Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supplementary Information

The Development of Supramolecular Assemblies for Photocatalytic Hydrogen Generation from Water.

^{1}H NMR spectroscopy

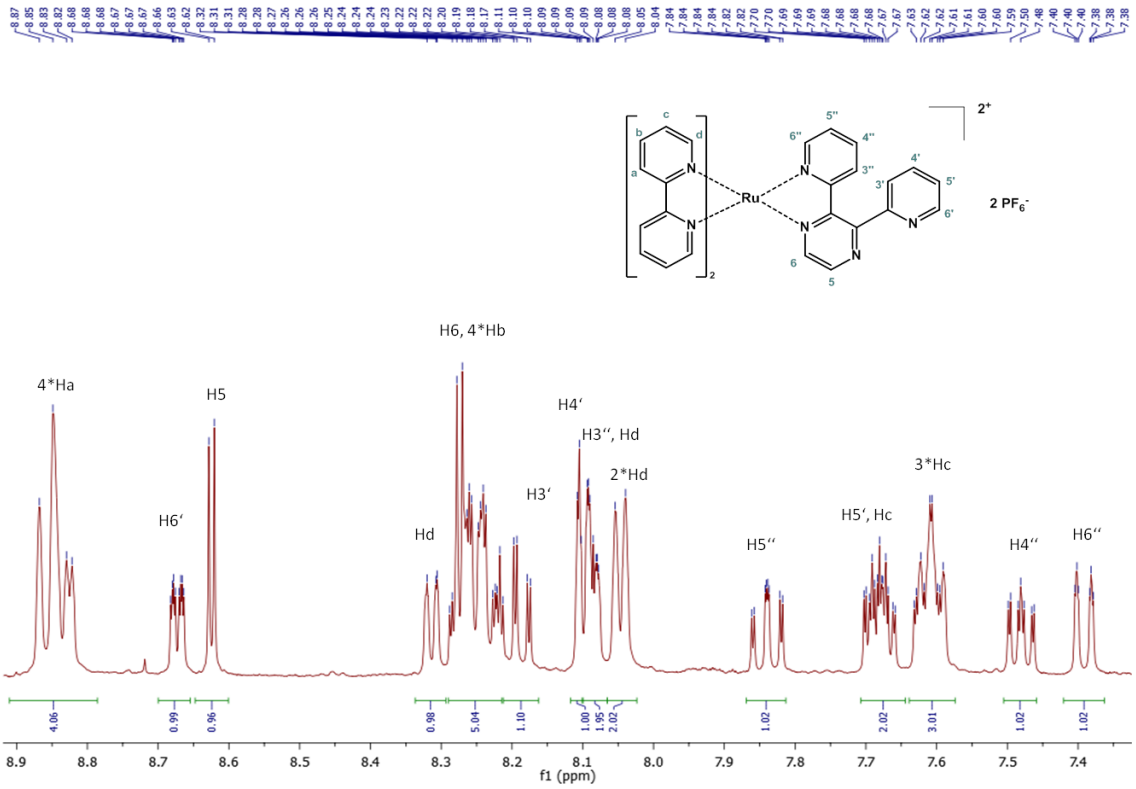

Figure S1: ^{1}H NMR spectrum of $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$ in acetone-d_6.

