Electronic Supporting Information

A Mononuclear Ruthenium Complex Showing Multiple Proton-Coupled Electron Transfer toward Multi-electron Transfer Reactions

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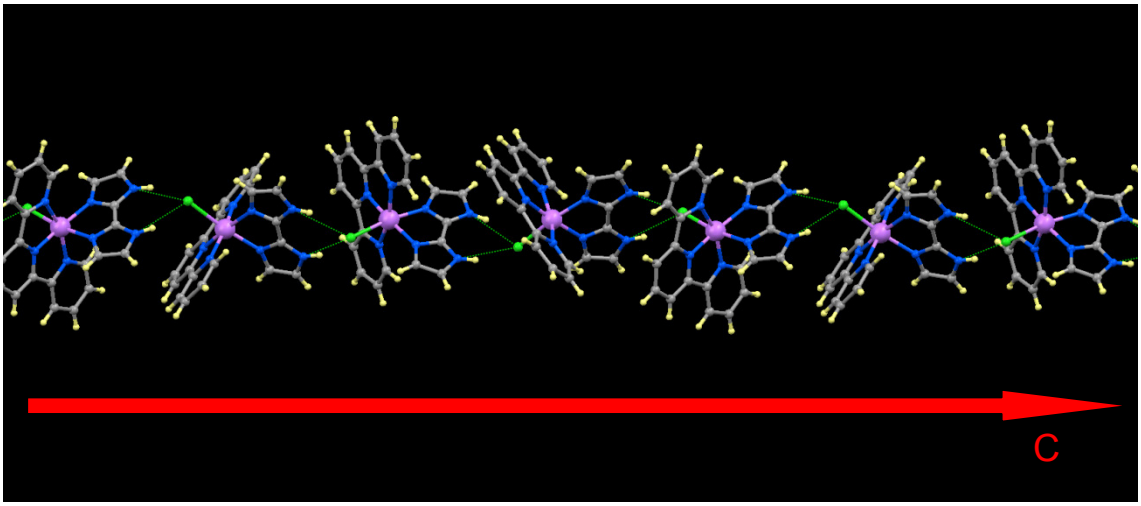

Fig. S1. Hydrogen-bonded one-dimensional network of the cationic moieties of **1** in the crystal.

