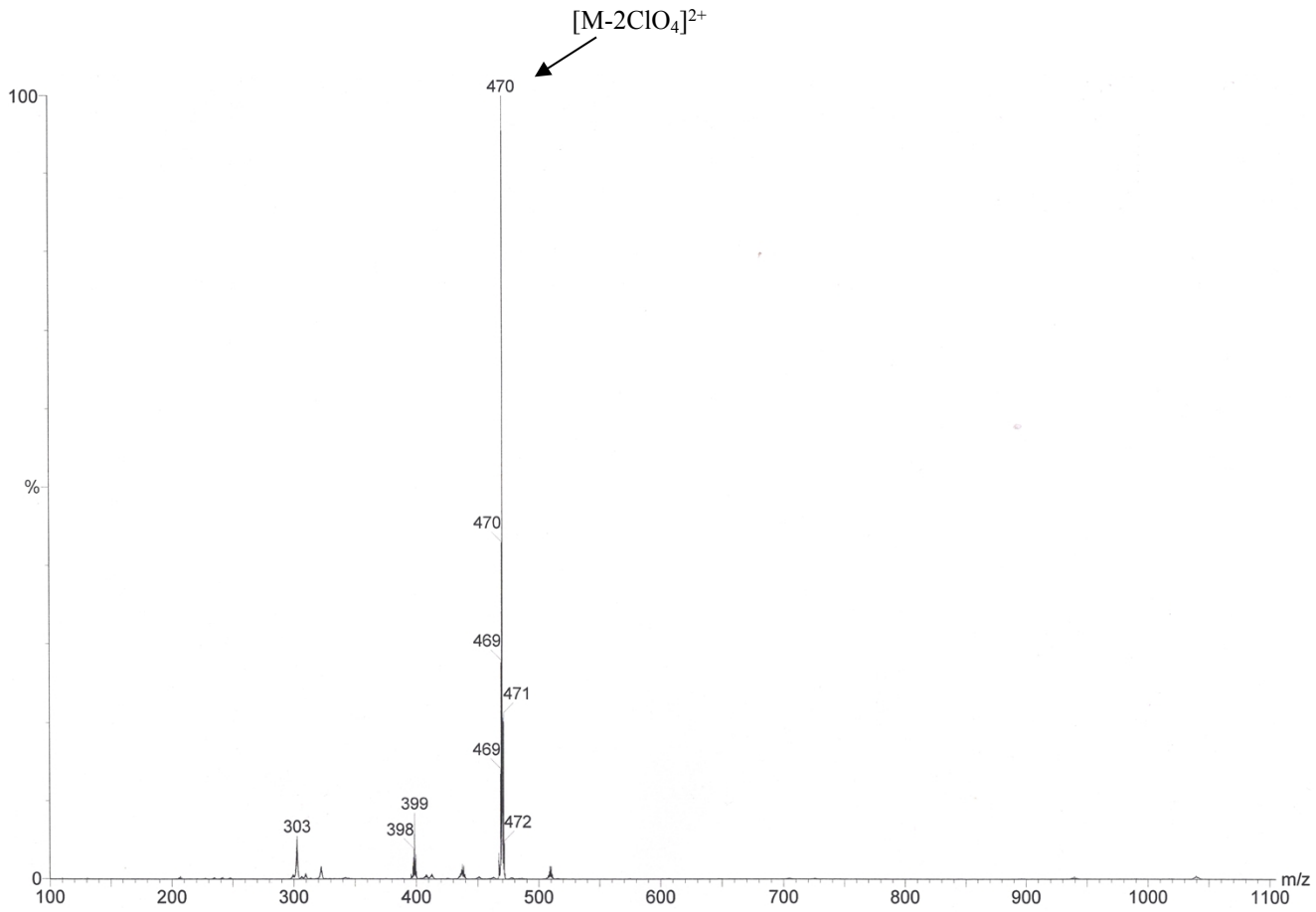


Figure S6. ESI Mass spectrum of **1**.