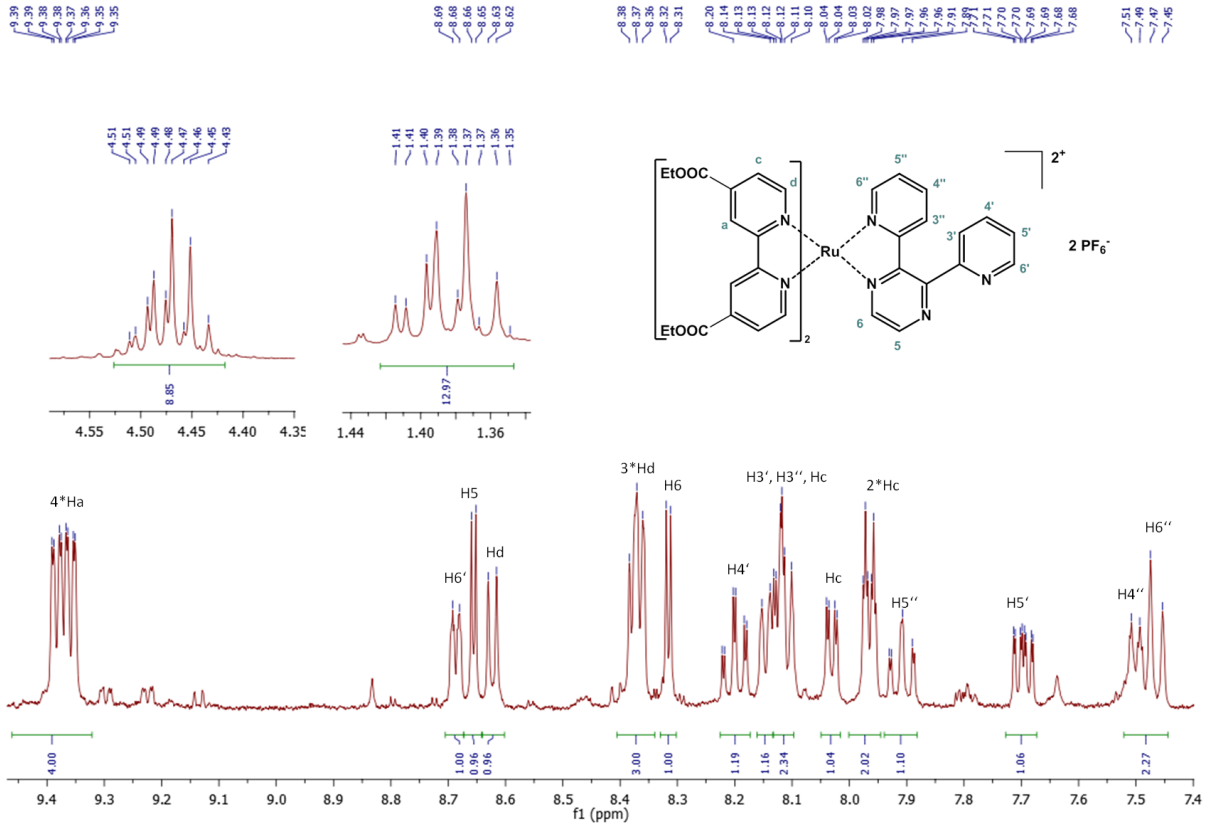

Figure S2: ^{1}H NMR spectrum of $[Ru(dceb)_2(2,3\text{-}dpp)]^{2+}$ in acetone-d_6.

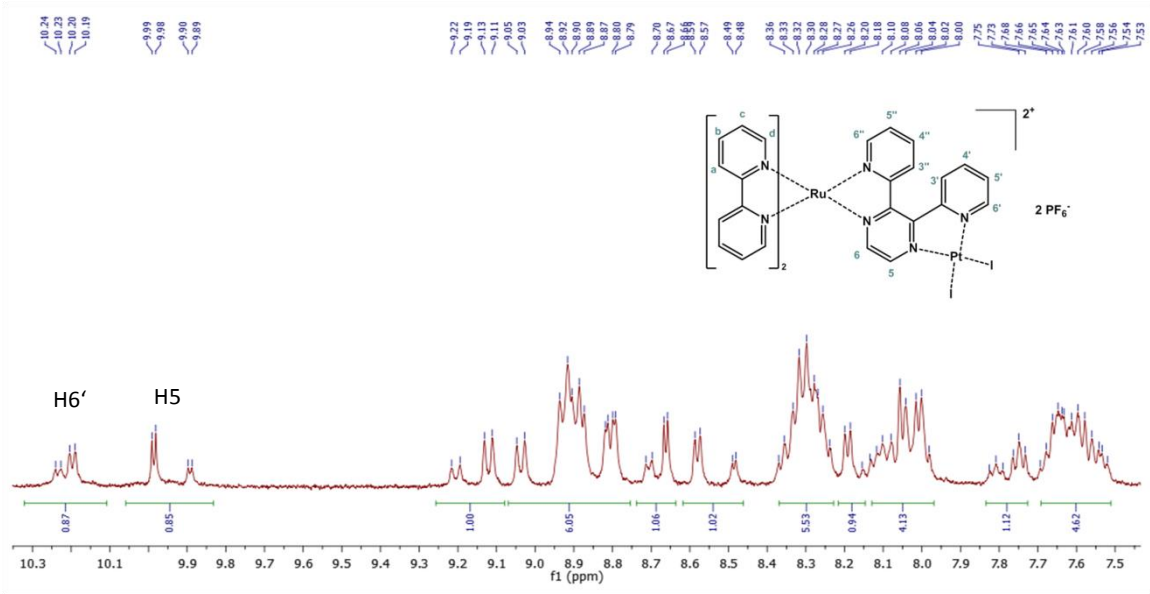

Figure S3: ^{1}H NMR spectrum of $[Ru(bpy)_2(2,3\text{-}dpp)PtI_2]^{2+}$ in acetone-d_6.