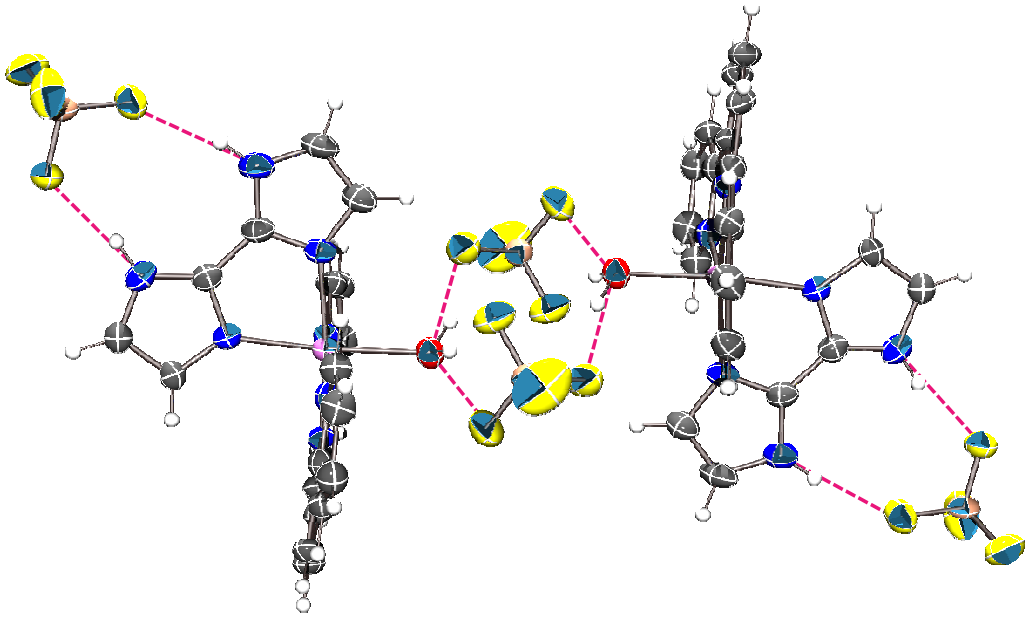

Fig. S2. Hydrogen-bonded dimeric structure of the complex **2'** in the crystal. Thermal ellipsoids are displayed at the 50% probability level.

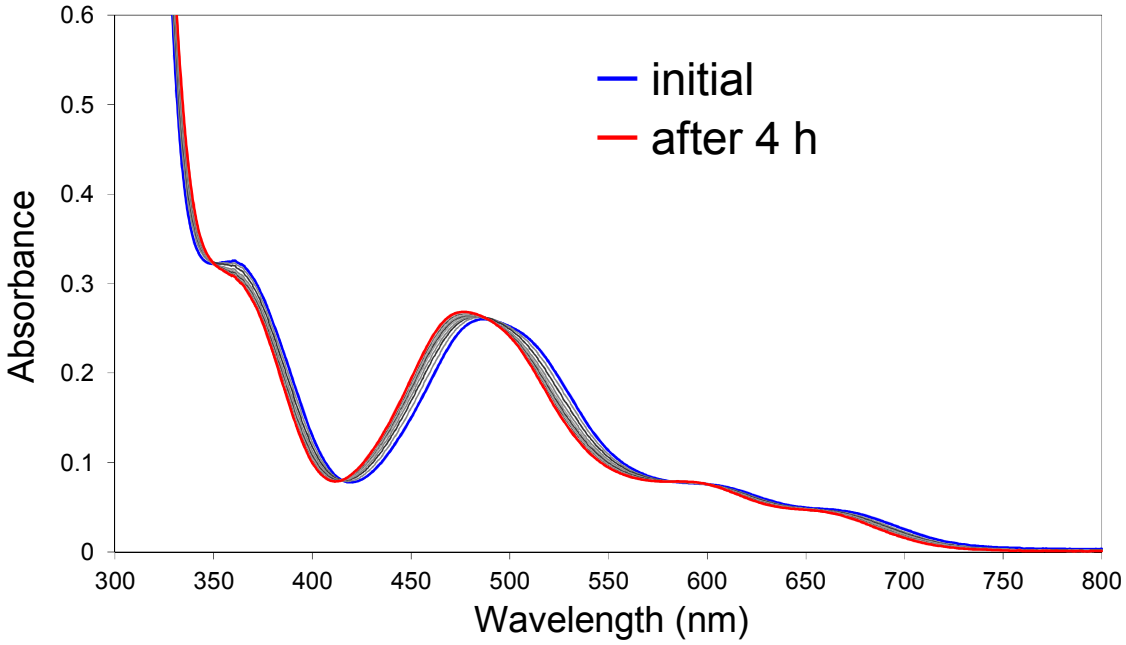

Fig. S3. Time course of absorption spectra after dissolution of **1** (0.5 mM) in water.

