Supporting Information

Photochemistry of ruthenium (II) complexes based on 1,4,5,8-tetraazaphenanthrene and 2,2'-bipyrazine: a comprehensive experimental and theoretical study

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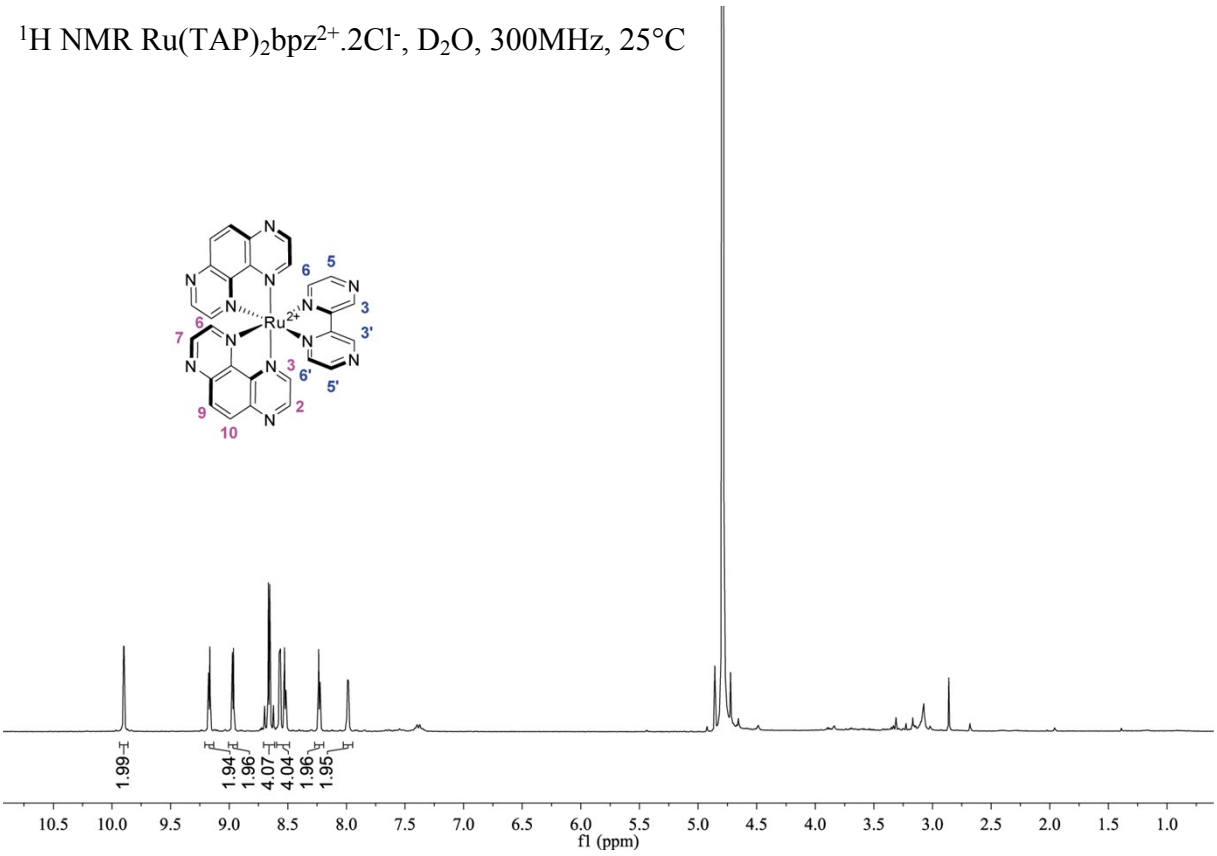
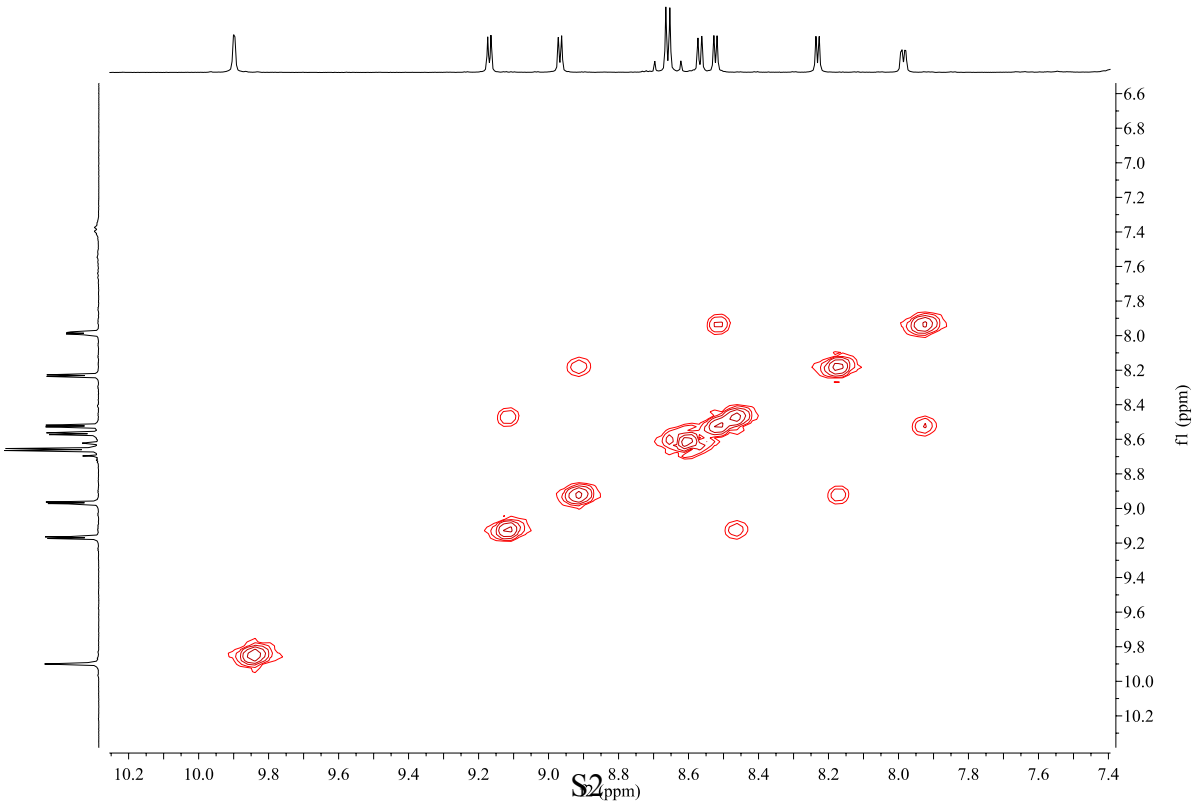
SI X1 : ^{1}H NMR of $[Ru(TAP)_2bpz]^{2+}$

