

Electronic Supplementary Information

Plasmon-Catalysed Decarboxylation of Dicarboxybipyridine Ligands in Ru(II) Complexes Chemisorbed on Ag Nanoparticles: Conditions, Proposed Mechanism and Role of Ag(0) Adsorption Sites

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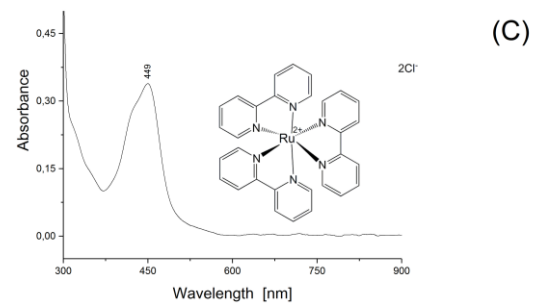
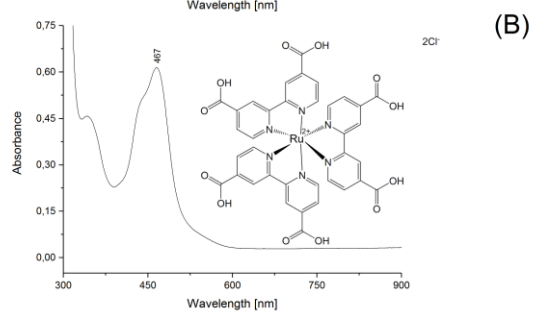
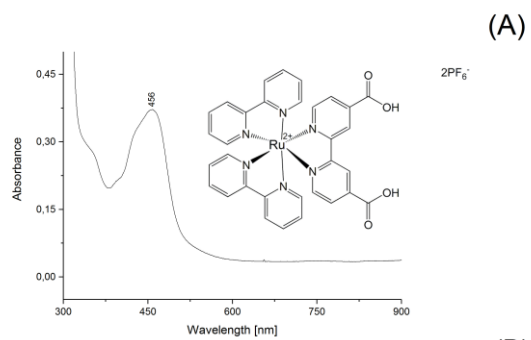


Fig. S1. Structure and electronic absorption spectra of (A) $\text{Ru}(\text{bpy})_2(\text{dcbpy})$, (B) $\text{Ru}(\text{dcbpy})_3$, (C) $\text{Ru}(\text{bpy})_3$ complexes.

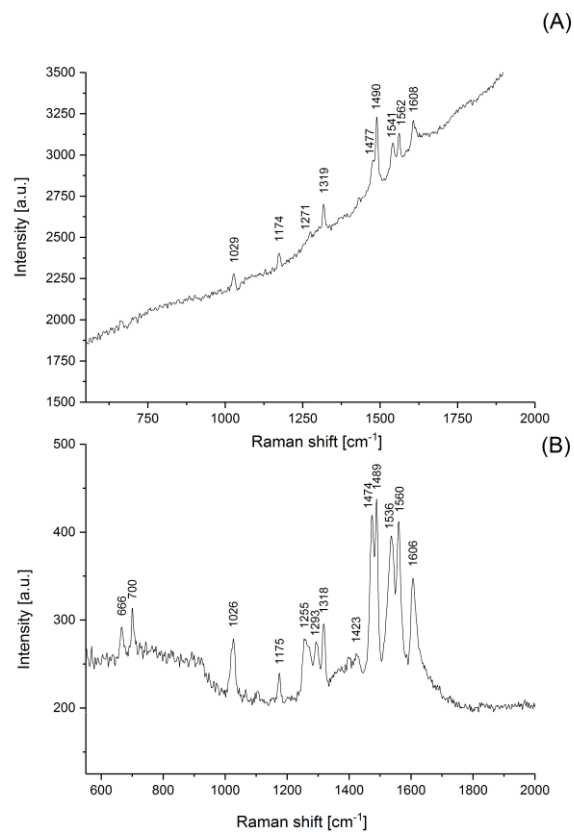


Fig. S2. (A) RRS of Ru(bpy)₂(dcbpy) in a 1x10⁻⁴ M aqueous solution, (B) SERRS spectra of Ag NP hydrosol/Ru(bpy)₂(dcbpy) (1x10⁻⁶ M) system, both spectra measured at 445 nm excitation.

