Supplementary Information for

Heterodinuclear ruthenium(II)-cobalt(III) complexes as models for a new approach to selective cancer treatment

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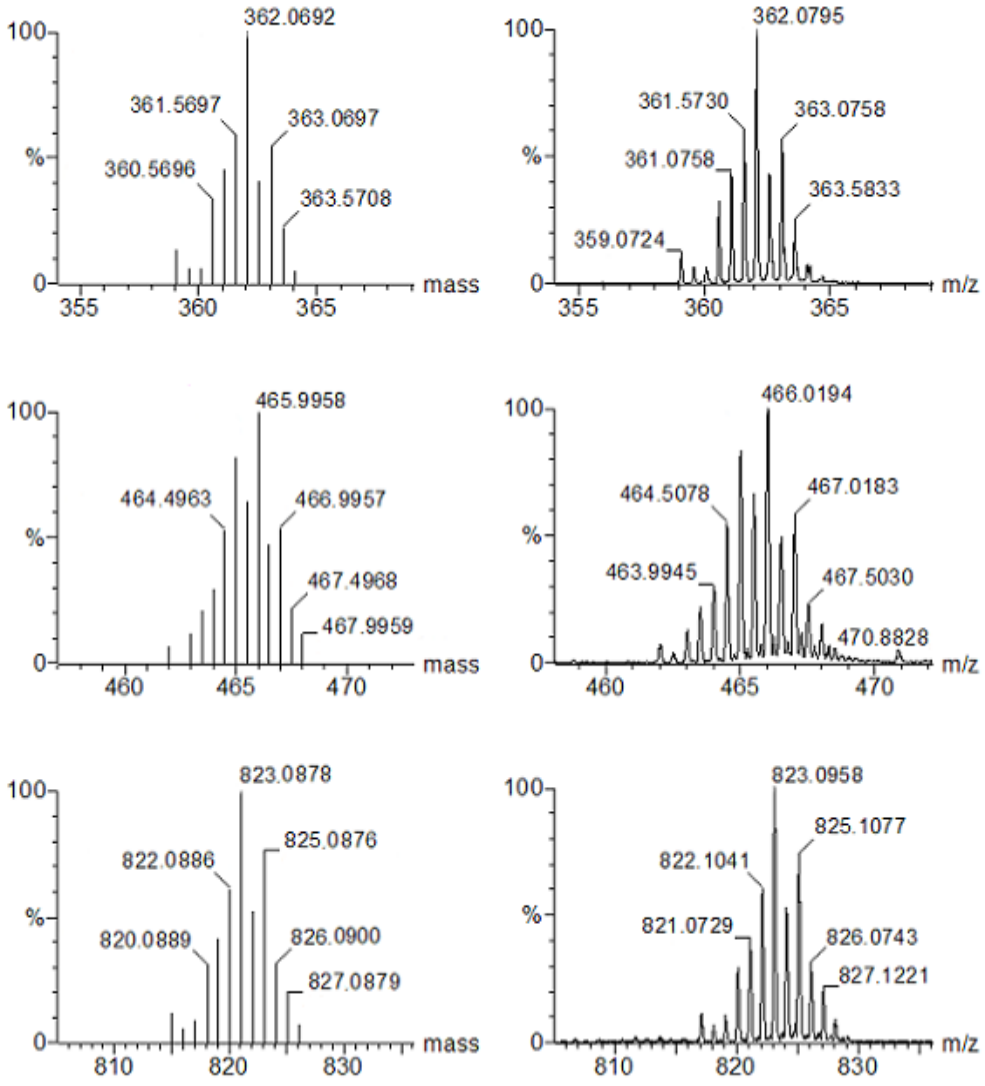

Figure S1: Modelled and experimental ESI-MS isotope patterns for $[Ru(bpy)_2(pytp)]^{2+}$, $[(bpy)_2Ru(pytp)Ag](ClO_4)^{2+}$ and $[Ru(bpy)_2(pytp)](ClO_4)+$ resulting from the addition of $AgClO_4$ to $[Ru(bpy)_2(pytp)](PF_6)_2$ in CH_3CN