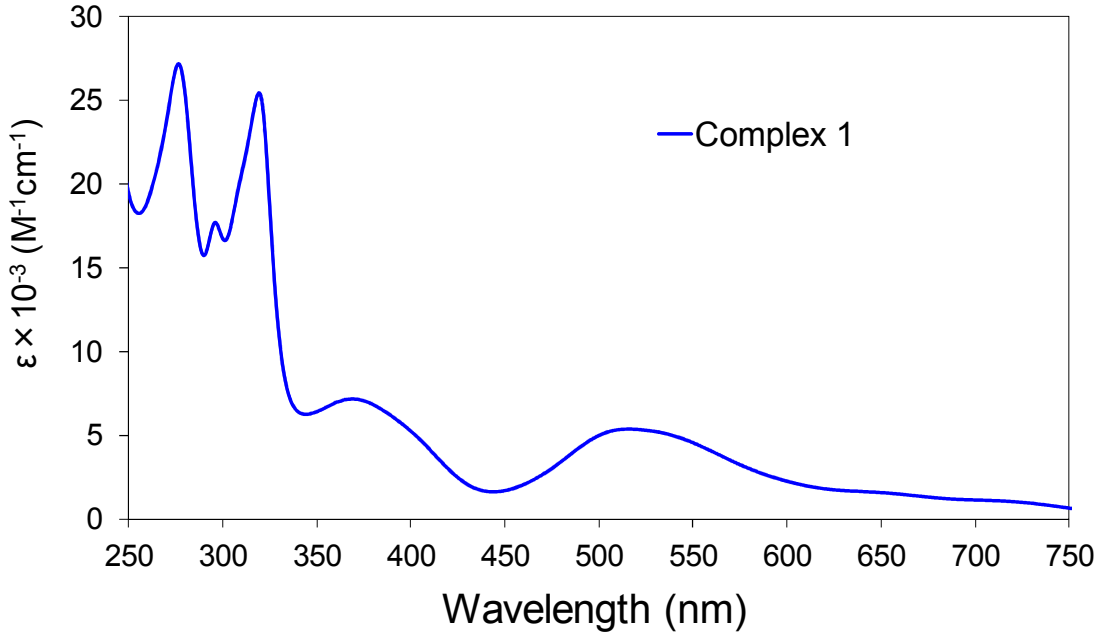

Fig. S4. UV-visible spectrum of an acetonitrile solution of **1** (0.5 mM).