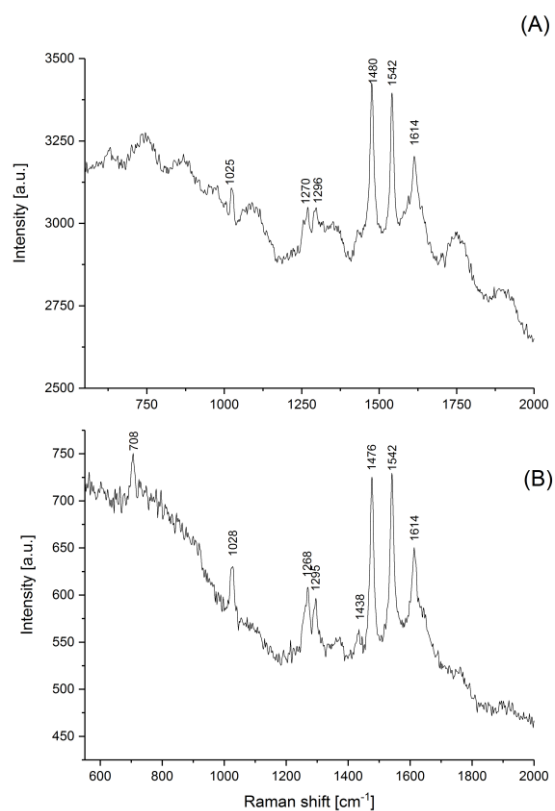


Fig. S3. (A) RRS of Ru(dcbpy)₃ in a 1x10⁻⁴ M aqueous solution, (B) SERRS spectra of Ag NP hydrosol/Ru(dcbpy)₃ (1x10⁻⁵ M) system, both spectra measured at 445 nm excitation.

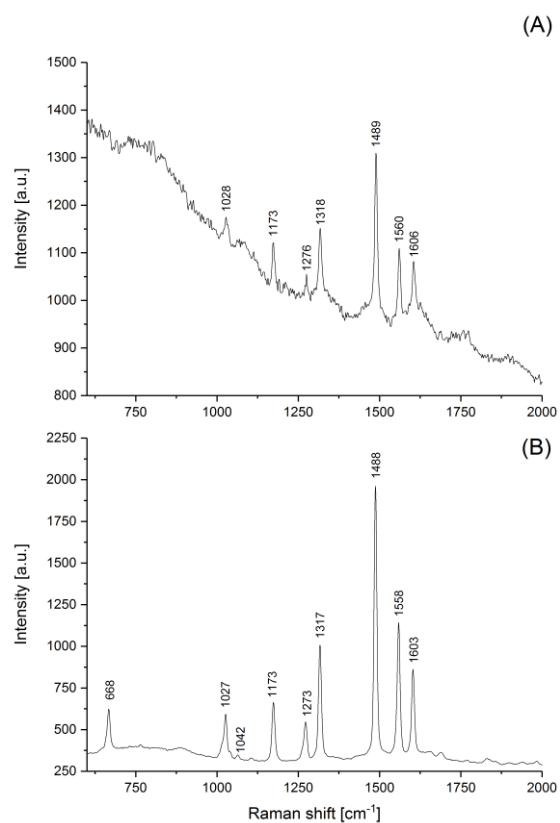


Fig. S4. (A) RRS of $\text{Ru}(\text{bpy})_3$ in a 1×10^{-4} M aqueous solution, (B) SERRS spectra of Ag NP hydrosol/ $\text{Ru}(\text{bpy})_3$ (1×10^{-6} M) system, both spectra measured at 445 nm excitation.

Tab. S1. Wavenumbers [cm^{-1}] of RRS and SERRS spectral bands of $\text{Ru}(\text{bpy})_2(\text{dcbpy})$.

$\text{Ru}(\text{bpy})_2(\text{dcbpy})$ RRS	$\text{Ru}(\text{bpy})_2(\text{dcbpy})$ SERRS
1029	1026
1174	1175
1271	1255
	1293
1319	1318
1477	1474
1490	1489
1541	1536
1562	1560
1608	1606

Tab. S2. Wavenumbers [cm^{-1}] of RRS and SERRS spectral bands of $\text{Ru}(\text{dcbpy})_3$.