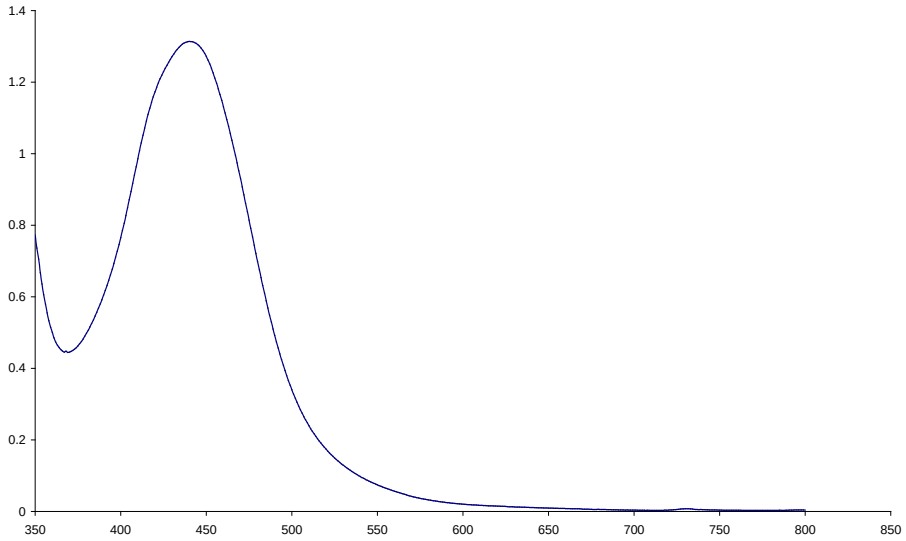

Figure S2: UV-vis absorption spectrum of $[Ru(bpy)_2(pytp)]^{2+}$ in CH_3CN

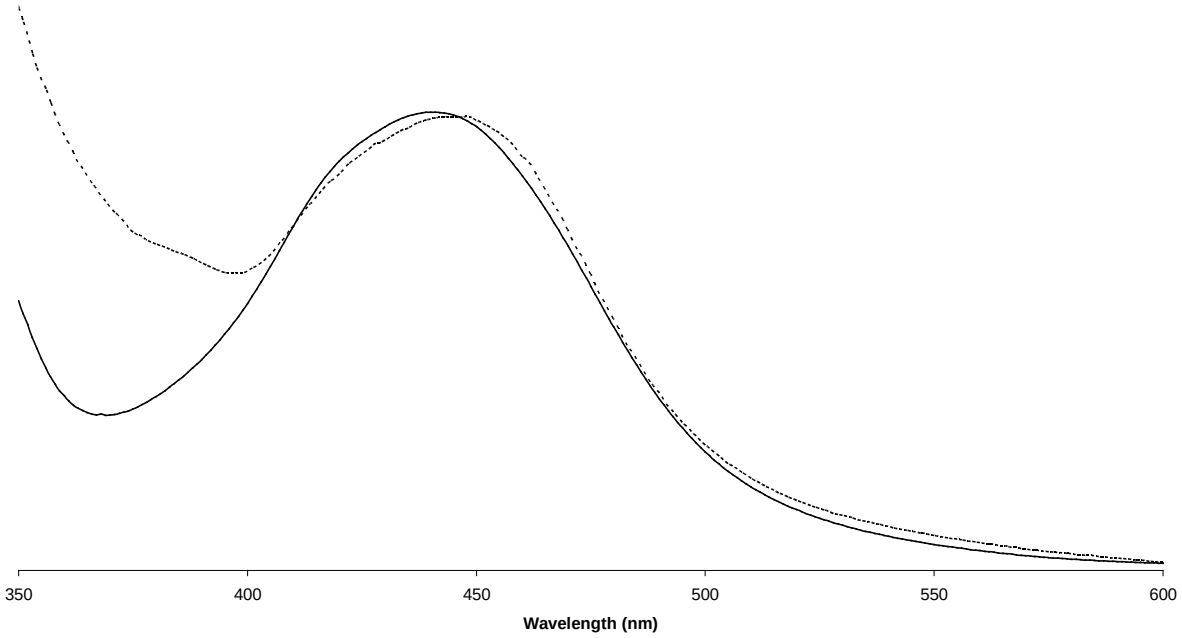

Figure S3: UV-visible spectra of $[Ru(bpy)_2(pytp)]^{2+}$ before (solid line) and after (dotted line) coordination of $[Co(en)_2]^{3+}$ in CH_3CN. The traces have been scaled to give a similar absorbance.

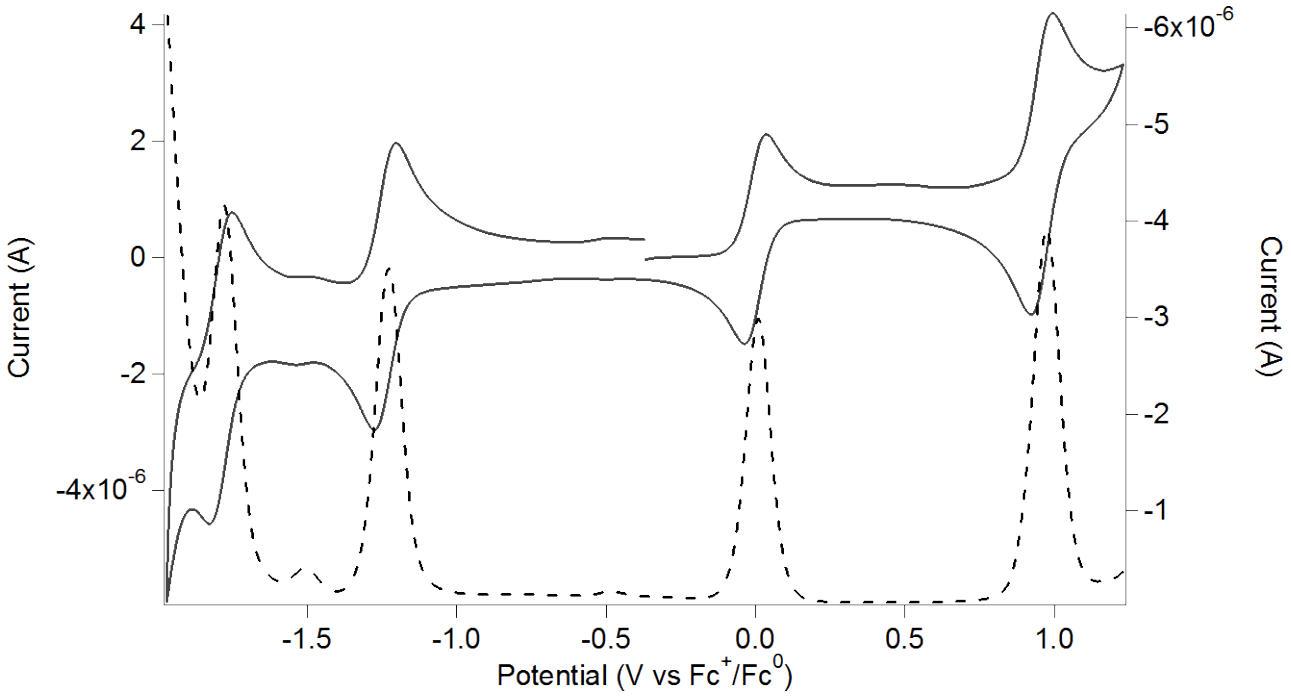

Figure S4: Cyclic voltammogram (solid line/left axis) and square wave voltammogram (dashed line/right axis) of $[Ru(bpy)_2(pytp)](PF_6)_2$, referenced to an internal Fc^+/Fc^0 standard.