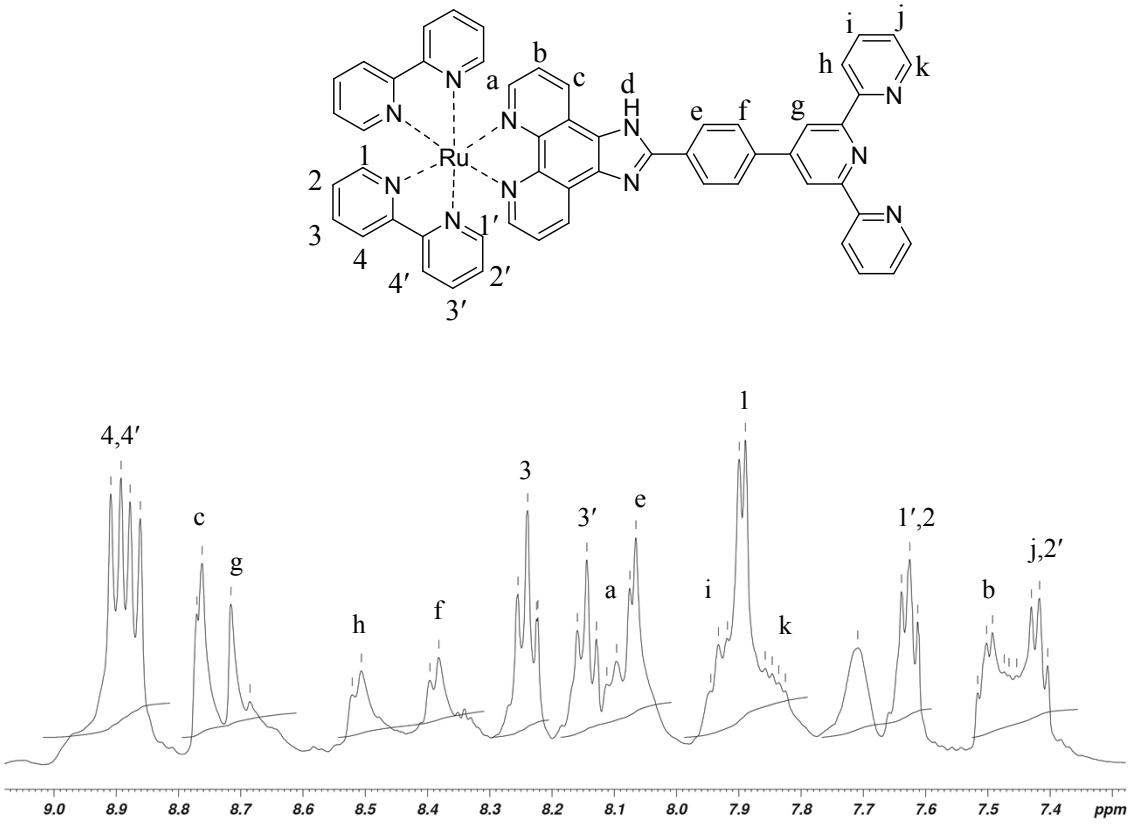


Figure S7. ^{1}H NMR spectrum of **1** in DMSO-d_6.

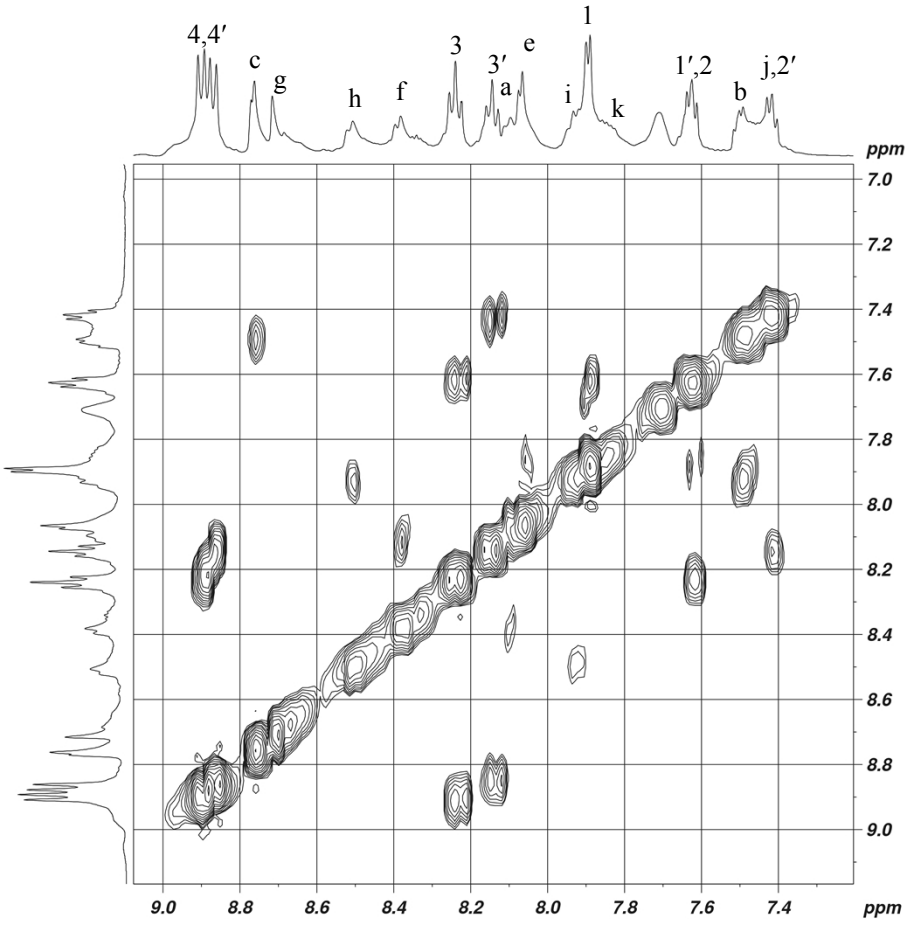
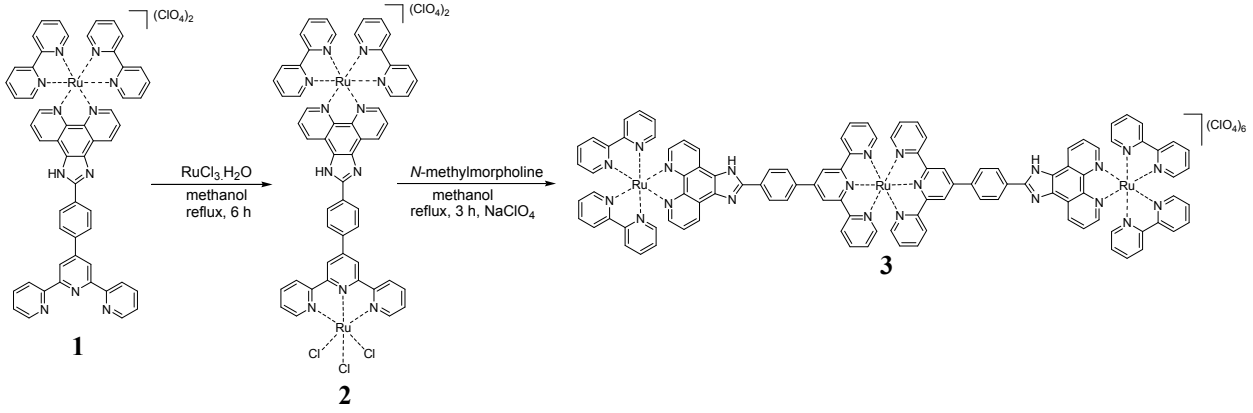