$\text{Ru}(\text{dcbpy})_3$ RRS	$\text{Ru}(\text{dcbpy})_3$ SERRS
1025	1028
1270	1268
1296	1295
1480	1476
1542	1542
1614	1614

Tab. S3. Wavenumbers [cm^{-1}] of RRS and SERRS spectral bands of $\text{Ru}(\text{bpy})_3$.

$\text{Ru}(\text{bpy})_3$ RRS	$\text{Ru}(\text{bpy})_3$ SERRS	$\text{Ru}(\text{bpy})$ NCA, PED [%] ^{[26]#}
1028	1027	$\nu(\text{C}_4\text{-C}_5)$, 25; $\nu(\text{C}_2\text{-C}_3)$, 23; $\nu(\text{C}_3\text{-C}_4)$, 13; $\delta(\text{CCH})$, 12
1173	1173	$\delta(\text{CCH})$, 81
1276	1273	$\nu(\text{C}_2\text{-C}_3)$, 50; $\nu(\text{C-N})$, 45; $\nu(\text{C}_3\text{-C}_4)$, 30; $\nu(\text{C}_4\text{-C}_5)$, 21
1318	1317	$\delta(\text{C}_2\text{C}_3\text{H})$, 36; $\delta(\text{CCH})$, 23; $\nu(\text{C}_2\text{-C}_2')$, 17
1489	1488	$\delta(\text{CCH})$, 25; $\nu(\text{C}_2\text{-C}_3)$, 20; $\nu(\text{C}_2\text{-C}_2')$, 20; $\nu(\text{C-N})$, 18; $\delta(\text{C}_2\text{C}_3\text{H})$, 18
1560	1558	$\nu(\text{C}_4\text{-C}_5)$, 42; $\nu(\text{C-N})$, 22; $\delta(\text{CCH})$, 18
1606	1603	$\nu(\text{C}_2\text{-C}_3)$, 43; $\nu(\text{C}_2\text{-C}_2')$, 14; $\nu(\text{C-N})$, 14; $\nu(\text{C}_3\text{-C}_4)$, 11

[#] NCA, PED taken from ref. 26

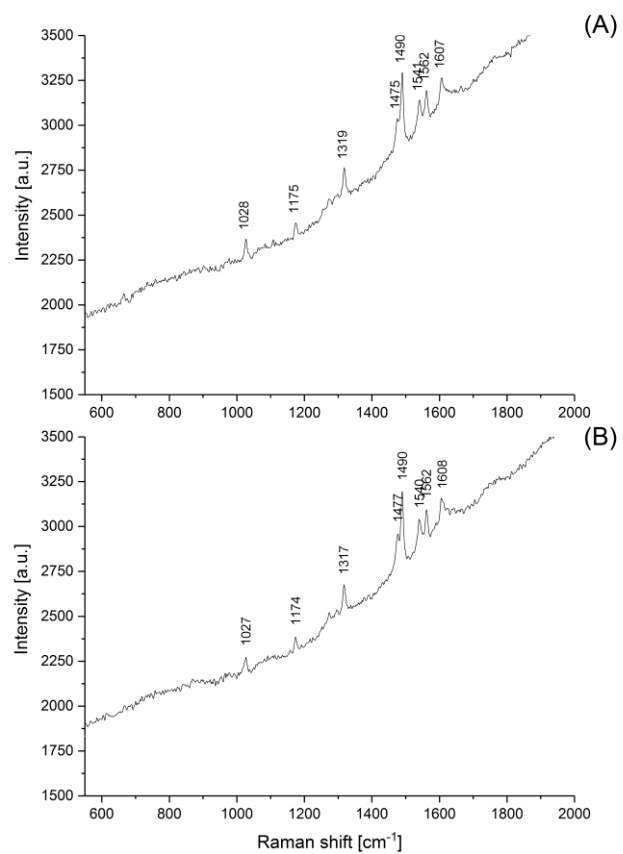


Fig. S5. RRS spectrum of Ru(bpy)₂(dcbpy) in an aqueous solution (A) prior, (B) after addition of aqueous NaCl solution (5×10^{-2} M final concentration of NaCl in the system).