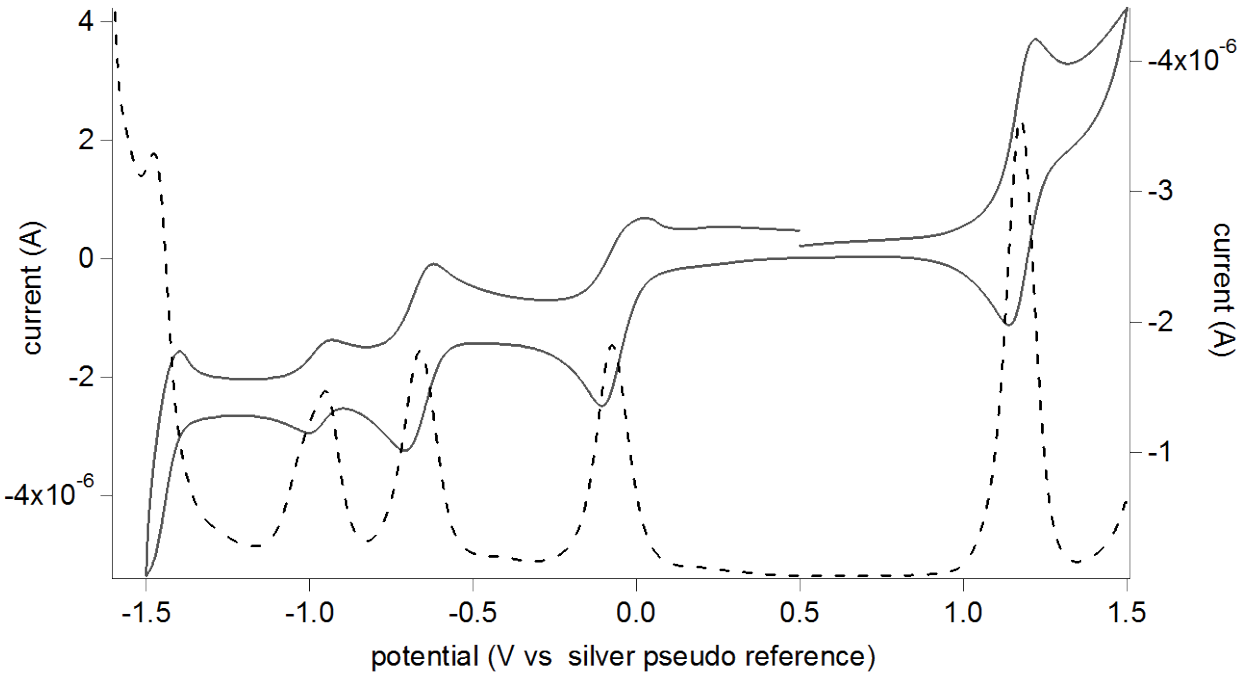

Figure S5: Unreferenced cyclic voltammogram (solid line/left axis) and square wave voltammogram (dashed line/right axis) of $[(bpy)_2Ru(pytp)Co(tren)](PF_6)_5$. The couple at approximately -1.0 V is likely due to the pytp based reduction of $[Ru(bpy)_2(pytp)]^{2+}$ resulting from either electrochemical or photo induced reduction of the Co(III) centre followed by ligand exchange.

