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SUPPLEMENTARY MATERIAL

In Situ Spectroelectrochemical Investigations of Ru^{II} Complexes with Bispyrazolyl Methane Triarylamine Ligands

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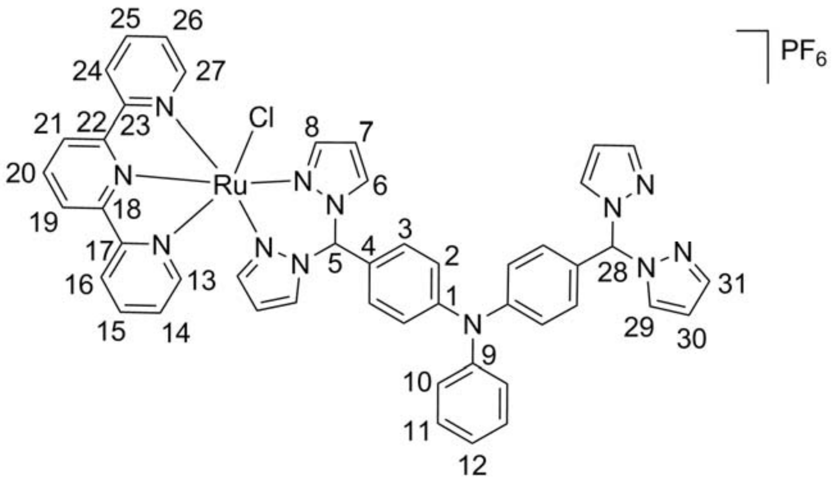
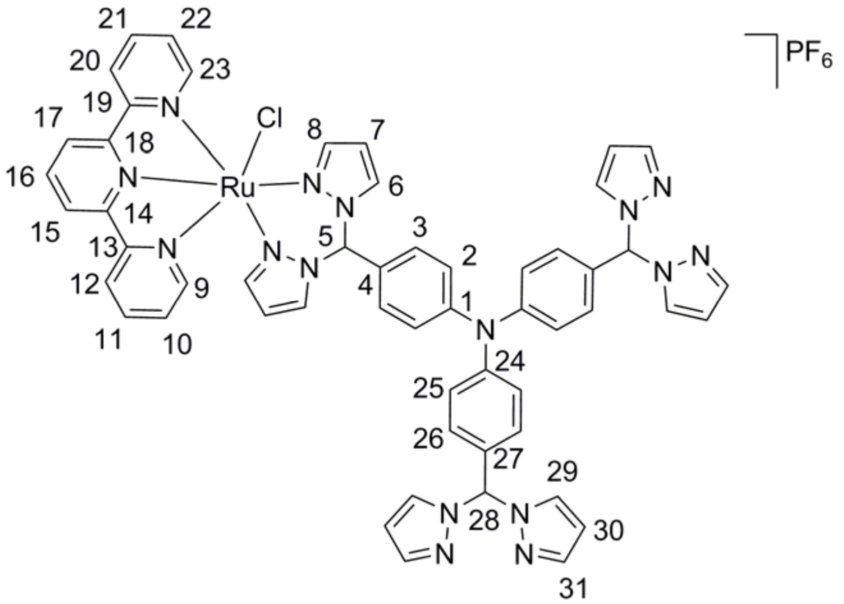
Experimental

[RuCl(tpy)(TPA-2bpm)]PF_6



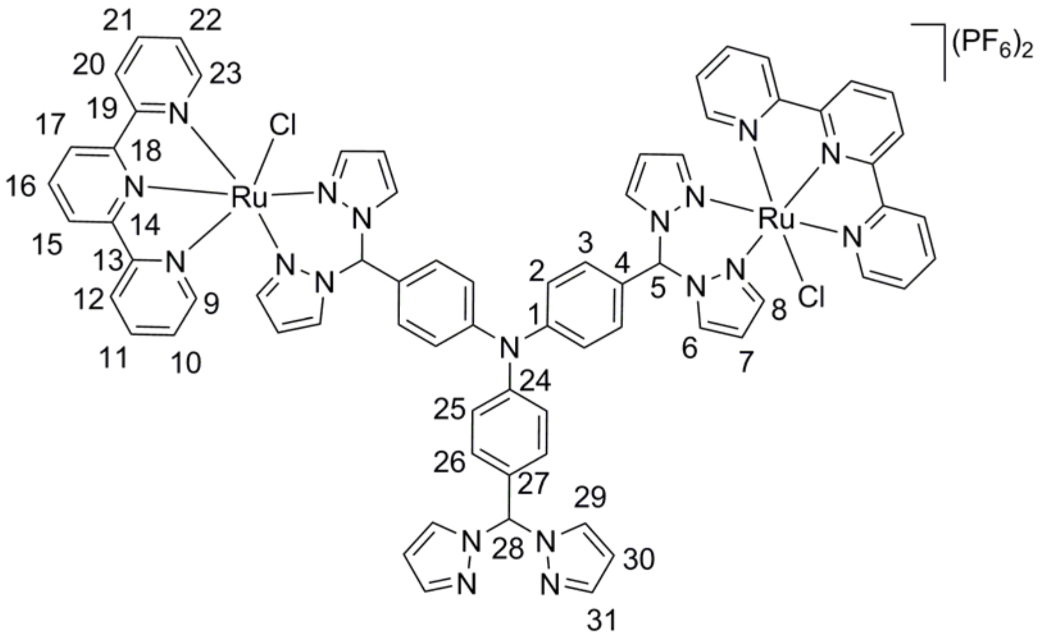
[1]H NMR (CD_3CN, 500 MHz): δ 9.01 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, **H6/H8**), 8.43 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, **H6/H8**), 8.38 (d, $^3J_{H-H}$ = 3.5 Hz, 1H, **H19**), 8.36 (d, $^3J_{H-H}$ = 3.5 Hz, 1H, **H21**), 8.30 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, **H16**), 8.24 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, **H24**), 7.99 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, **H20**), 7.93 (s, 1H, **H5**), 7.83 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, **H15**), 7.79 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, **H25**), 7.76 (br s, 3H, **H21**, **H29/H31**), 7.62 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, **H13**), 7.55 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, **H27**), 7.38 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, **H14**), 7.33 (t, $^3J_{H-H}$ = 6.0 Hz, 1H, **H12**), 7.18 (t, $^3J_{H-H}$ = 6.0 Hz, 1H, **H26**), 7.11 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, **H10/H11**), 7.04 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, **H10/H11**), 6.96 (t, $^3J_{H-H}$ = 2.5 Hz, 2H, **H7**), 6.77 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, **H2/H3**), 6.44 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, **H22/H24**), 6.26 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, **H2/H3**), 6.07 (t, $^3J_{H-H}$ = 2.0 Hz, 2H, **H23**) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 161.2 (**C18**), 161.1 (**C22**), 160.0 (**C17**), 159.6 (**C23**), 154.5 (**C9**), 149.9 (**C22/C24**), 148.7 (**C1**), 148.2 (**C6/C8**), 145.9 (**C6/C8**), 141.3 (**C13**), 137.7 (**C6/C8**, **C15**, **C29/C31**, **C28**), 137.0 (**C15'**), 134.6 (**C20**), 130.9 (**C14**), 130.8 (**C13'**), 129.4 (**C10/C11**), 128.1 (**C12**), 127.9 (**C4**), 127.5 (**C10/C11**), 126.3 (**C14'**), 124.4 (**C16**), 124.1 (**C16'**),123.1 (**C19**), 123.0 (**C19'**), 121.6 (**C2/C3**), 109.0 (**C7**), 108.8 (**C30**), 107.2 (**C2/C3**), 77.7 (**C21**), 76.5 (**C5**) ppm. Elemental Analysis: Found C, 53.54; H, 3.52 and N, 15.82%; Calculated for $C_{47}H_{38}ClF_6N_{12}PRu$: C, 53.64; H, 3.64; N, 15.97%. ESI-MS (ESI^+, MeOH): 906.93 (Calculated $[M-PF_6]^+$ = 907.21, 100%) amu.