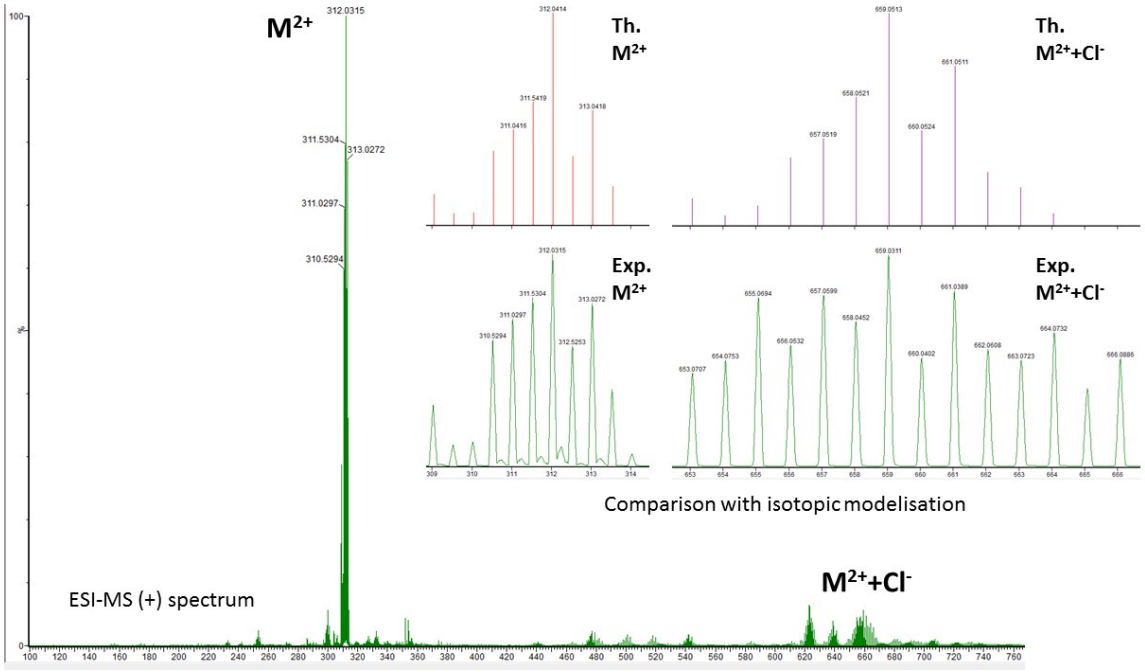
^{1}H NMR $Ru(TAP)_2bpz^{2+}.2Cl^{-}$, D_2O, 300MHz, 25°C