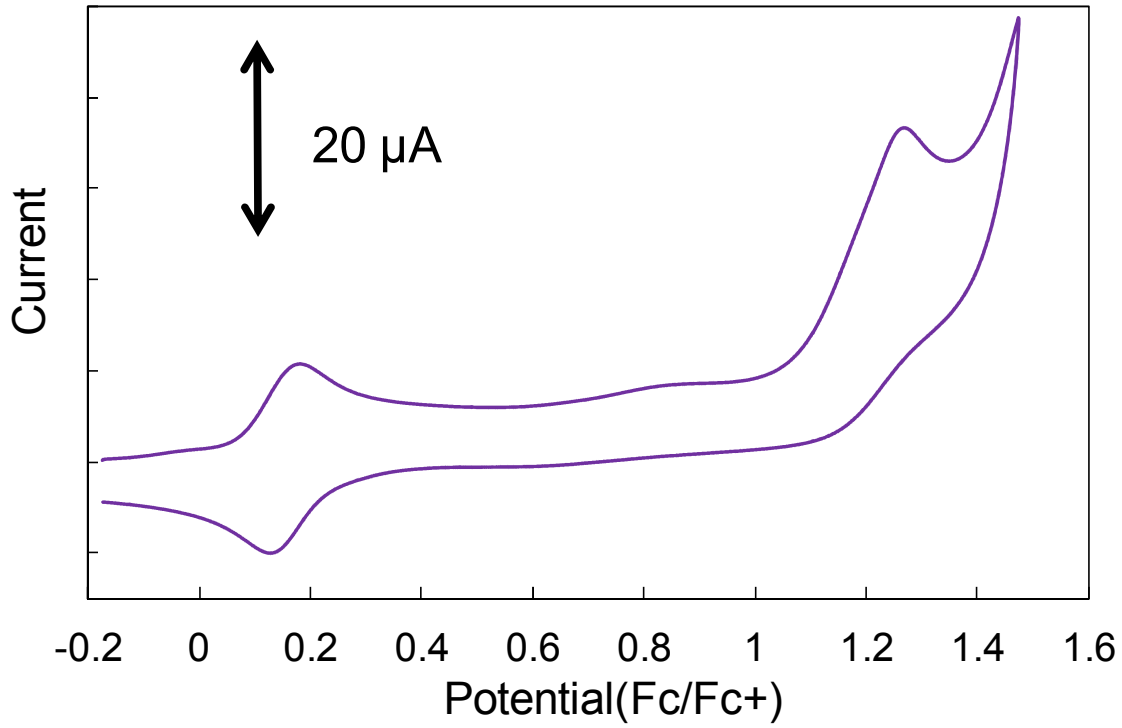

Fig. S5. Cyclic voltammogram of **1** (0.5 mM) in 0.1 M TBAP/acetonitrile solution under Ar atomosphere (WE: GC, CE: Pt wire, RE: SCE; Scan rate: 100 mV/s).