[RuCl(tpy)(TPA-3bpm)]PF_6



^{1}H NMR (CD_3CN, 500 MHz): δ 9.01 (br s, 2H, **H6**/**H8**), 8.46 (br s, 2H, **H6**/**H8**), 8.39 (t, $^3J_{H\text{-}H}$ = 3.8 Hz, 1H, **H16**), 8.32 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H12**), 8.25 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H20**), 8.03-7.95 (m, 2H, **H15**, **H17**), 7.95 (s, 1H, **H5**), 7.87 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H11**), 7.79 (br s, 4H, **H29**/**H31**), 7.77 (s, 2H, **H28**), 7.75 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H21**), 7.64 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H9**), 7.56 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H22**), 7.34 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H10**), 7.11 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, **H25/H26**), 7.09 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, **H23**), 7.07 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, **H25/H26**), 6.96 (t, $^3J_{H\text{-}H}$ = 2.0 Hz, 2H, **H7**), 6.83 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, **H3**), 6.45 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 4H, **H29/H31**), 6.30 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, **H2**), 6.08 (t, $^3J_{H\text{-}H}$ = 2.0 Hz, 2H, **H30**) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 161.3 (**C14/C18**), 161.2 (**C14/C18**), 160.1 (**C13**/**C19**), 159.8 (**C13**/**C19**), 154.7 (**C24**), 153.5 (**C1**), 148.8 (**C6**/**C8**), 146.0 (**C29**/**C30**), 141.4 (**C22**), 137.8 (**C6**/**C8**), 137.7 (**C29**/**C31**), 137.7 (**C11**), 137.1 (**C21**), 134.7 (**C15**, **C17**), 133.6 (**C2**), 131.0 (**C9**), 129.7 (**C25**), 130.1 (**C27**), 128.2 (**C4**), 128.1 (**C10**), 127.5 (**C23**), 126.3 (**C26**), 125.0 (**C12**), 124.5 (**C20**), 123.1 (**C16**), 122.6 (**C3**), 109.1 (**C7**), 108.7 (**C30**), 107.3 (**C2**/**C3**), 77.8 (**C28**), 76.6 (**C5**) ppm. Elemental Analysis: Found C, 54.25; H, 3.95 and N, 18.72; Calculated for $C_{54}H_{44}ClF_6N_{16}PRu$: C, 54.12; H, 3.70; N, 18.70%. ESI-MS (ESI^+, MeOH): 1053.13 (Calculated $[M\text{-}PF_6]^+$ = 1053.27, 100%) amu.

[Ru_2Cl_2(tpy)$_2$(TPA-3bpm)](PF_6)$_2$



[1]H NMR (CD_3CN, 500 MHz): δ 9.02 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 1H, **H6/H8**), 8.57 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 4H, **H6/H8**), 8.42-8.38 (m, 4H, **H15** and **H17**), 8.33 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, **H12**), 8.23 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, **H20**), 8.17 (s, 1H, **H28**), 8.01 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, **H16**), 7.90-7.87 (m, 6H, **H29/H31**, **H11**), 7.83 (s, 2H, H5), 7.66-7.64 (m, 2H, **H21**), 7.56-7.54 (m, 2H, **H9**), 7.49 (d, $^3J_{H\text{-}H}$ = 5.5 Hz, 2H, **H23**), 7.34 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, **H10**), 7.19-7.16 (m, 4H, **H25**, **H26**), 6.99 (t, $^3J_{H\text{-}H}$ = 2.0 Hz, 2H, **H7**), 6.95 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, **H22**), 6.82 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, **H2/H3**), 6.47 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 2H, **H29/H31**), 6.253 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, **H2/H3**), 6.12 (t, $^3J_{H\text{-}H}$ = 2.0 Hz, 2H, **H30**) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 161.4 (**C14/C18**), 161.3 (**C14/C18**), 160.0 (**C13**), 159.8 (**C19**), 148.9 (**C4**), 148.8 (**C6/C8**), 147.2 (**C27**), 146.2 (**C29/C31**), 141.5 (**C9**), 141.4 (**C23**), 138.1 (**C11**), 138.1 (**C6/C8**), 137.9 (**C29/C31**), 134.8 (**C16**), 131.1 (**C21**), 131.0 (**C1**), 130.1 (**C24**), 129.7 (**C25/C26**), 128.3 (**C10**), 128.3 (**C25/C26**), 127.8 (**C2/C3**), 126.3 (**C22**), 124.6 (**C12**), 123.9 (**C20**), 123.8 (**C2/C3**), 123.2 (**C15/C17**), 123.1 (**C15/C17**), 109.2 (**C30**), 108.9 (**C7**), 77.7 (**C5**), 76.4 (**C28**) ppm. Elemental Analysis: Found C, 48.21; H, 3.22 and N, 15.73; Calculated for $C_{69}H_{55}Cl_2F_{12}N_{19}P_2Ru_2$: C, 48.37; H, 3.24; N, 15.53%. ESI-MS (ESI$^+$, MeOH): 712.33 (Calculated $[M\text{-}2PF_6]^{2+}$ = 711.62, 100%) amu.