^{1}H-^{1}H COSY $Ru(TAP)_2bpz^{2+}.2Cl^{-}$, D_2O, 300MHz, 25°C

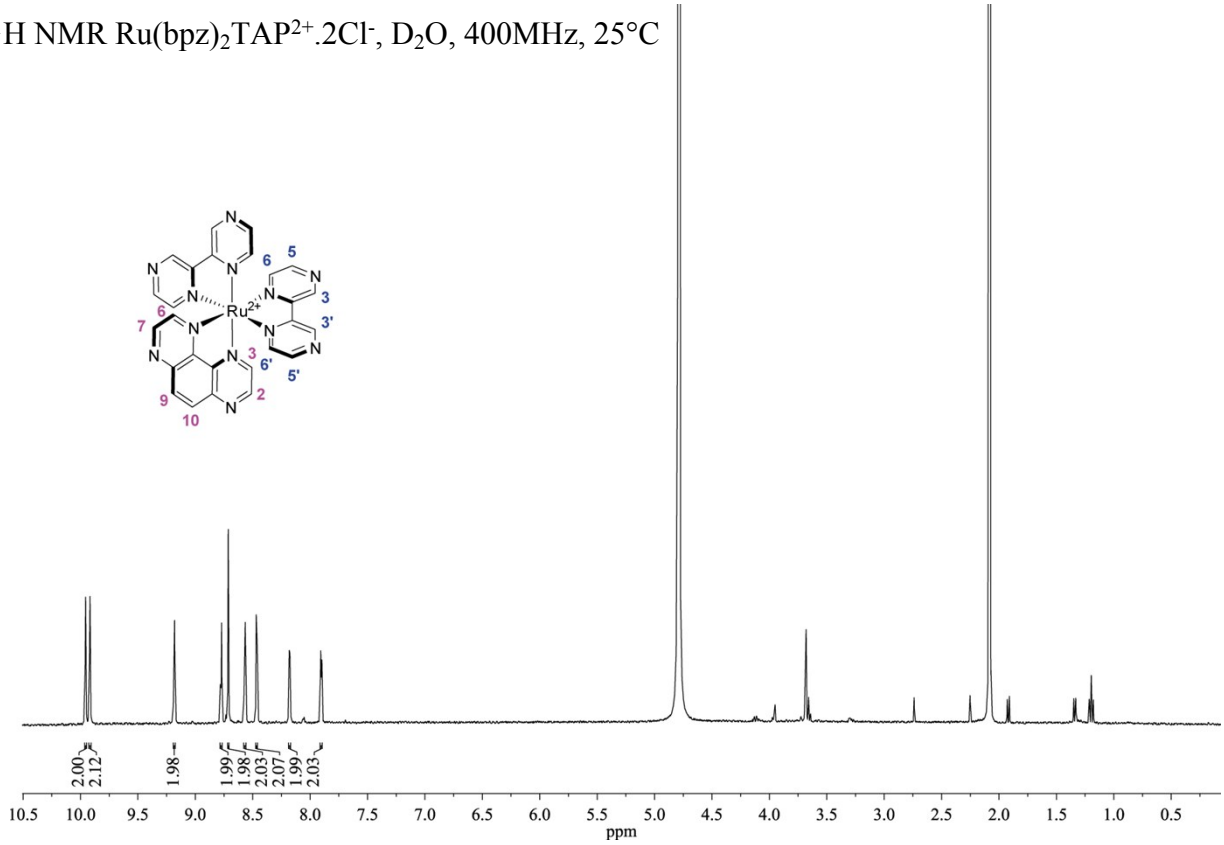


SI X2 : HR-MS of $[Ru(TAP)_2bpz]^{2+}$