Figure S8. ^{1}H-^{1}H COSY spectrum of **1**.

[Ru((ttpy-Izphen)Ru(bpy)$_2$)$_2$](ClO$_4$)$_6$ (3). A solution of **1** (0.20 g, 0.16 mmol) and $RuCl_3.H_2O$ (0.04 g, 0.18 mmol) in methanol (100 mL) was refluxed for 6 h. The reaction mixture was cooled to room temperature, and the red solid that separated out was filtered, washed with water and dried in vacuo to give **2** as a red powder (0.14 g, 58%). A solution of **2** (0.14 g, 0.10 mmol) and **1** (0.12 g, 0.10 mmol) in methanol (100 mL) was refluxed and stirred in the presence of few drops of *N*-methyl morpholine under argon atmosphere for 3 h. The dark red solution was cooled to room temperature and filtered. An aqueous solution of sodium perchlorate was added to the filtrate with stirring whereupon a black solid separated out. The compound was filtered, washed with water, dried in vacuo and recrystallised in hot CH_3CN. Black crystalline solid (0.24 g, 84%). IR (KBr, ν_{max}/cm^{-1}): 3403 ν_s(N-H), 3067, 2926 ν_s(C-H) (aromatic), 1606 ν(C=N), 1408 ν_s(C-H) (pyridine), 1087 $\nu(ClO_4)$, 763 (β-ring) (pyridine), 627 (C-C) (ring). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.63 (s, 2H, H_g), 9.19 (d, 2H, H_h), 8.92-8.75 (br, 8H, H_c, H_f, H_4, $H_{4'}$), 8.25 (t, 2H, H_3), 8.14-8.08 (br, 6H, H_i, H_k, $H_{3'}$), 7.97 (br, 2H, H_a, H_e), 7.88 (nr, 2H, H_1), 7.67-7.62 (br, 6H, H_b, $H_{1'}$, H_2), 7.40 (t, 2H, H_j), 7.34 (t, 2H, $H_{2'}$). ESI MS: *m/z* 694 $[M\text{-}5ClO_4]^{3+}$ $(C_{108}H_{74}N_{22}ClO_4Ru_3)^{3+}$, 495 $[M\text{-}6ClO_4]^{4+}$ $(C_{108}H_{74}N_{22}Ru_3)^{4+}$, 397 $[M\text{-}6ClO_4]^{5+}$ $(C_{108}H_{74}N_{22}Ru_3)^{5+}$, 331 $[M\text{-}6ClO_4]^{6+}$ $(C_{108}H_{74}N_{22}Ru_3)^{6+}$.



Scheme S4. Synthesis of [Ru((ttpy-Izphen)Ru(bpy)$_2$)$_2$](ClO$_4$)$_6$ (**3**).