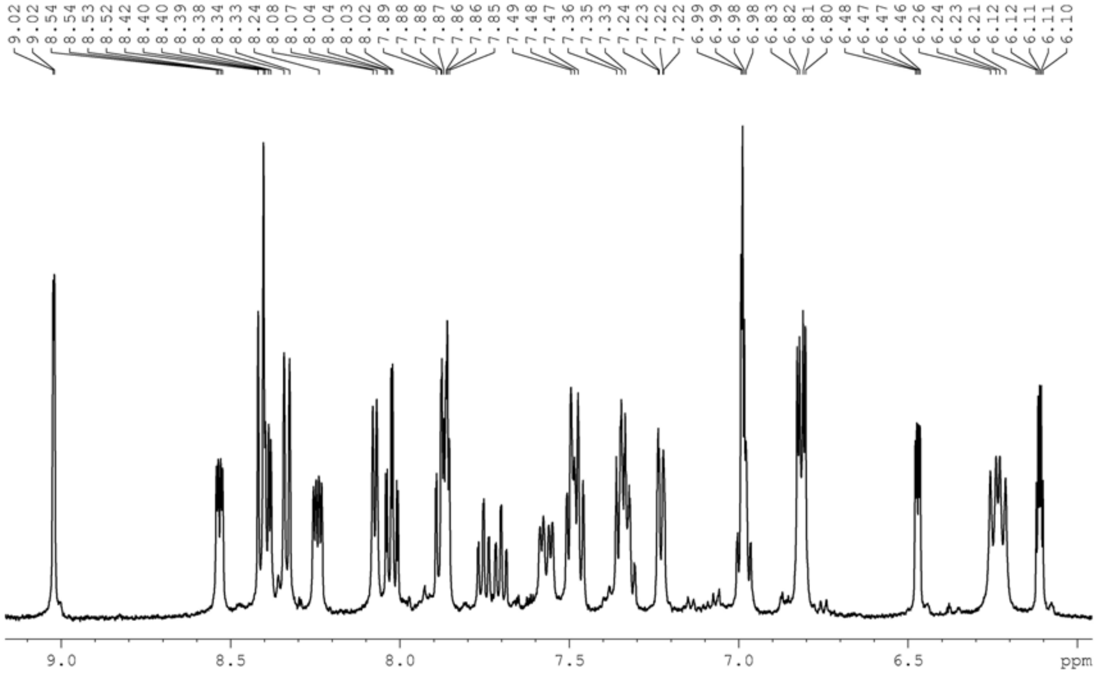


Figure S1. Solution state [1]H NMR spectrum of $[Ru_2Cl_2(tpy)_2(TPA\text{-}2bpm)](PF_6)_2$ recorded at 500 MHz in CD_3CN.

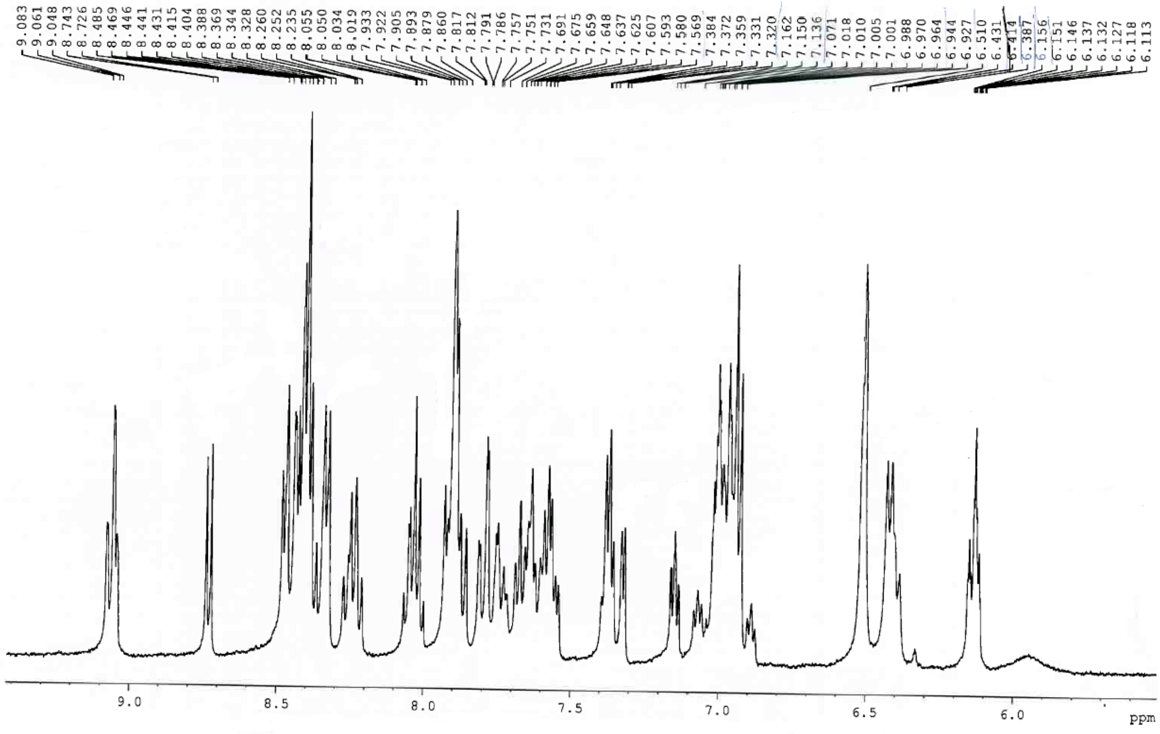


Figure S2. Solution state [1]H NMR spectrum of $[Ru_3Cl_3(tpy)_3(TPA\text{-}3bpm)](PF_6)_3$ recorded at 500 MHz in CD_3CN.

Table A1.1. Crystal data and structure refinement details for **TPA-2bpm**

Parameter	
Formula	$C_{32}H_{27}N_9$
M/g mol^{-1}	537.63
Temperature (K)	150(2)
Crystal system	Triclinic
Crystal size (mm^3)	0.188 × 0.144 × 0.100
Crystal colour	Colourless
Crystal Habit	Block
a (Å)	9.9607(3)
b (Å)	12.2145(3)
c (Å)	12.9010(4)
α (°)	110.727(3)
β (°)	102.826(2)
γ (°)	101.316(2)
V (Å^3)	1364.85(7)
Z	2
ρ_{calc} (mg/mm^3)	1.308
λ(CuKα)	1.54178 Å
μ(CuKα)	0.652 mm^{-1}
T(CRYSALISPRO)$_{min,max}$	0.93508, 1.000000
$2\theta_{max}$	151.82°
hkl range	-12 12, -15 14, -16 16
Reflections collected	24161/5651[R(int) = 0.0196]
Data/parameters	5022/370
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1369
Goodness-of-fit on F^2	1.076
Residual Extrema	-0.508, 0.570 $e^-Å^{-3}$

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.0452P)^2+0.9594P]$ where $P=(F_o^2+2F_c^2)/3$

Table A1.2. Crystal data and structure refinement details for **TPA-3bpm**

Parameter	
Formula	$C_{39}H_{33}N_{13}O_{1.62}$
M/g mol^{-1}	709.65
Temperature (K)	100(1)
Crystal system	Hexagonal
Crystal size (mm^3)	0.10 × 0.10 × 0.06
Crystal colour	Colourless
Crystal Habit	plate
a (Å)	11.903(2)
b (Å)	11.903(2)
c (Å)	14.466(3)
γ (°)	120
V (Å^3)	1775.0(7)
Z	2
ρ_{calc} (mg/mm^3)	1.328
λ(Synchrotron)	0.7109 Å
μ(Synchrotron)	0.087 mm^{-1}
hkl range	-15 15, -15 15, -18 18
Reflections collected	27876/1410[R(int) = 0.0701]
Data/parameters	1286/152
Final R indexes [all data]	R_1 = 0.0761, wR_2 = 0.1801
Goodness-of-fit on F^2	1.124
Residual Extrema	-0.186, 0.189 e$^-$Å^{-3}

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2/\Sigma\{w(F_o^2)^2\}]^{1/2}$, $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/S(wF_c^2)^2)^{1/2}$ all reflections $w=1/[s^2(F_o^2)+(0.0560P)^2+1.1154P]$ where $P=(F_o^2+2F_c^2)/3$