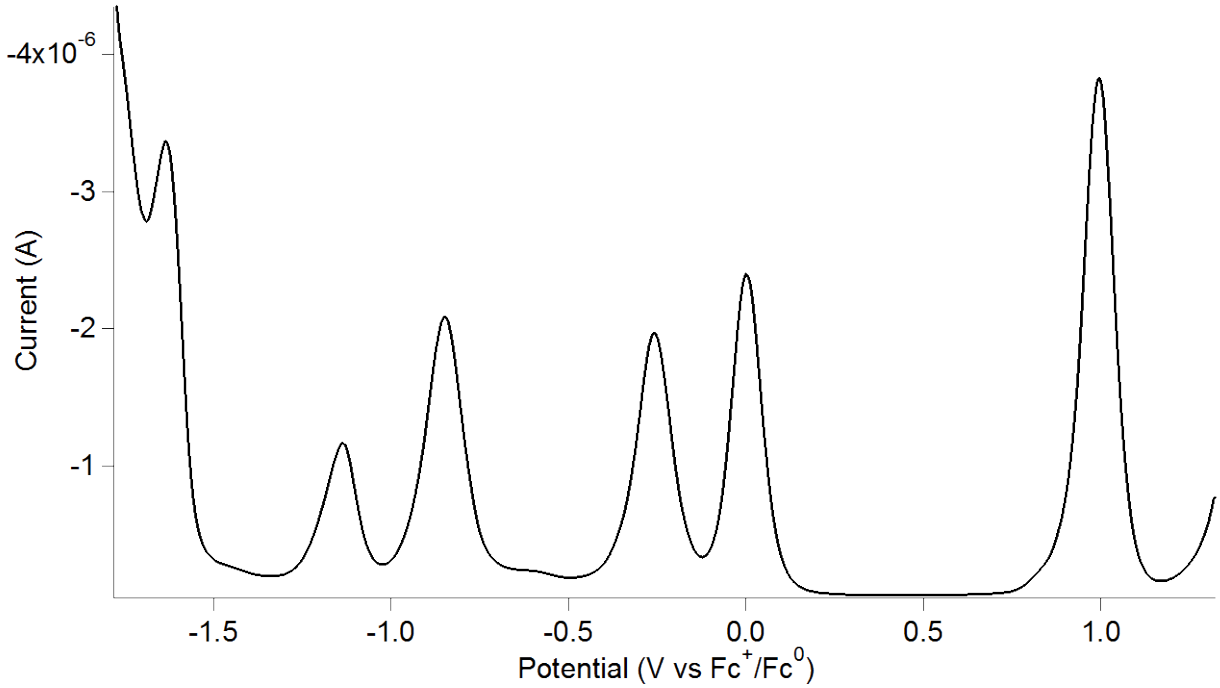

Figure S6: Square wave voltammogram of $[(bpy)_2Ru(pytp)Co(tren)](PF_6)_5$ with internal Fc^+/Fc^0 standard, as used for referencing of redox potentials.

Table S1: Crystal data and structure refinements

Identification code	pytp.2HCl	$Ru[(bpy)_2(pztp)](PF_6)_2 \cdot 1.5(CH_3CN)$
Empirical formula	$C_{18}H_{14}Cl_2N_6O$	$C_{40}H_{29.5}F_{12}N_{12.5}P_2Ru$
Formula weight	401.25	1076.27
Temperature/K	118(2)	118(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	8.3203(2)	11.8919(7)
b/Å	9.8047(3)	12.3372(7)
c/Å	11.3191(4)	15.9036(10)
α/°	112.3820(10)	81.000(4)
β/°	93.764(2)	77.789(4)
γ/°	93.041(2)	66.668(4)
Volume/$Å^3$	848.93(4)	2087.1(2)
Z	2	2
$\rho_{calc}mg/mm^3$	1.570	1.713
m/mm^{-1}	0.406	0.556
F(000)	412.0	1078.0
Crystal size/mm^3	0.24 × 0.19 × 0.17	0.24 × 0.19 × 0.17
2Θ range for data collection	4.92 to 60°	4.38 to 50.1°
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 13, -15 \leq l \leq 15$	$-14 \leq h \leq 14, -14 \leq k \leq 14, -18 \leq l \leq 18$
Reflections collected	22950	34975
Independent reflections	4919[R(int) = 0.0863]	7380[R(int) = 0.1090]
Data/restraints/parameters	4919/4/256	7380/0/636
Goodness-of-fit on F^2	1.030	1.003
Final R indexes [I>=2σ (I)]	$R_1 = 0.0366$, $wR_2 = 0.1012$	$R_1 = 0.0559$, $wR_2 = 0.1121$
Final R indexes [all data]	$R_1 = 0.0427$, $wR_2 = 0.1054$	$R_1 = 0.1193$, $wR_2 = 0.1393$
Largest diff. peak/hole /e $Å^{-3}$	0.51/-0.29	0.56/-0.57