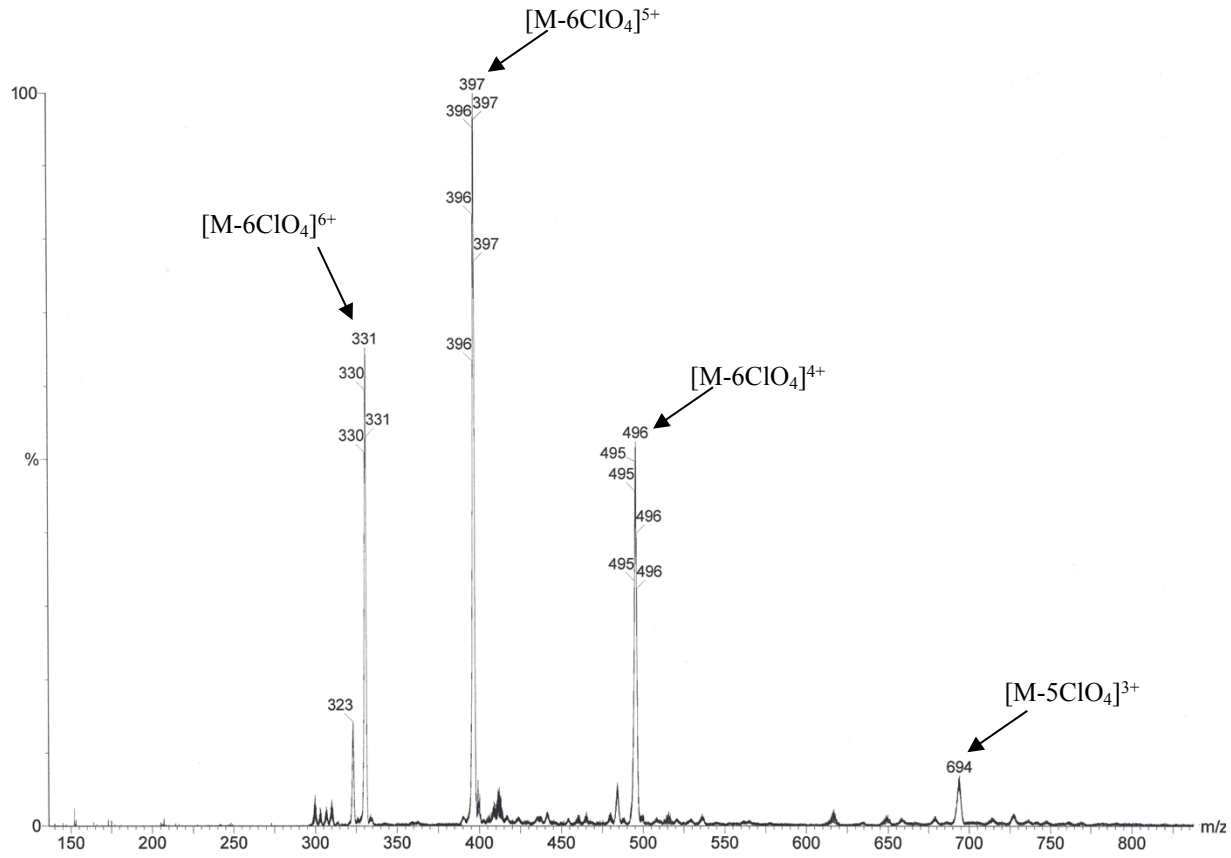


Figure S9. ESI Mass spectrum of **3**.

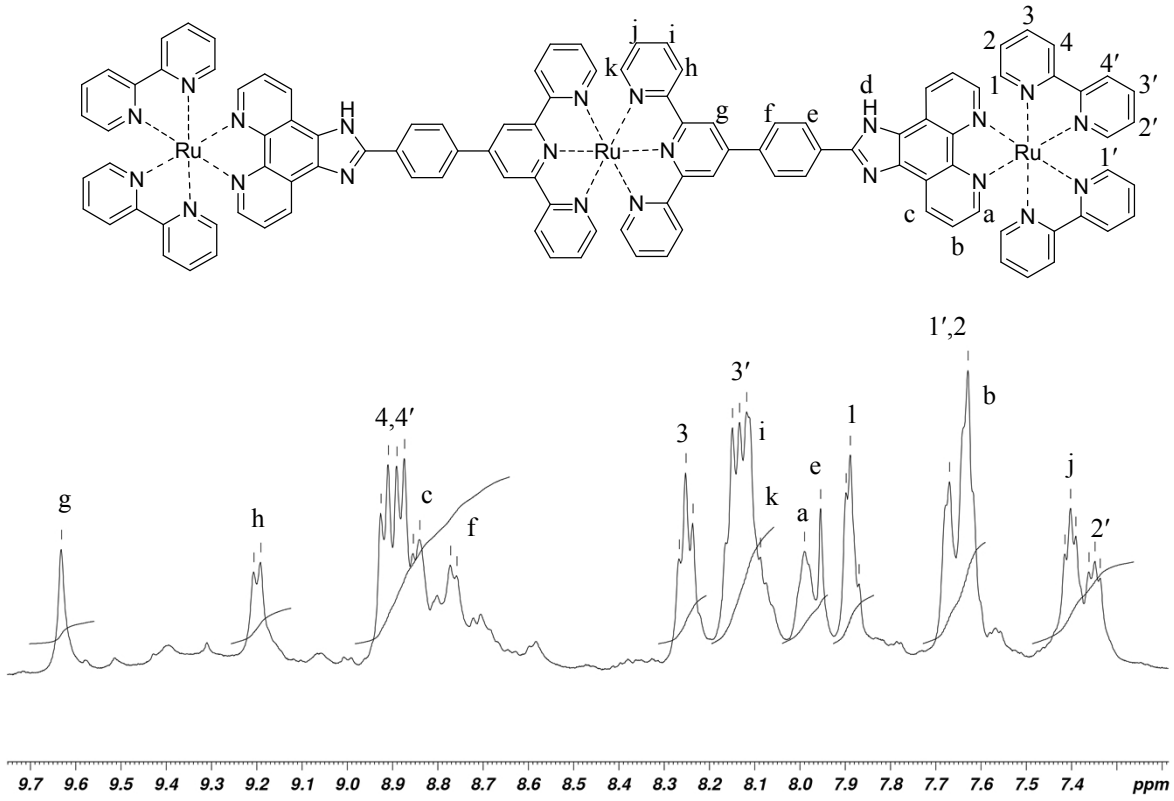


Figure S10. ^{1}H NMR spectrum of **3** in DMSO-d_6.