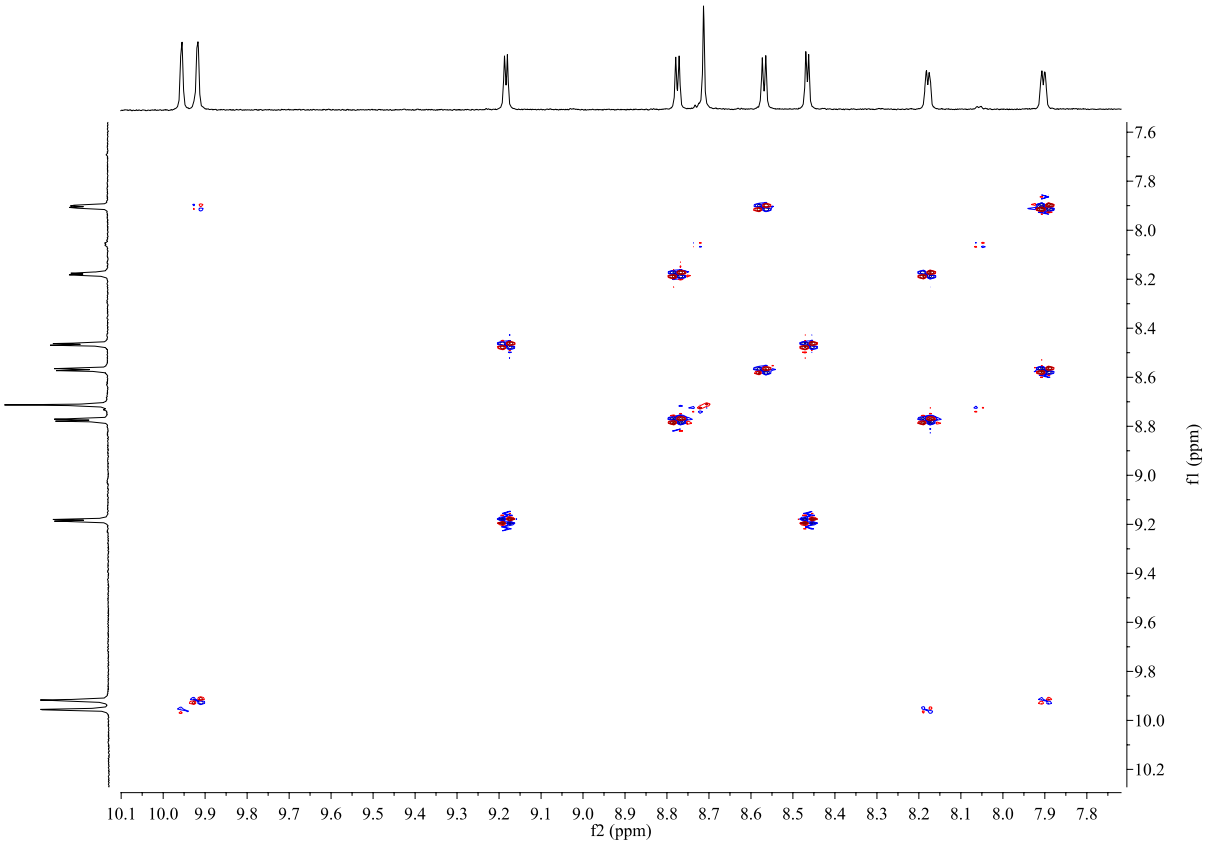


SI X3 : ^{1}H NMR of [Ru(bpz)$_2$TAP]$^{2+}$

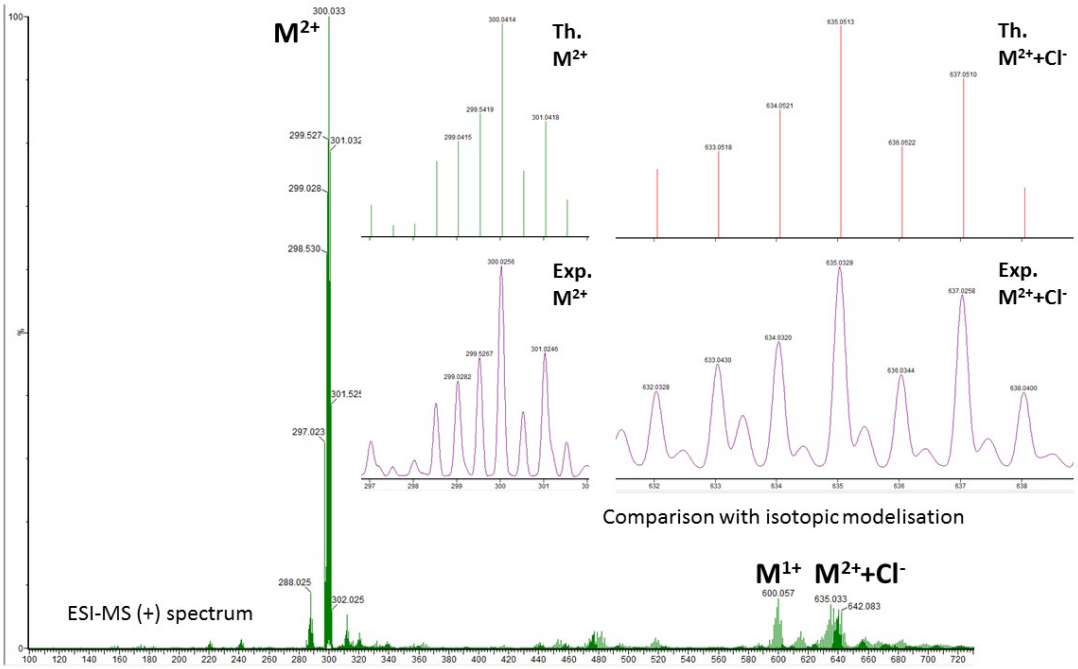