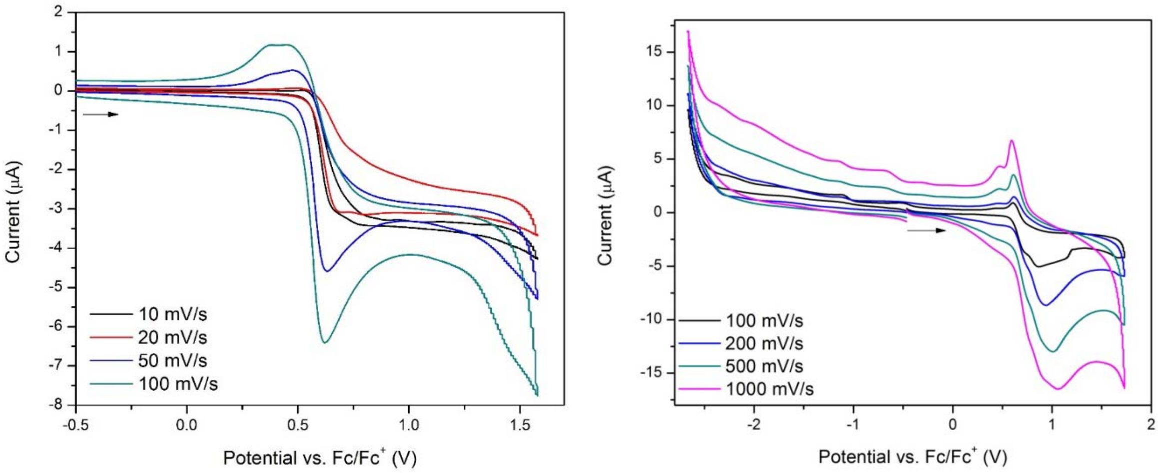


Figure S3. Solution state electrochemistry on **TPA-2bpm** in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte at scan rates of a) 10-100 mV/s and b) $[(n\text{-}C_4H_9)_4N]PF_6/CH_2Cl_2$ electrolyte at scan rates of 100-1000 mV/s where the arrow indicates the direction of the forward scan.

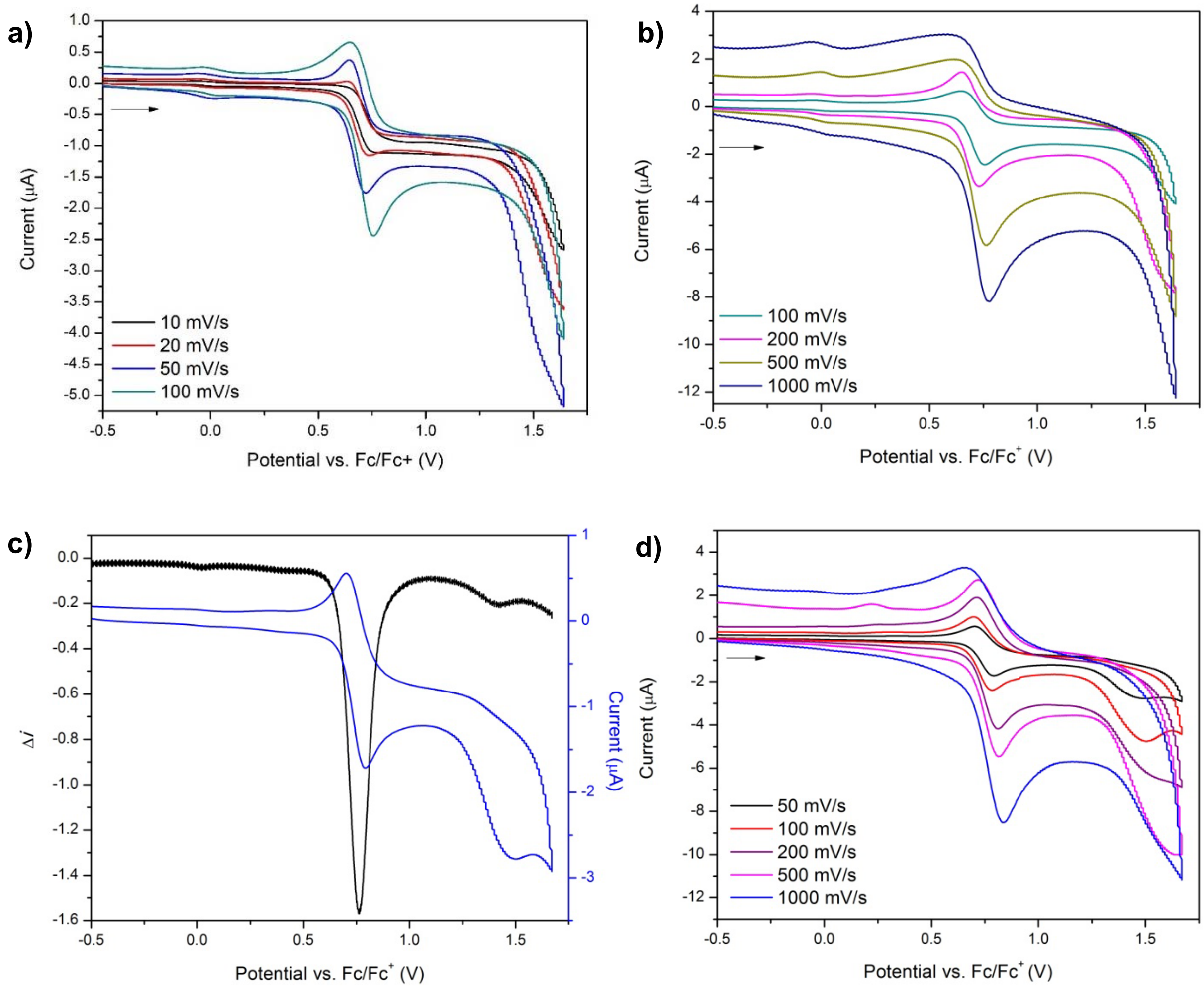


Figure S4. Solution state electrochemistry on **TPA-3bpm** in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte, referenced against the Fc/Fc^+ couple at scan rates of a) 10-100 mV/s, b) 100-1000 mV/s, c) square wave voltammogram at 10 mV and 39 Hz against the cyclic voltammogram at 50 mV/s and d) scan rates of 50-1000 mV/s in $[(n\text{-}C_4H_9)_4N]PF_6/CH_2Cl_2$ electrolyte.