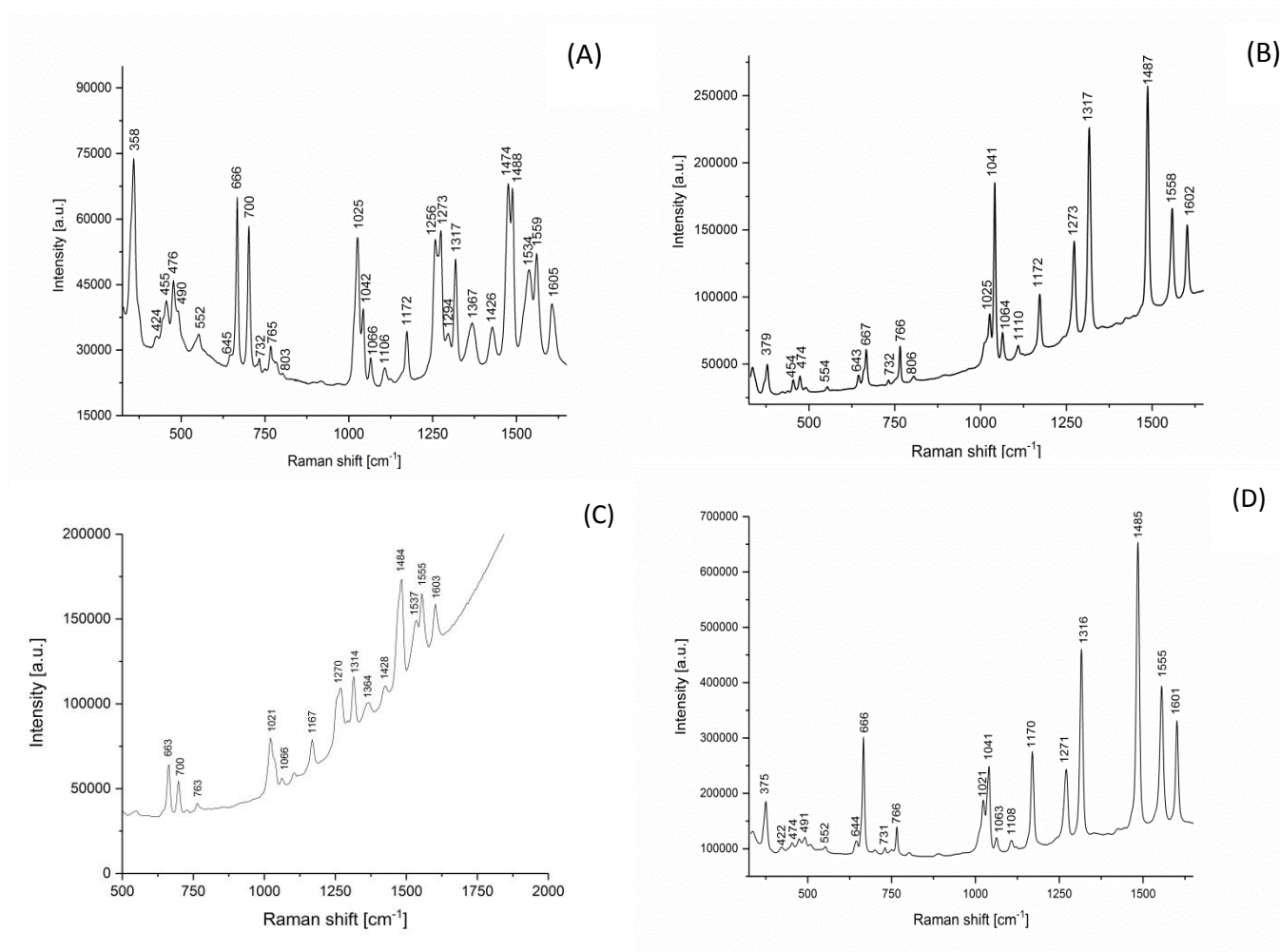


Fig. S6. SERS spectra of Ru(bpy)₂(dcbpy) (A), of Ru(bpy)₃ (B), SERS spectrum of Ru(bpy)₂(dcbpy)/NaBH₄/AgNO₃ system measured 5 min. after preparation (C) and SERS spectrum of Ru(bpy)₂(dcbpy) after addition of chlorides (D). All spectra measured at 532 nm.