^{1}H NMR Ru(bpz)$_2$TAP^{2+}.2Cl^{-}, D$_2$O, 400MHz, 25°C



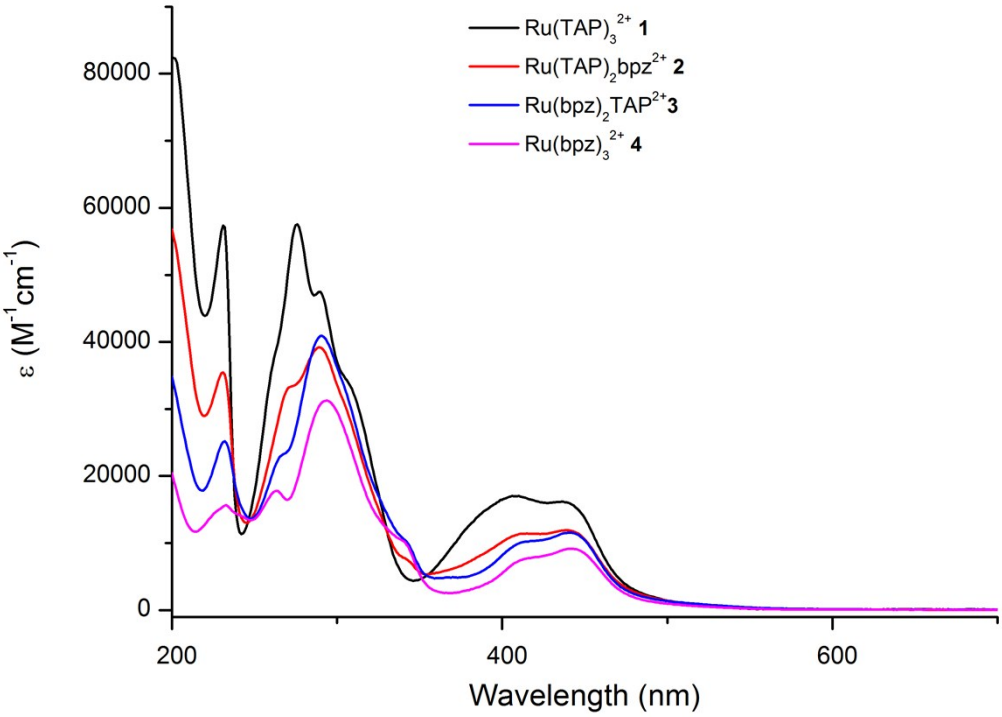
^{1}H-^{1}H COSY Ru(bpz)$_2$TAP^{2+}.2Cl^{-}, D$_2$O, 400MHz, 25°C