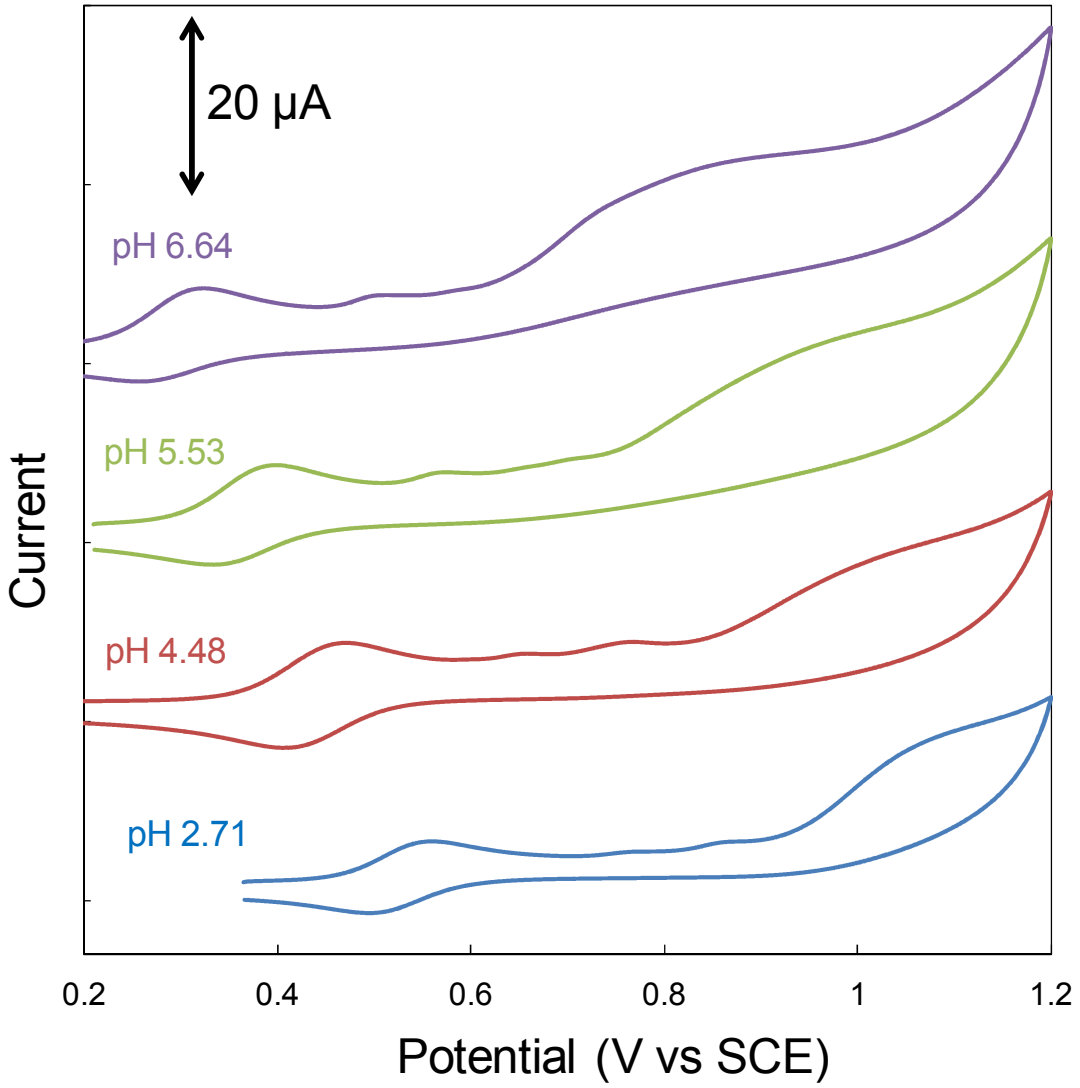

Fig. S6. pH-dependence of cyclic voltammograms of $[Ru(trpy)(H_2bim)(OH_2)](PF_6)_2$ (0.5 mM) in aqueous solution under various pH conditions (WE : GC, CE : Pt wire, RE : SCE ; Scan rate :100 mV/s)