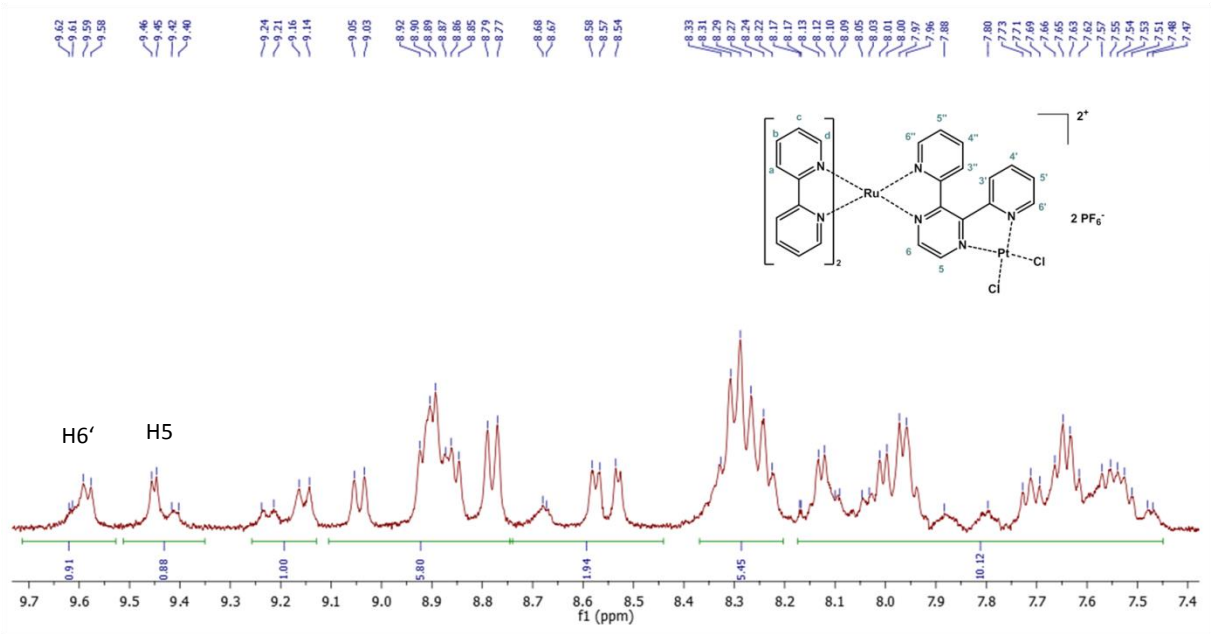

Figure S4: ^{1}H NMR spectrum of $[Ru(bpy)_2(2,3dpp)PtCl_2]^{2+}$ in acetone-d_6.