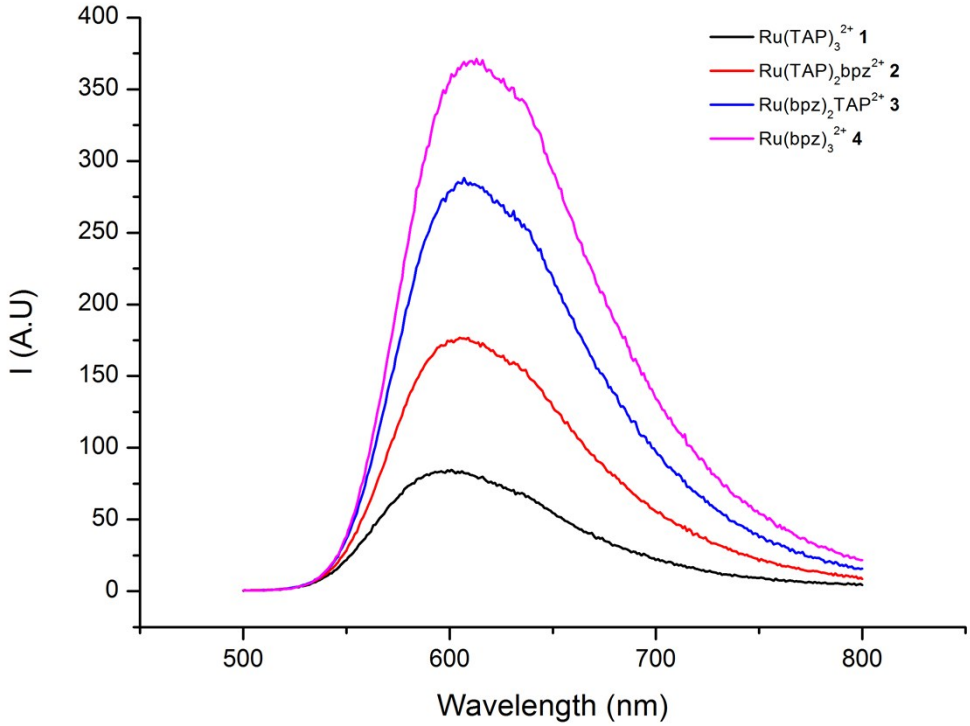


SI X4 : HR-MS of $[Ru(bpz)_2TAP]^{2+}$



SI X5 : Absorption and emission data in water





Absorption and emission data for $[Ru(TAP)_n(bpz)_{3-n}]^{2+}$ (n = 0-3) complexes measured in water. Extinction coefficient measured for the bathochromic transition.

Complex	Absorption (ε_λ, 10^3 L.mol^{-1}.cm^{-1})	Maximum of emission (nm)
$[Ru(\mathbf{TAP})_3]^{2+}$ **(1)**	231 nm (53.9 ± 11.8)	601
	276 nm, 289 nm (44.4 ± 9.2)	
	406 nm (16,2 ± 2.0)	
	440 nm (15.7 ± 5.9)	
$[Ru(\mathbf{TAP})_2\mathbf{bpz}]^{2+}$ **(2)**	231 nm (32.1 ± 1.8)	609
	269 nm, 289 nm (39.7 ± 2.3)	
	409 nm (11.4 ± 0.6)	
	439 nm (12.0 ± 0.7)	
$[Ru(\mathbf{bpz})_2\mathbf{TAP}]^{2+}$**(3)**	232 nm (24.9 ± 6.7)	607
	290 nm (40.1 ± 10.9)	
	417 nm (10.1 ± 2.7)	
	441 nm (11.4 ± 3.1)	
$[Ru(\mathbf{bpz})_3]^{2+}$ **(4)**	238 nm (14.4 ± 1.8)	611
	294 nm (32.7 ± 6.7)	
	411 nm (14.4 ± 1.8)	
	441 nm (9.2 ± 1.1)	

SI X6: Luminescence lifetimes and quantum yield of emission for $[Ru(TAP)_n(bpz)_{3-n}]^{2+}$ (n = 0-3) complexes measured under air at room temperature.