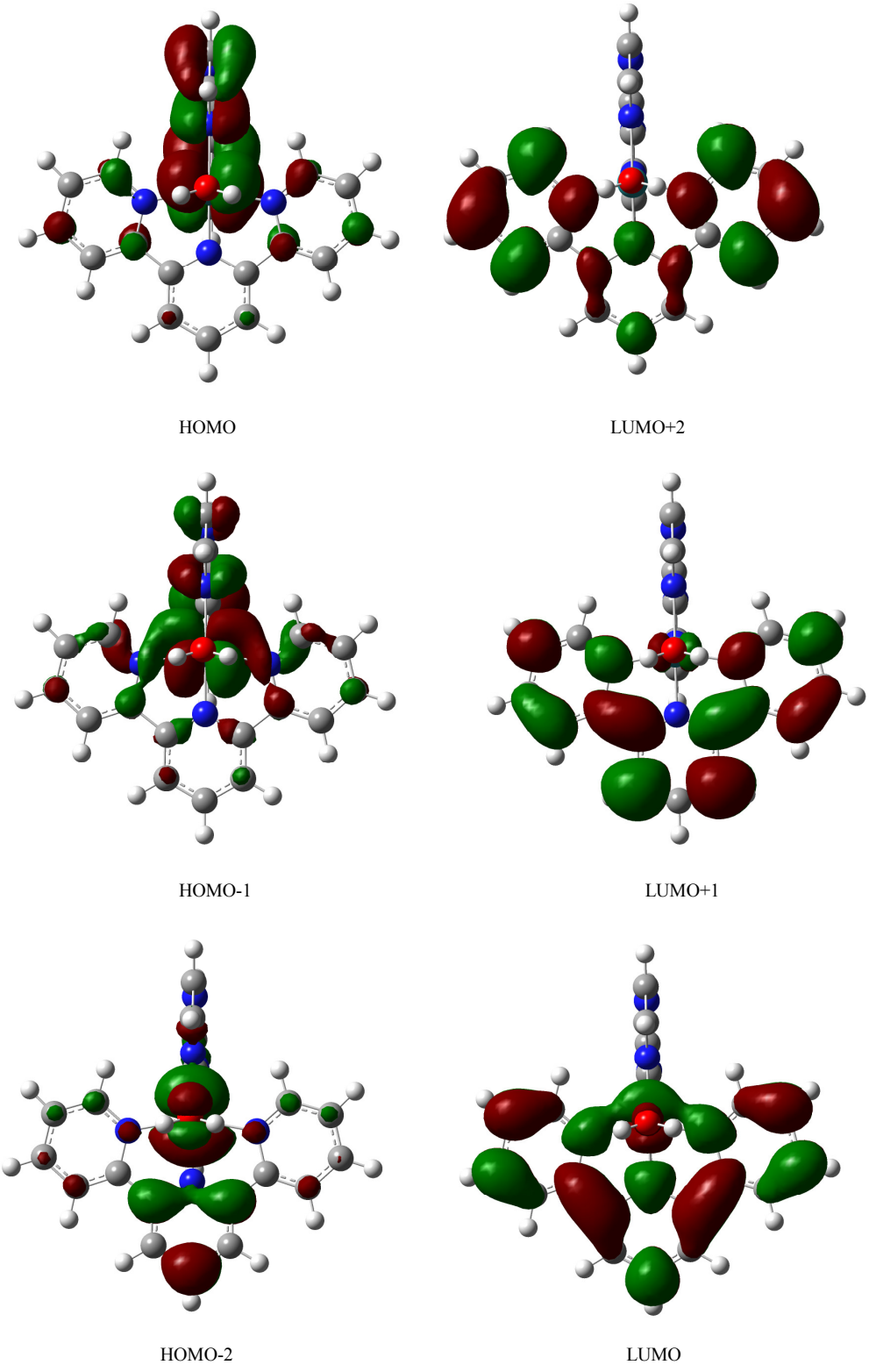

Fig. S7. Isodensity surface plots of selected frontier molecular orbitals of $[Ru(trpy)(Hbim)(OH_2)]^+$ based on the optimized ground-state geometry.