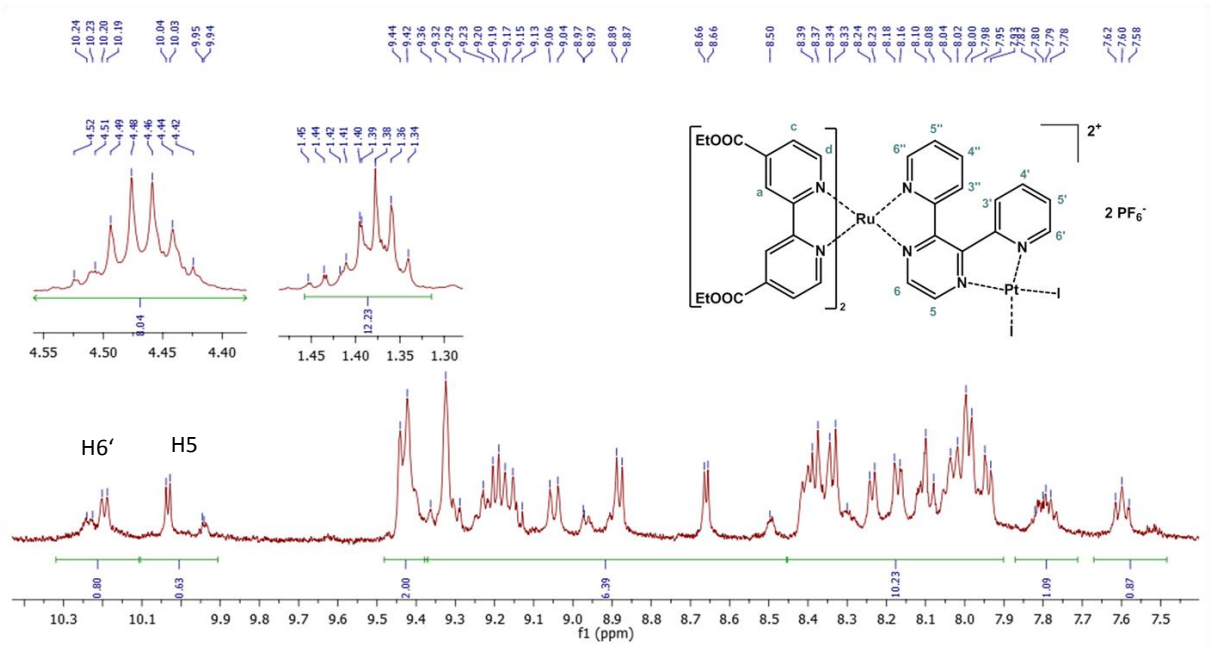

Figure S5: ^{1}H NMR spectrum of $[Ru(dceb)_2(2,3\text{-}dpp)PtI_2]^{2+}$ in acetone-d_6.

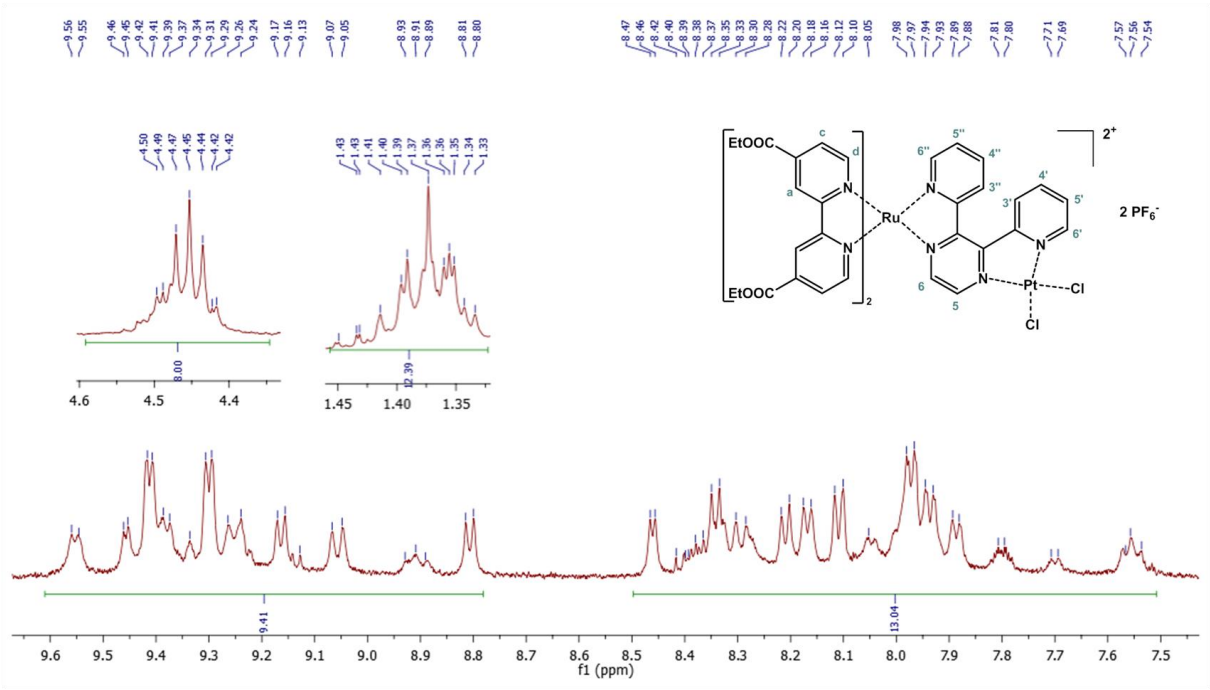

Figure S6: ^{1}H NMR spectrum of $[Ru(dceb)_2(2,3\text{-}dpp)PtCl_2]^{2+}$ in acetone-d_6.