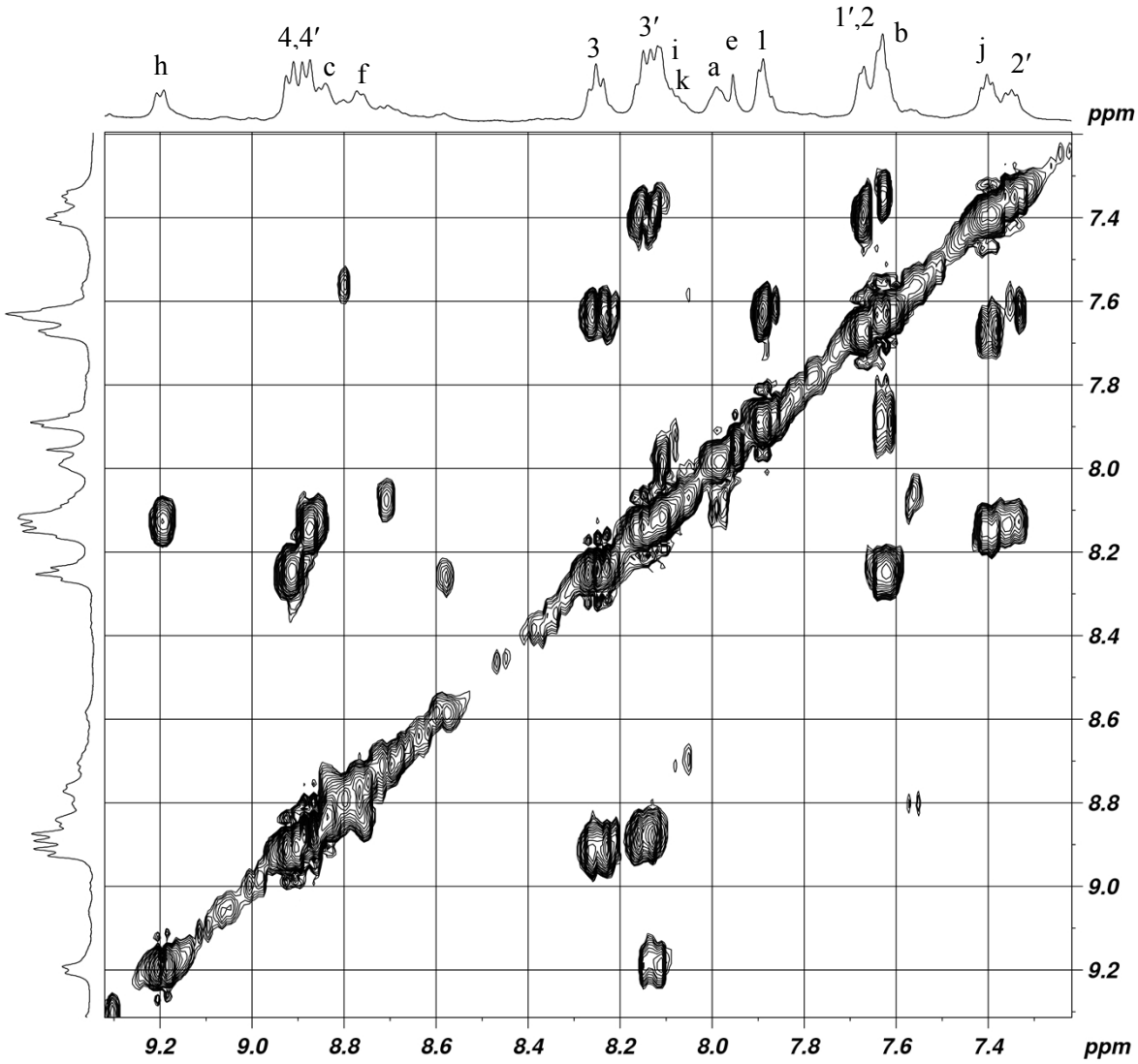


Figure S11. ^{1}H-^{1}H COSY spectrum of **3**.