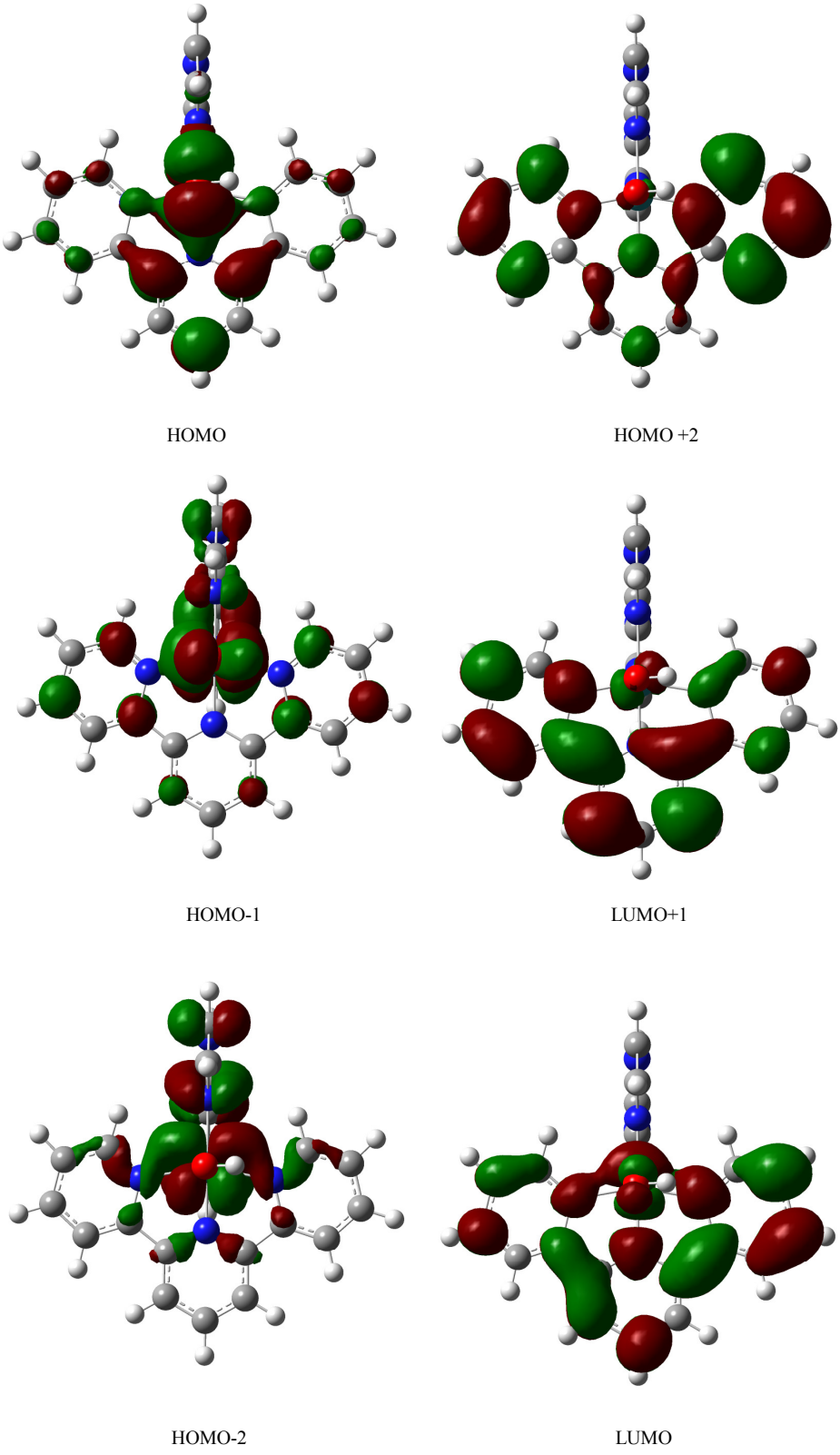

Fig. S8. Isodensity surface plots of selected frontier molecular orbitals of $[Ru(trpy)(Hbim)(OH)]^0$ based on the optimized ground-state geometry.

Table S1. Wavelength and oscillator strengths of both isomers at MLCT band from TD-DFT calculated absorption spectra.

Complex	Wavelength (nm)	Oscillator strength	Transition	|CI coef| (> 0.3)
$[Ru(trpy)(H_2bim)(OH_2)]^{2+}$	466	0.0469	HOMO-2→LUMO+1	0.68751
	442	0.0912	HOMO-2→LUMO	0.34681
			HOMO-1→LUMO+1	0.39629
			HOMO→LUMO+1	0.36473
	364	0.0606	HOMO-1→LUMO+2	0.42111
			HOMO→LUMO+4	0.39707
$[Ru(trpy)(Hbim)(OH_2)]^{+}$	500	0.0486	HOMO-2→LUMO+1	0.68547
	477	0.0652	HOMO-2→LUMO	0.44248
			HOMO→LUMO+1	0.33187
	389	0.0381	HOMO→LUMO+2	0.65208
$[Ru(trpy)(Hbim)(OH)]^{0}$	660	0.056	HOMO→LUMO+1	0.60367
	414	0.117	HOMO-1→LUMO+2	0.66706

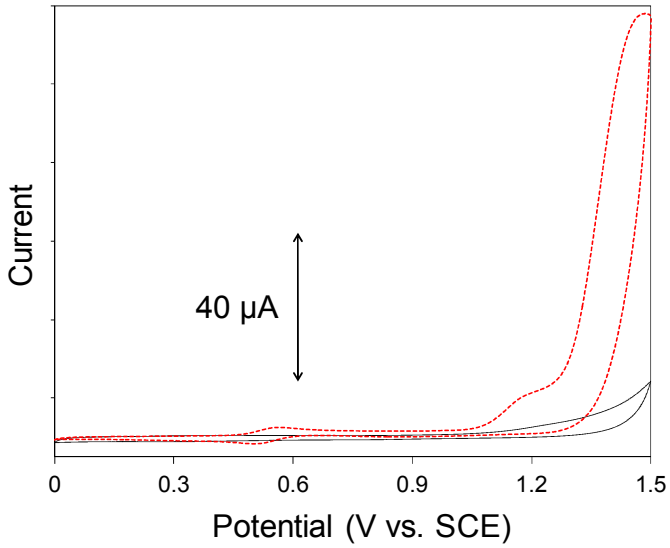

Fig. S9 Cyclic voltammograms (0.5 mM) of **2** in an aqueous 1 N H_2SO_4 solution (red dotted line) and blank solution (black line) under Ar atmosphere. (WE : GC, CE : Pt wire, RE : SCE ; Scan rate : 10 mV/s)