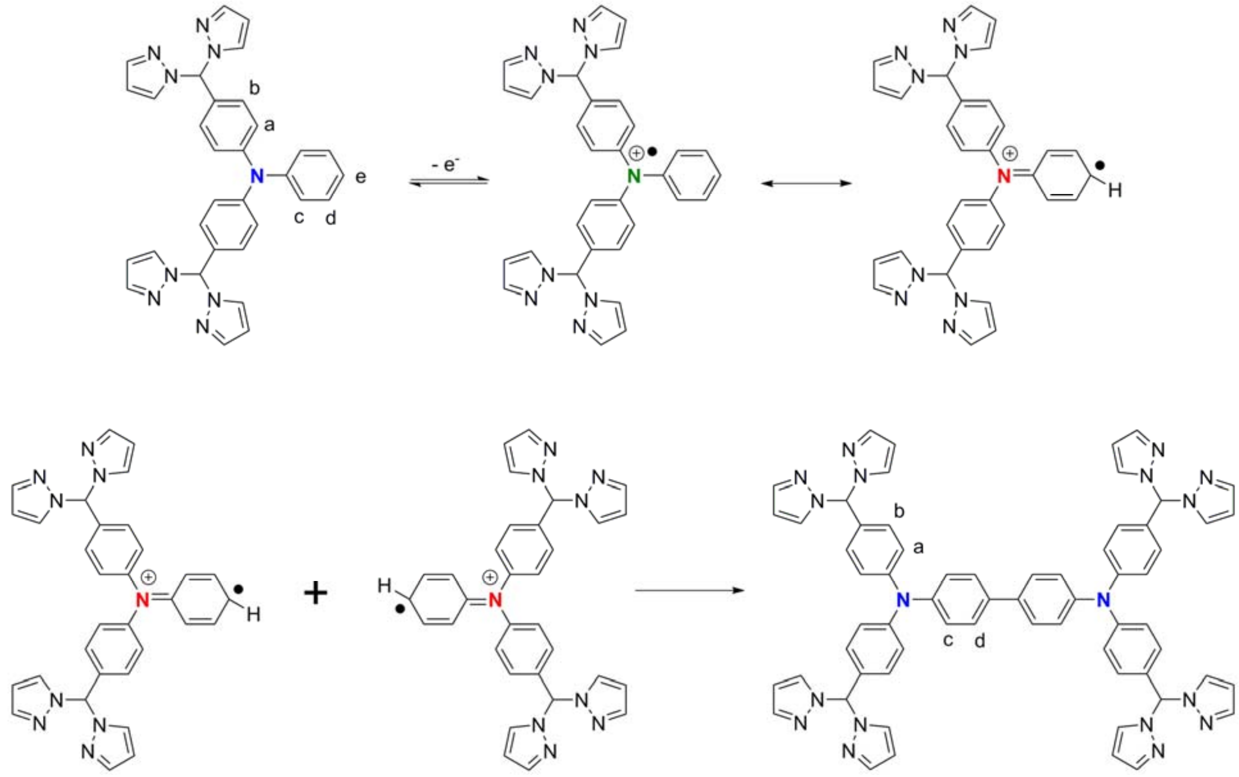


Figure S5. Mechanism of the dimerisation of **TPA-2bpm** upon oxidation to form the triarylamine radical cation.

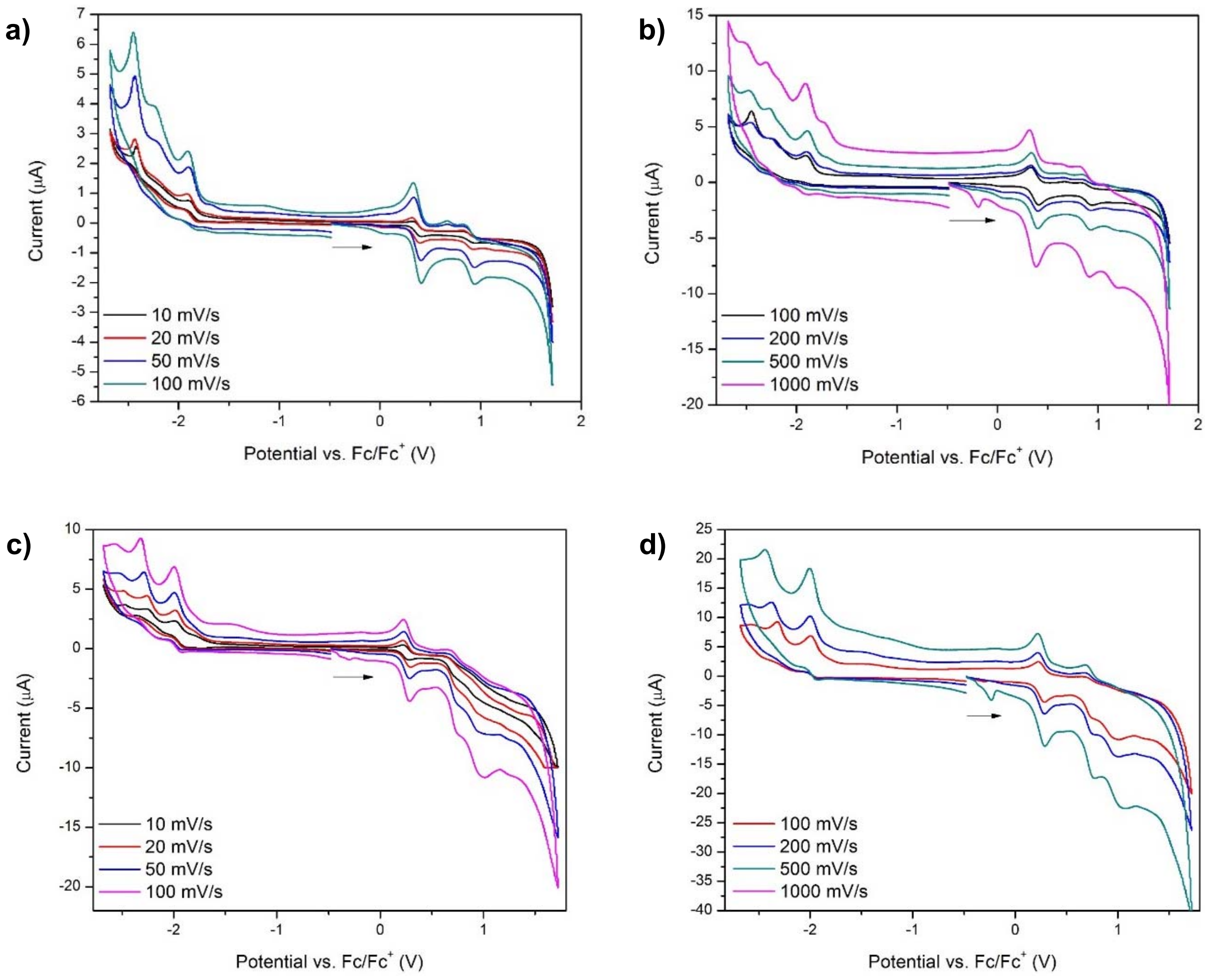


Figure S6. Cyclic voltammograms of $[Ru_2Cl_2(tpy)_2(TPA\text{-}2bpm)](PF_6)_2$ at scan rates of a) 10-100 mV/s and b) 100-1000 mV/s and $[RuCl(tpy)(TPA\text{-}3bpm)]PF_6$ at different scan rates where c) 10-100 mV/s and d) 100-1000 mV/s in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte.