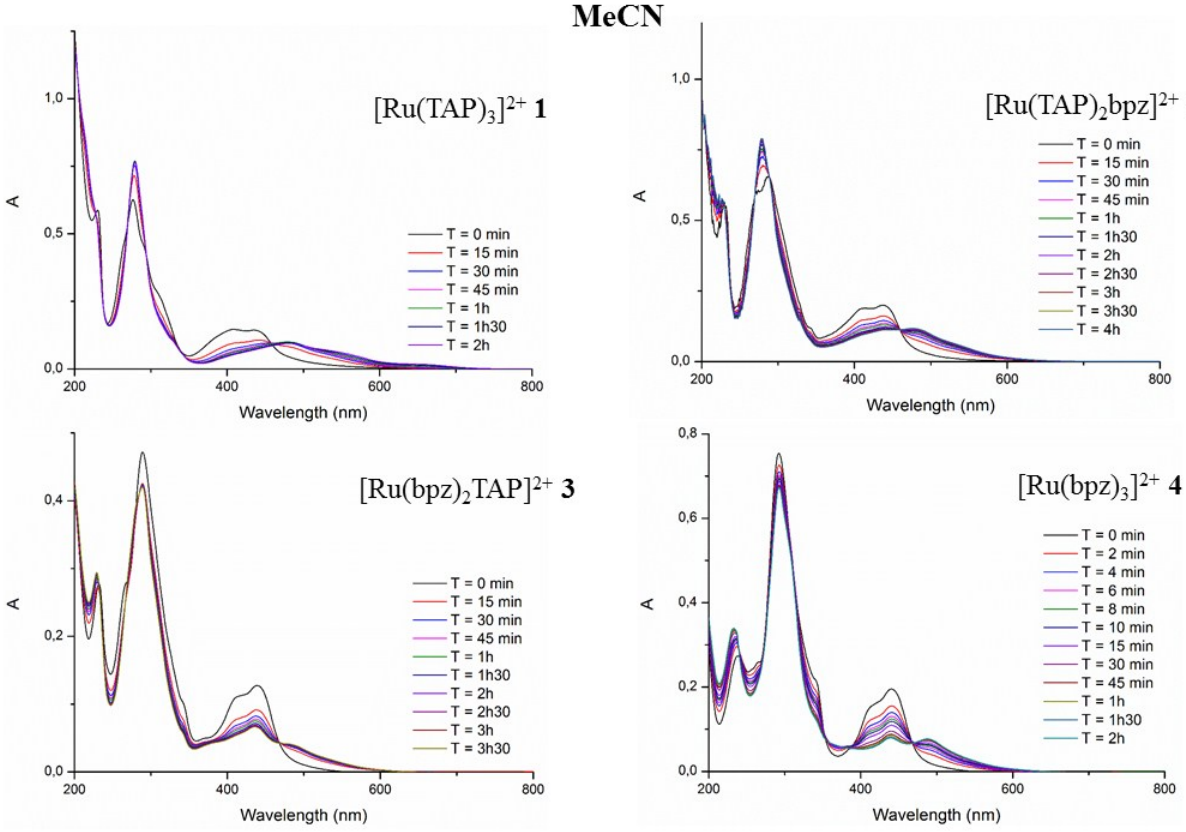
	Luminescence lifetimes (ns)		Luminescence quantum yield
	Water	MeCN	Water
	Air	Air	Air
Ref	-	-	0.028[34, 67]
1	174	55	0.013
2	353	101	0.029
3	635	242	0.043
4	810	480	0.055

SI X7: Deactivation rate constants for $[Ru(TAP)_n(bpz)_{3-n}]^{2+}$ (n = 0-3) complexes determined in water under air at room temperature.