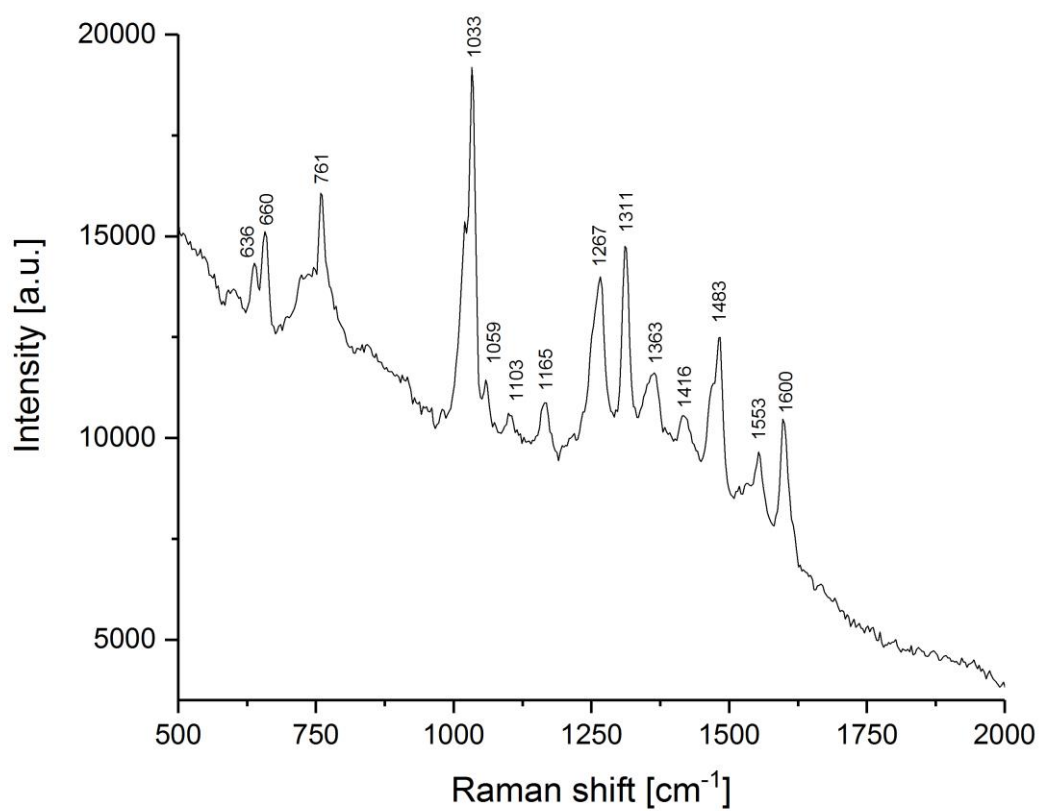


Fig. S7. SERS spectrum of Ru(bpy)₂(dcbpy) /NaBH₄/AgNO₃ system measured 5 min. after preparation at 780 nm excitation.