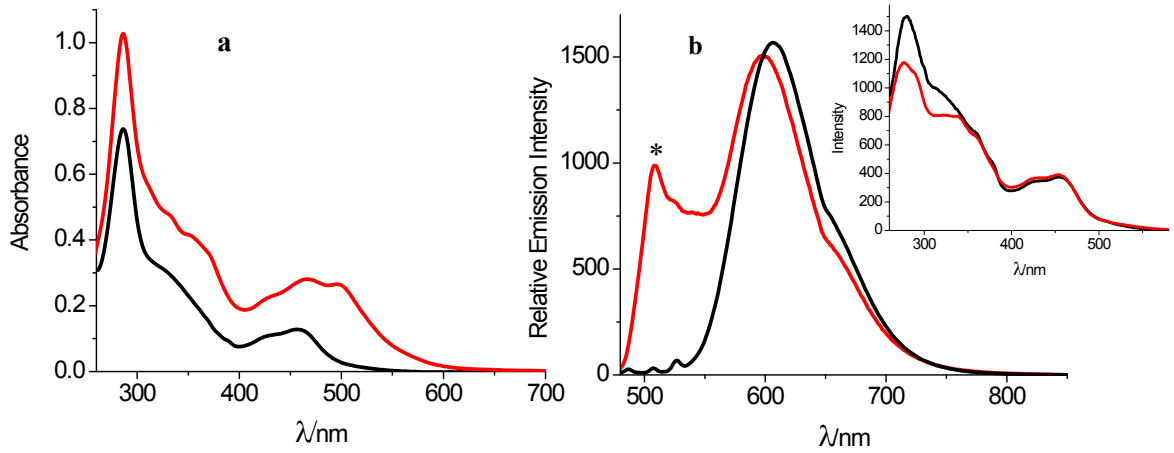


Figure S12. (**a**) The absorption spectrum of **1** (black) and **3** (red). (**b**) Emission spectrum of **1** and **3** in CH_3CN at 298 K (* denotes the Raman peak of CH_3CN); inset: excitation spectrum.

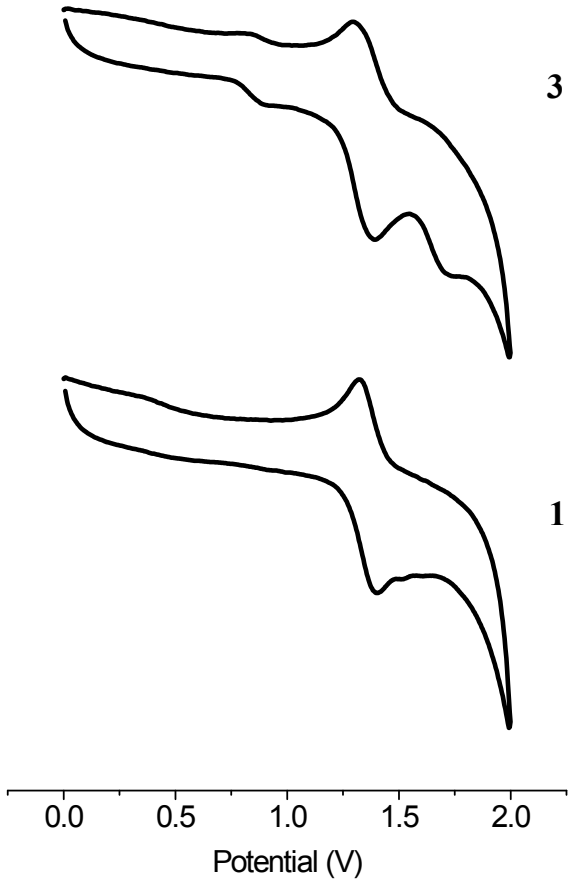


Figure S13. Cyclic voltammogram of **1** (bottom) and **3** (top) on a glassy carbon millielectrode in CH_3CN (Et_4NClO_4) versus Ag/Ag^+ at 25 °C.