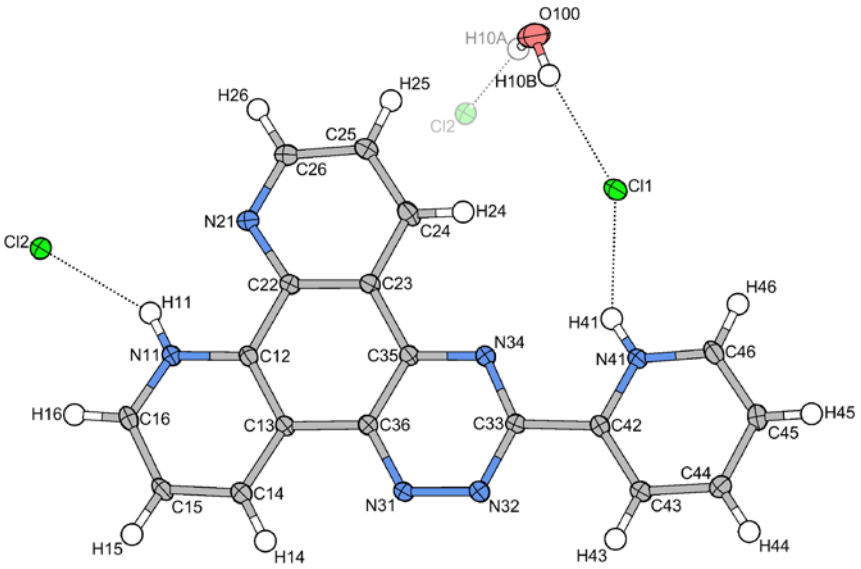

Figure S7: Numbering scheme for **pytp.2HCl**

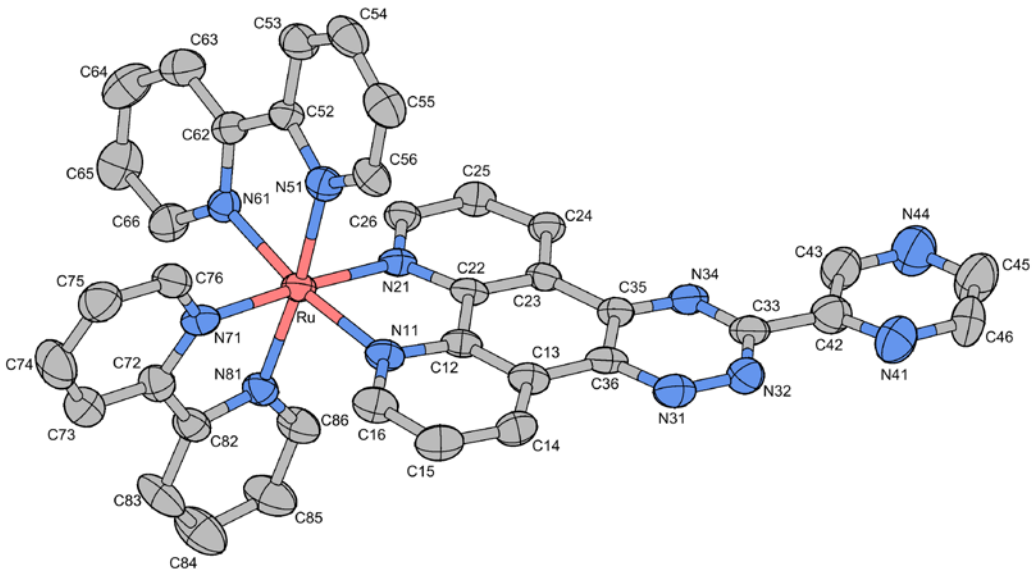

Figure S8: Numbering scheme for **Ru[(bpy)$_2$(pztp)](PF$_6$)$_2$•1.5(CH$_3$CN)**