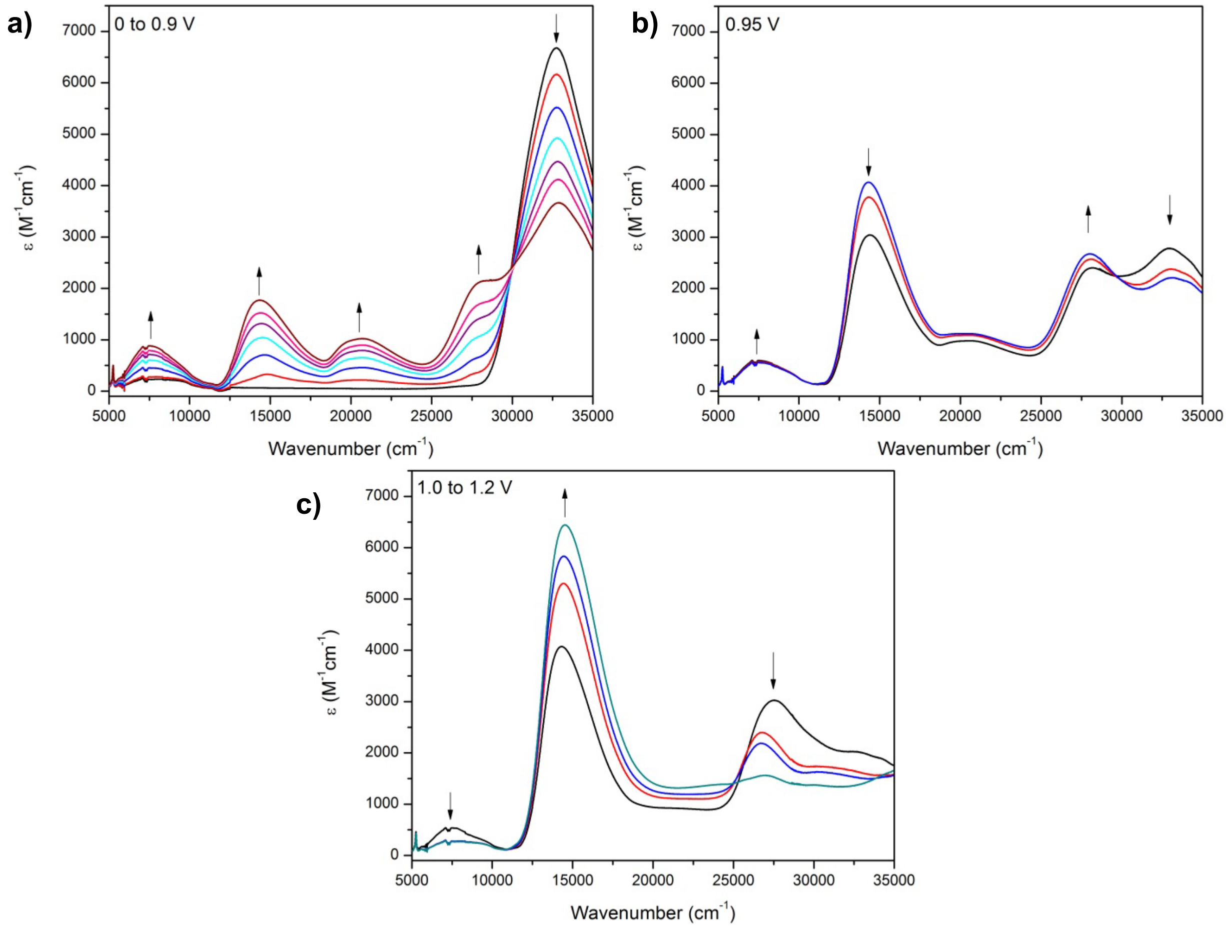


Figure S7. Solution state spectroelectrochemistry of **TPA-2bpm** in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte a) upon increasing the potential from 0 to 0.9 V, b) holding at 0.95 V and c) increasing the potential from 1.0 to 1.2 V.

Table S3. Parameters used in the IVCT analysis of the NIR bands of the TPA-2bpm ligand and $[Ru_2Cl_2(tpy)2(TPA\text{-}2bpm)](PF_6)_2$.

	ν_{max}/cm^{-1}	ε_{max}/$M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$/cm^{-1}	$\nu_{1/2}$ (high) /cm^{-1}	$\Delta\nu_{1/2}°$/cm^{-1}	H_{ab}/cm^{-1}	r_{ab}/Å
TPA-2bpm	7582	881	3325	1896	4185	337	9.72
$[Ru_2Cl_2(tpy)_2(TPA\text{-}2bpm)](PF_6)_2$	7783	2620	3495	1974	4240	566	9.72

Calculation of $\Delta\nu_{1/2}°$ [1-3]

$$\Delta\nu_{1/2}° = [16RT \times \log_e(2) \times \nu_{max}]^{1/2}$$

$$= [2310 \times \nu_{max}]^{1/2}$$

Calculation of H_{ab} [1-3]

$$H_{ab} = 0.0206(\nu_{max} \times \varepsilon_{max} \times \Delta\nu_{1/2})^{1/2} / r_{ab}$$