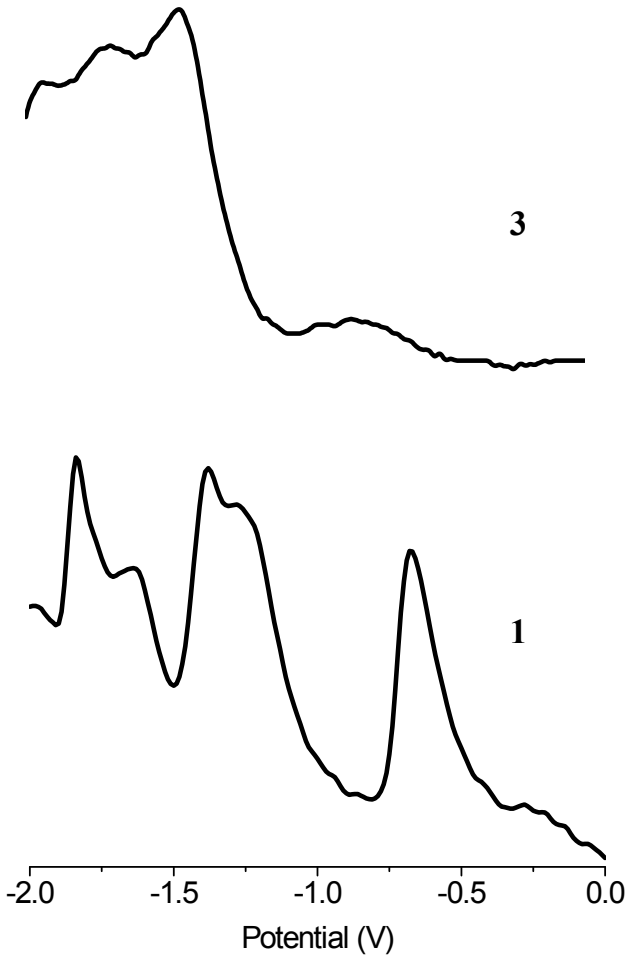
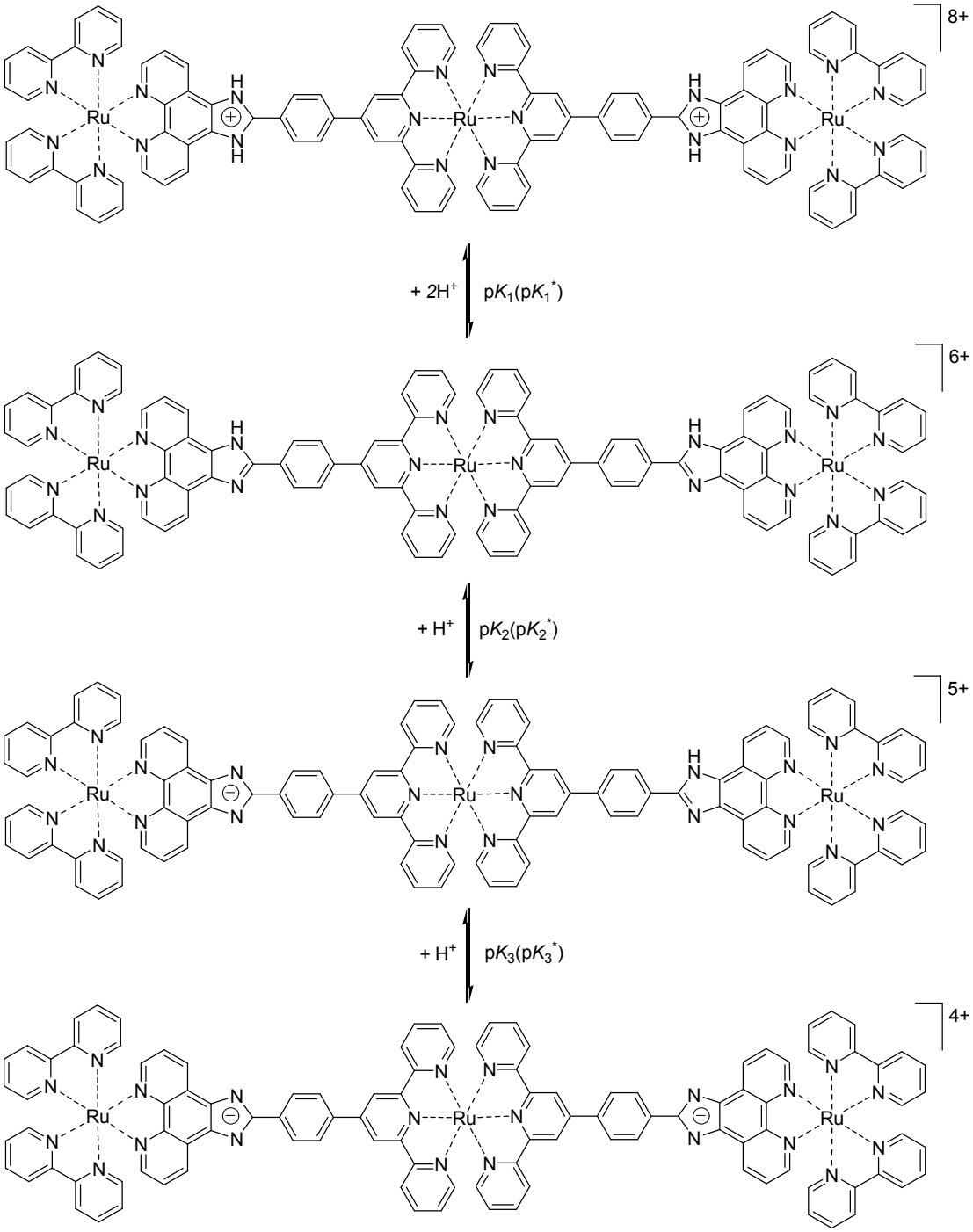


Figure S14. Square wave voltammogram of **1** and **3** on a glassy carbon millielectrode in CH_3CN (Et_4NClO_4) versus Ag/Ag^+ at 25 °C.

Table S1. Electrochemical Data[a]

	$E_{1/2}$ (V)	
Compound	oxidation	reduction[b]
1	1.36	-0.68, -1.28, -1.38, -1.64, -1.84
3	0.86, 1.34	-0.82, -1.45, -1.70, -1.92

[a]The data are computed from cyclic voltammogram recorded on a glassy carbon millielectrode in acetonitrile (10^{-3} M) using tetraethylammonium perchlorate as the supporting electrolyte (0.1 M) at 298 K at the scan rate of 100 mV s^{-1}. Potentials are reported in volts versus Ag/Ag^+. [b]$E_{1/2}$ values obtained from square wave voltammetry.