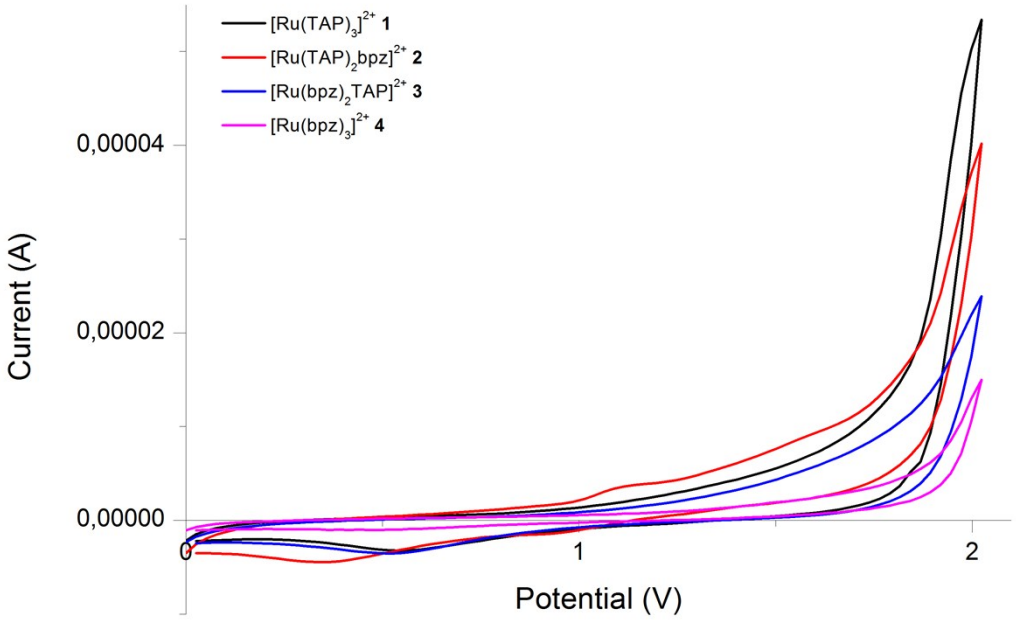
Complex	Water	
	Air	
	k_r	k_{nr}
1	6.64	481
2	7.52	250
3	6.36	141
4	6.37	111

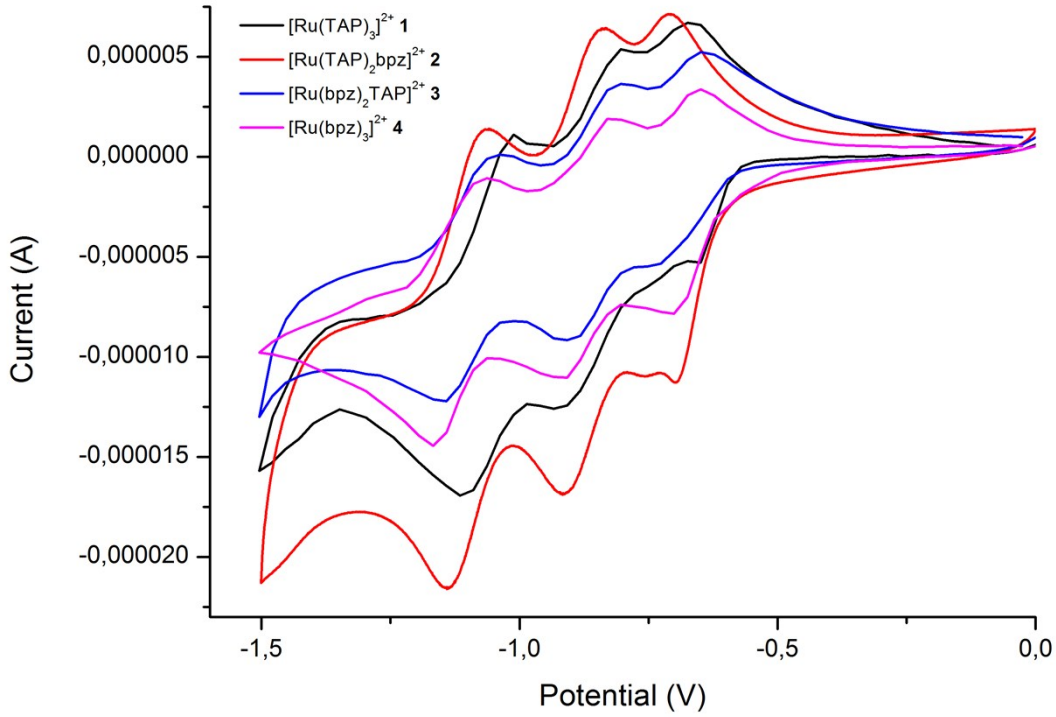
SI X8: Photostability study of the four complexes in acetonitrile. Illumination was performed using a 500W Xe lamp for maximum 4 hours.

MeCN



SI X9: Voltammogram of $[Ru(TAP)_n(bpz)_{3-n}]^{2+}$ (n = 0-3)





SI X10: HOMO and LUMO levels modelisation for $[Ru(TAP)_n(bpz)_{3-n}]^{2+}$ (n = 0-3)