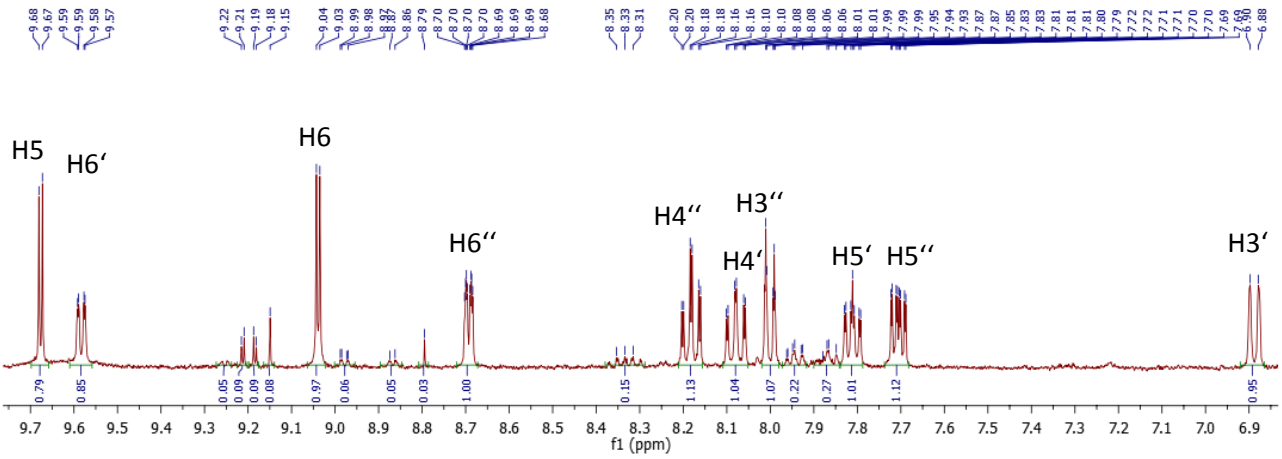

Figure S7: ^{1}HNMR spectrum of $[Pt(2,3dpp)Cl_2]$ in dmso-d_6.