Scheme S5. Successive deprotonation steps of **3**.

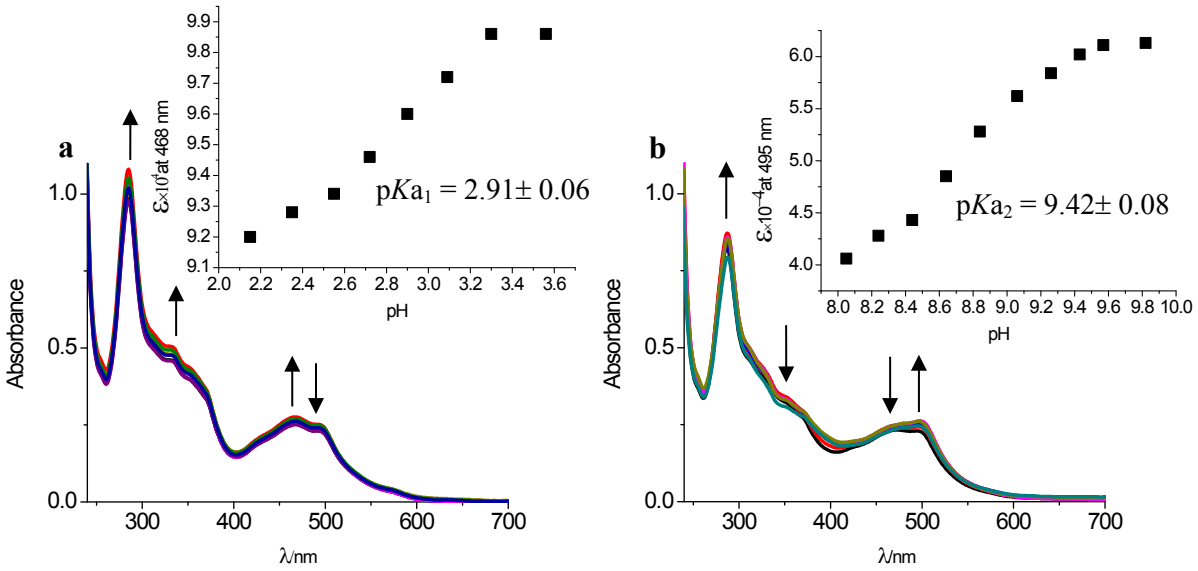


Figure S15. The absorption spectra of **3** (5 μM) in acetonitrile/Britton-Robinson buffer solution (3:2, v/v) as a function of pH: (a) pH 2.15-3.59, (b) pH 8.06-9.74. Insets: molar absorptivity (ε) at 428 and 495 nm as a function of pH.

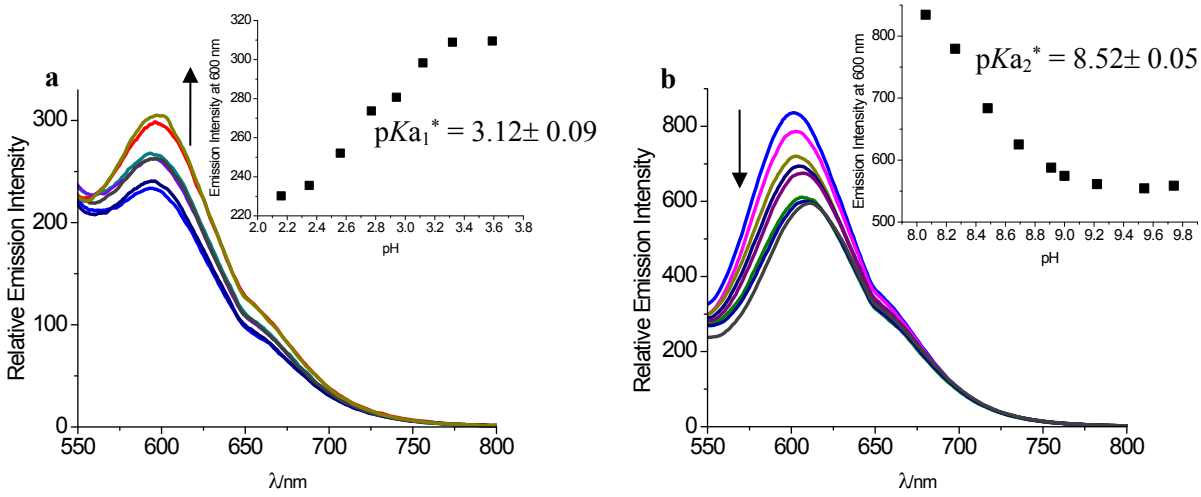


Figure S16. The emission spectra of **3** (5.0 μM) in acetonitrile/Britton-Robinson buffer (3:2, v/v) as a function of pH: (a) pH 2.15-3.59, (b) pH 8.06-9.74. Insets: relative emission intensity at 600 nm (λ_{ex} = 455 nm) as a function of pH.