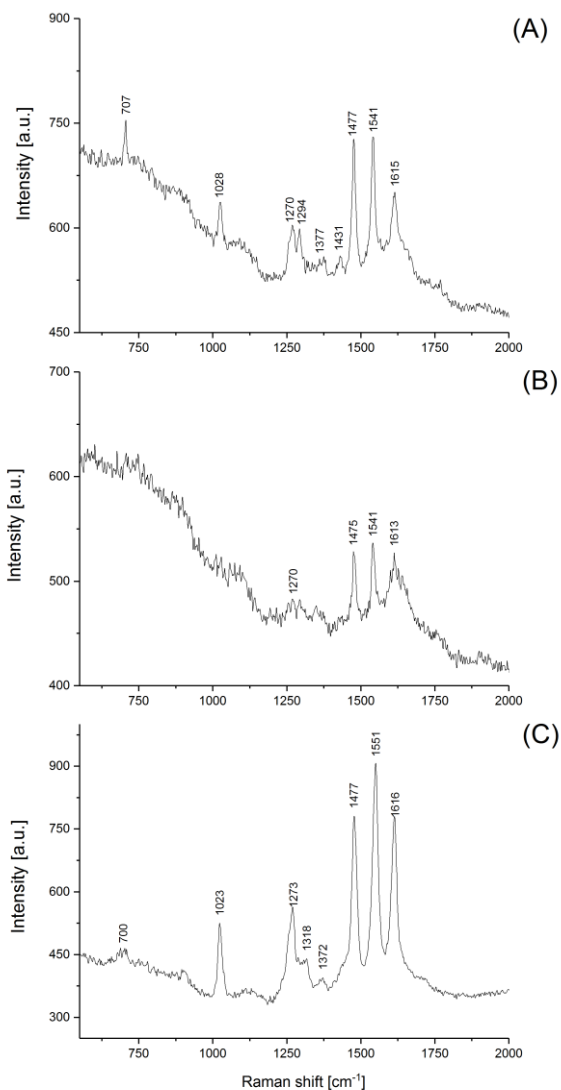


Fig. S8. SERRS spectra of (A) Ag NP hydrosol/Ru(dcbpy)₃ system, (B) Ag NP hydrosol/Ru(dcbpy)₃/NaCl (2x10⁻² M) system, and (C) Ag NP hydrosol/Ru(dcbpy)₃/NaCl (2.5x10⁻² M)/HCl (1x10⁻² M) system.

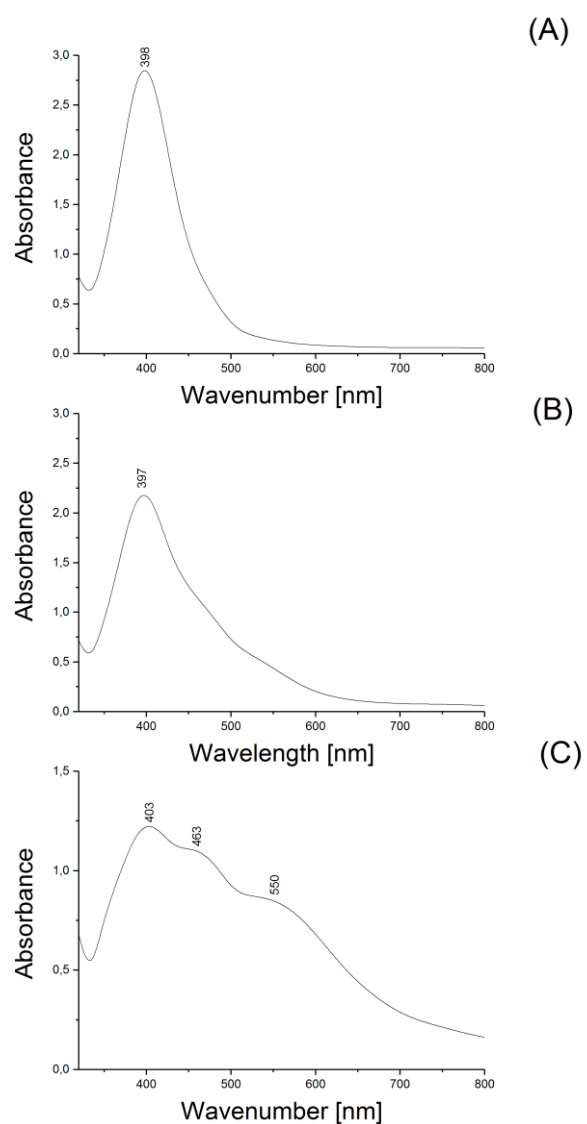


Fig. S9. UV/vis absorption spectra depicting SPE of Ag NPs in (A) Ag NP hydrosol/Ru(dcbpy)₃ system, (B) Ag NP hydrosol/Ru(dcbpy)₃/NaCl (2x10⁻² M) system, and (C) Ag NP hydrosol/Ru(dcbpy)₃/NaCl (2.5x10⁻² M)/HCl (1x10⁻² M) system.