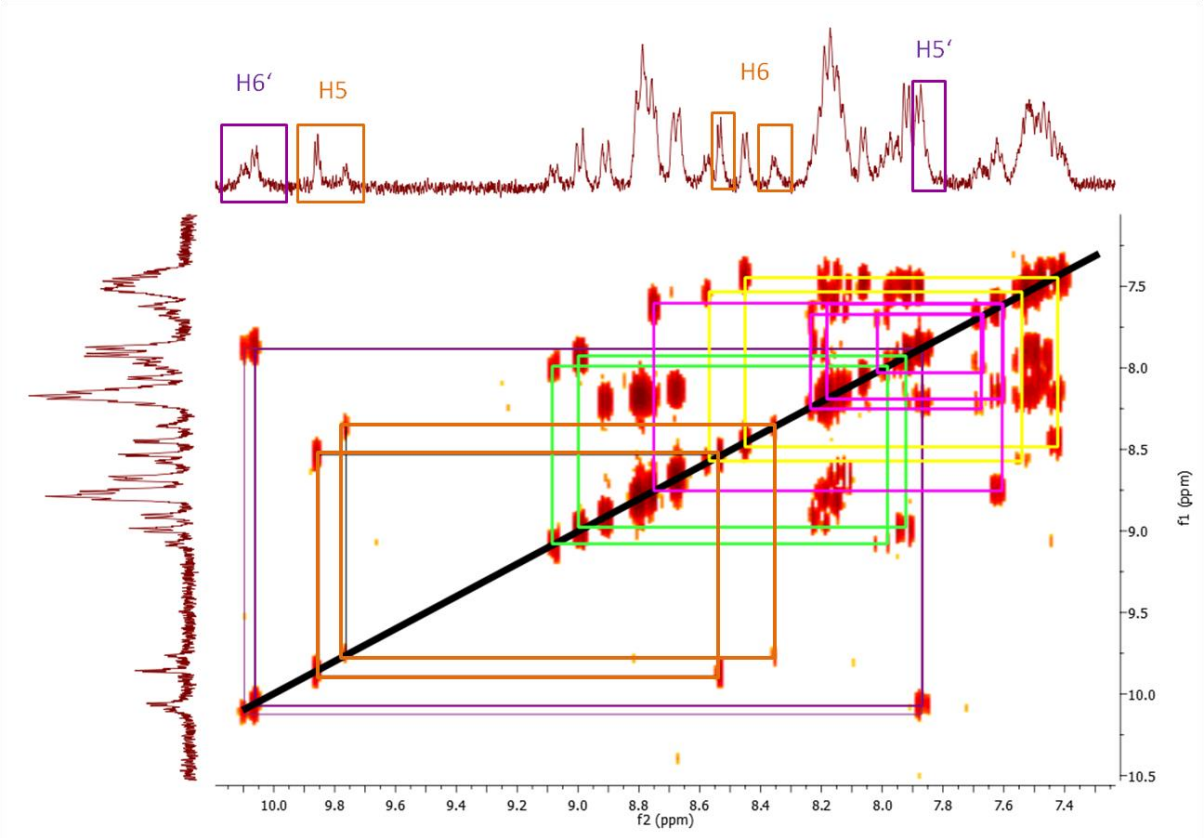

Figure S8: ^{1}H-^{1}H COSY spectrum of $[Ru(bpy)_2(2,3\text{-dpp})PtI_2]^{2+}$ in acetone-d_6.

Resonance Raman Spectroscopy

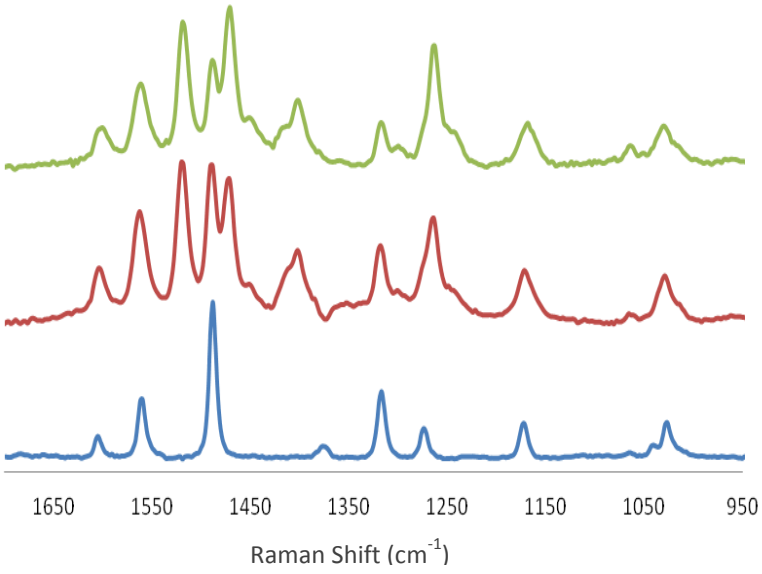

Figure S9: RR spectra (normalised) of $[Ru(bpy)_3]^{2+}$ (blue, λ_{exc}. 473 nm) and $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$ (red λ_{exc}. 457 nm and green λ_{exc}. 473 nm) in acetonitrile.

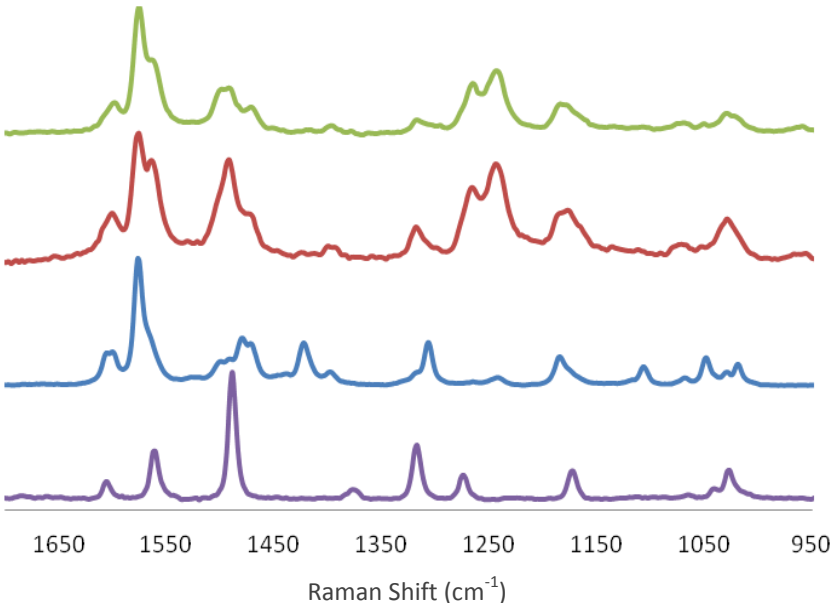

Figure S10a: RR spectra (normalised) of $[Ru(bpy)_3]^{2+}$ (purple, λ_{exc}. 473 nm) and $[Ru(bpy)_2(2,3dpp)PtCl_2]^{2+}$ λ_{exc}. 355 nm (blue), 457 nm (red) and 473 nm (green) in acetonitrile.