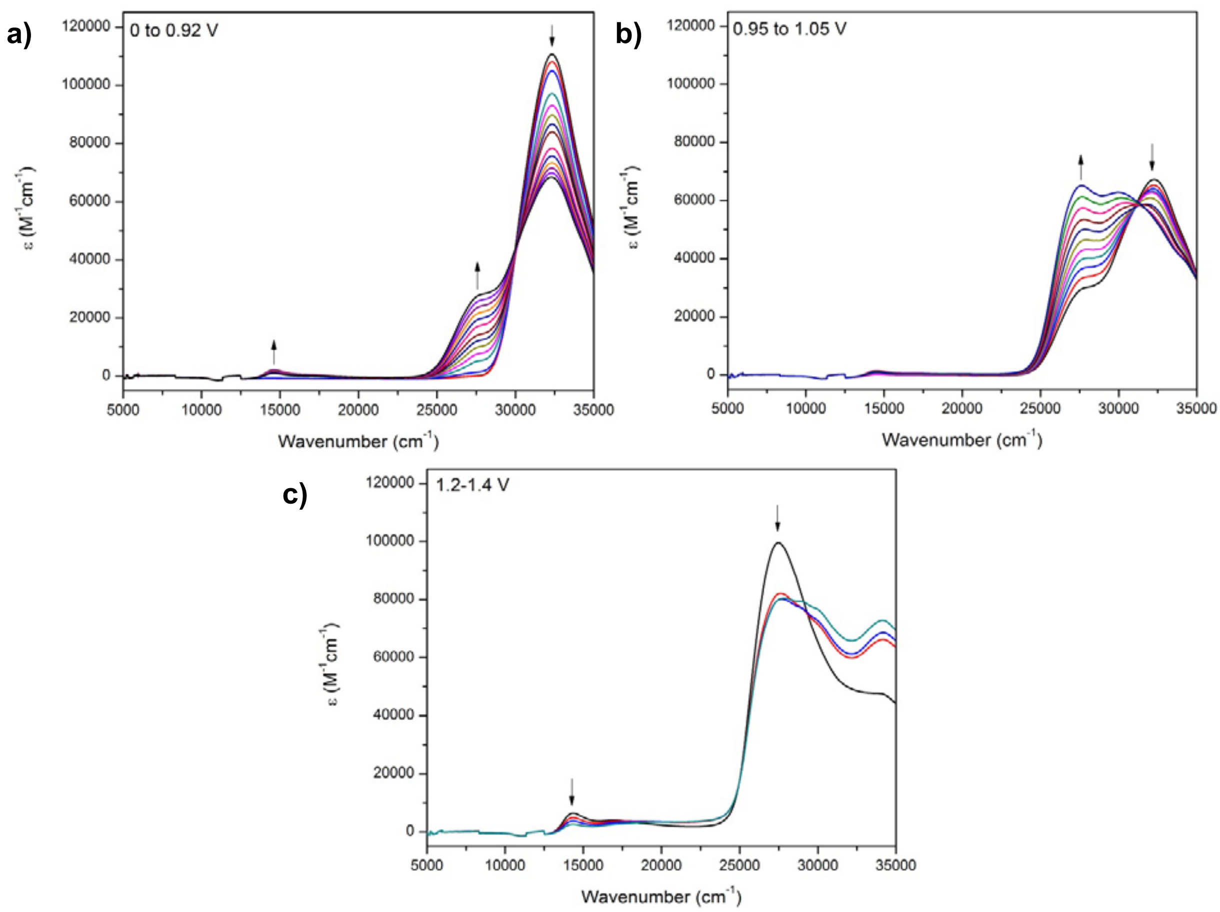


Figure S8. Solution state spectroelectrochemistry of **TPA-3bpm** in [(*n*-$C_4H_9)_4N]PF_6/CH_3CN$ electrolyte upon increasing the potential from a) 0 to 0.92 V, b) 0.95 to 1.05 V and c) 1.0 to 1.15 V.

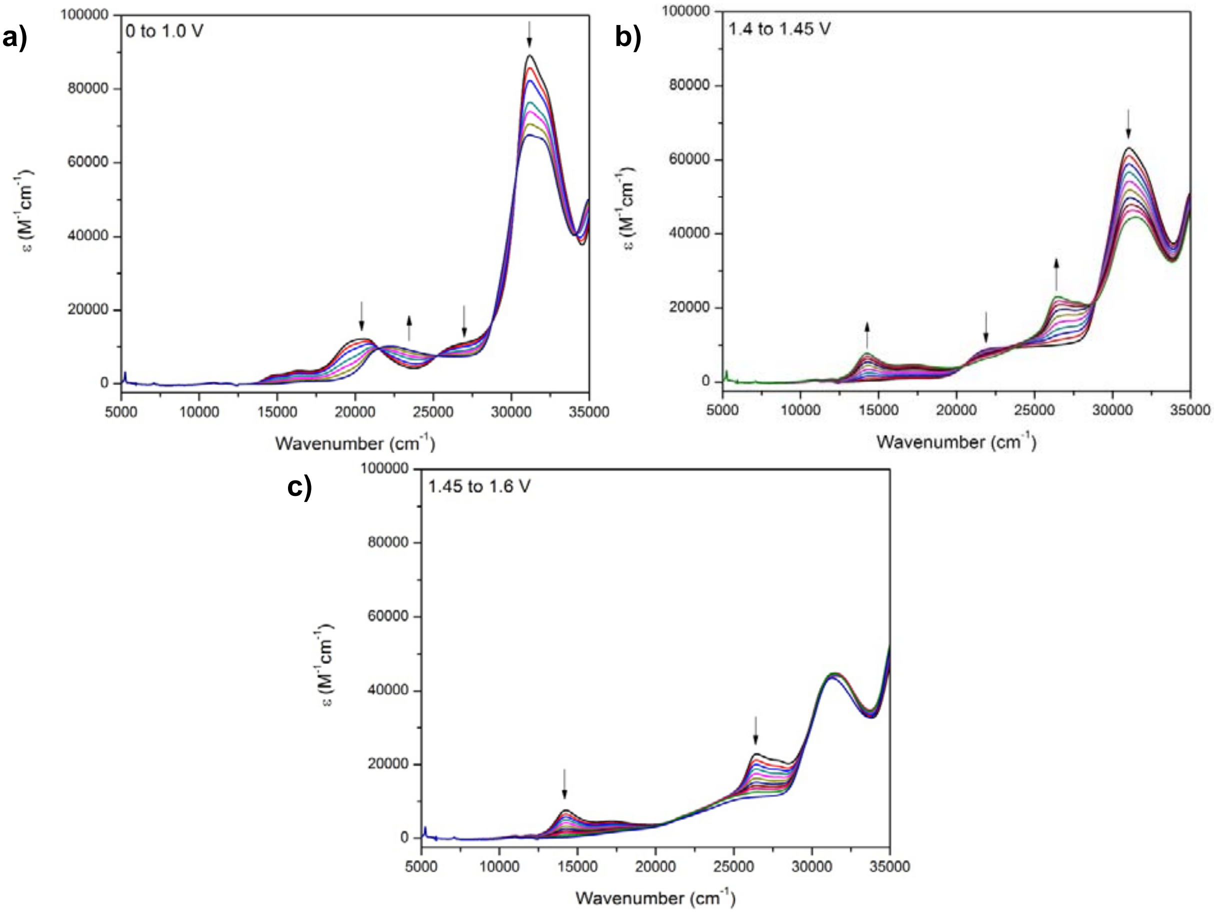


Figure S9. Solution state UV/Vis/NIR spectroelectrochemistry of $[Ru_3Cl_3(tpy)_3(TPA\text{-}3bpm)](PF_6)_3$ in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte where the potential was increased from a) 0 to 1.0 V, b) 1.4 to 1.45 V and c) 1.45 to 1.6 V.

Table S4. *g*-factor and hyperfine coupling values for the Ru(II) complexes containing the **TPA-3bpm** ligand.

Compound	**g-factor**	**A (MHz) for N**
$[Ru(tpy)Cl(TPA\text{-}3bpm)]PF_6$	2.0068	26.7
$[Ru_2(tpy)_2Cl_2(TPA\text{-}3bpm)](PF_6)_2$	2.0069	26.7
$[Ru_3(tpy)_3Cl_3(TPA\text{-}3bpm)](PF_6)_3$	2.0071	26.7

Table S5. Simulation parameters for the ^{14}N and ^{1}H nuclei in $[Ru(tpy)Cl(TPA\text{-}3bpm)]PF_6$ as a frozen solution at X-band and Q-band.

	g_x (N)	**g_y (N)**	**g_z (N)**	**A (MHz)**	**Line Broadening (Voigtian)**	**g (H)**	**A (MHz)**
X-band (5 K)	1.985	1.9985	2.0115	9.8	0.25, 0.25	1.9985	15.4
Q-band (50 K)	1.9915	1.9957	1.9995	9.8	0.25, 0.25	1.9957	15.4

Table S6. Simulation parameters for the ^{14}N and ^{1}H nuclei in [Ru(tpy)Cl(TPA-3bpm)]PF_6 as a solution at X-band.