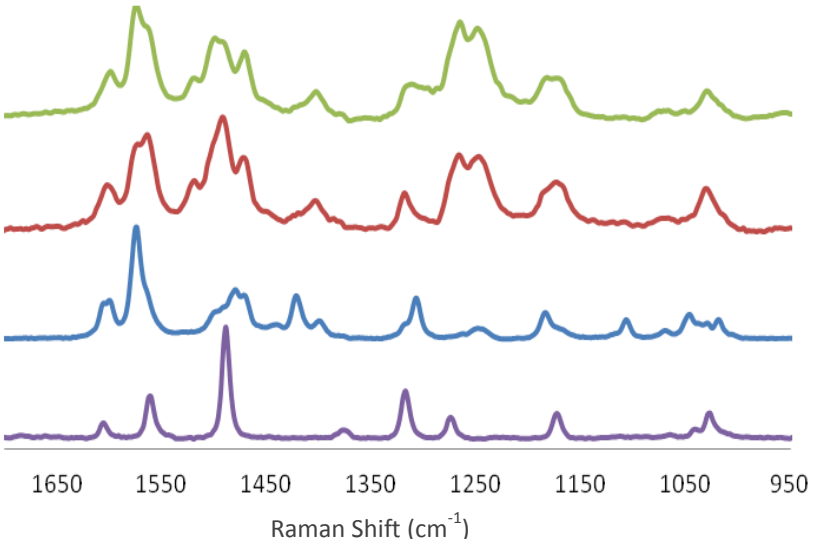

Figure S10b: RR spectra (normalised) of $[Ru(bpy)_3]^{2+}$ (purple, λ_{exc}. 473 nm) and $[Ru(bpy)_2(2,3dpp)PtI_2]^{2+}$ λ_{exc}. 355 nm (blue), 457 nm (red) and 473 nm (green) in acetonitrile.

ESI-MS data

m/z peaks / Complex	$[M\text{-}PF_6]^+$	$[M\text{-}2PF_6]^{2+}$	$[M\text{-}2PF_6\text{-}PtX_2]^{2+}$	Additional prominent peaks*
$[Ru(bpy)_2(2,3dpp)]^{2+}$	793.3 (792.7)	324.2 (323.9)	-	-
$[Ru(bpy)_2(2,3dpp)PtCl_2]^{2+}$	1059.0 (1058.7)	456.7 (456.8)	326.0 (323.9)	248.3, 265.6, 402.3, 658.3
$[Ru(bpy)_2(2,3dpp)PtI_2]^{2+}$	1241.1 (1241.5)	548.7 (548.3)	-	569.2, 779.7
$[Ru(dceb)_2(2,3dpp)]^{2+}$	1081.4 (1080.9)	468.4 (467.8)	-	-
$[Ru(dceb)_2(2,3dpp)PtI_2]^{2+}$	1531.2 (1529.8)	692.5 (692.4)	468.4 (467.8)	1349.5, 1258.7, 971,3, 824.4
$[Ru(phen)_2(2,3dpp)]^{2+}$	840.3 (840.7)	348.3 (347.9)	-	234.5
$[Ru(phen)_2(2,3dpp)PtCl_2]^{2+}$	1106.2 (1106.7)	481.3 (480.9)	-	689.9
$[Ru(phen)_2(2,3dpp)PtI_2]^{2+}$	1290.6 (1289.6)	572.7 (572.32)	348.3 (347.9)	593.6, 1465.8, 1270.9

Table S1 Prominent m/z peaks in the mass spectra of the 2,3dpp based complexes and their assignment to the calculated mol fragments (in brackets); (M = total molar mass, m /z = mass-to-charge ratio, X = Cl^-, I^-, * = peaks that couldn't be assigned to calc. mol fragments)