Nucleus	g	A (MHz)	Correlation Time (s)	Line broadening (Voigtian)	No. Of Nuclei
N	2.0069	25.3	1×10^{-8}	0.45, 0.4	1
H	2.005	15.4		0, 0.1	6

Table S7. Simulation parameters for Ru^{3+} in [Ru(tpy)Cl(TPA-3bpm)]PF_6 as a frozen solution at X-band.

	g_x (Ru^{3+})	g_y (Ru^{3+})	g_z (Ru^{3+})	$A_{\|\|}$ (MHz)	$A_{\perp}$ (MHz)	Line Broadening (Voigtian)
X-band (5 K)	2.5	2.32	1.99	238	11.2	4.5, 4.5

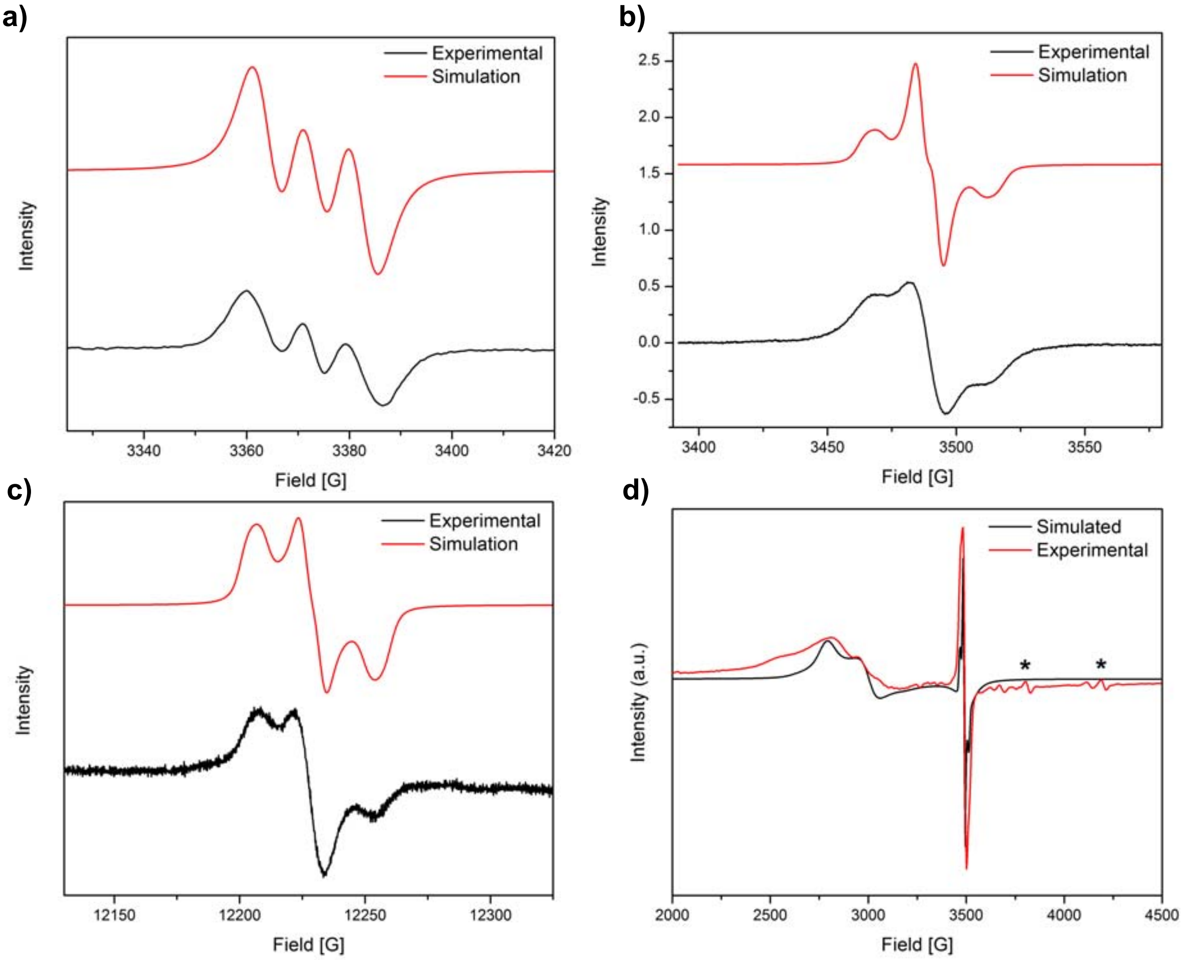


Figure S10. EPR spectroelectrochemistry of $[Ru(tpy)Cl(TPA\text{-}3bpm)]PF_6$ in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte showing the simulated vs. experimental spectrum of the radical a) in solution at 240 K at X-band, b) as a frozen solution at 5 K at X-band, c) as a frozen solution at 50 K at Q-band and d) the Ru^{3+} and radical at X-band at 5K where the signals indicated by * are due to the cavity.

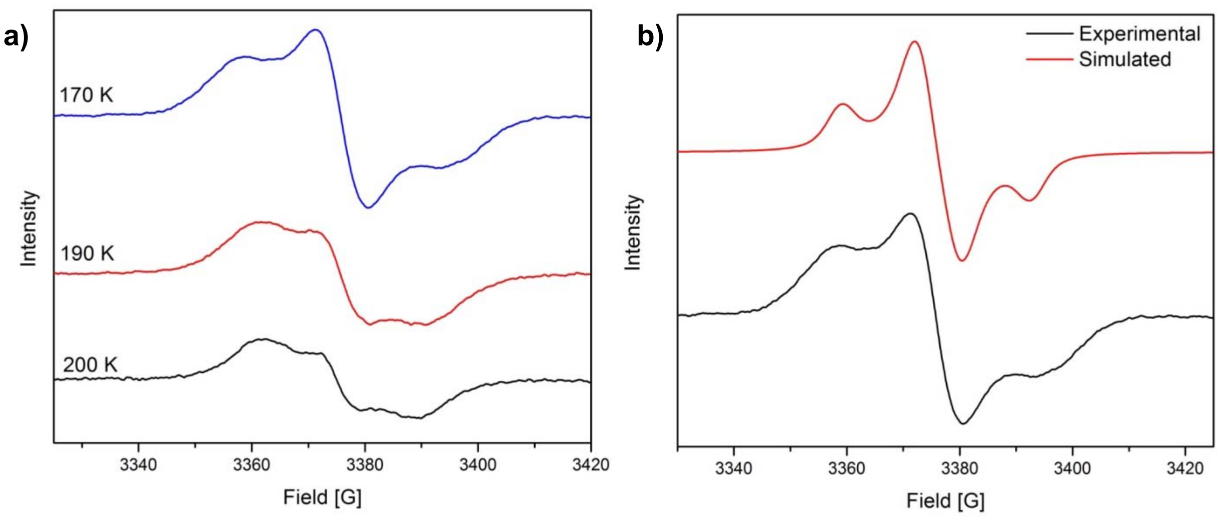


Figure S11. X-band EPR spectrum of the radical produced by the electrochemical experiment in $[(n\text{-}C_4H_9)_4N]PF_6/CH_2Cl_2$ electrolyte of **TPA-3bpm** a) at 170, 190 and 200 K and b) the simulated vs. experimental spectrum at 170 K as a frozen solution at a potential of 1.7 V.

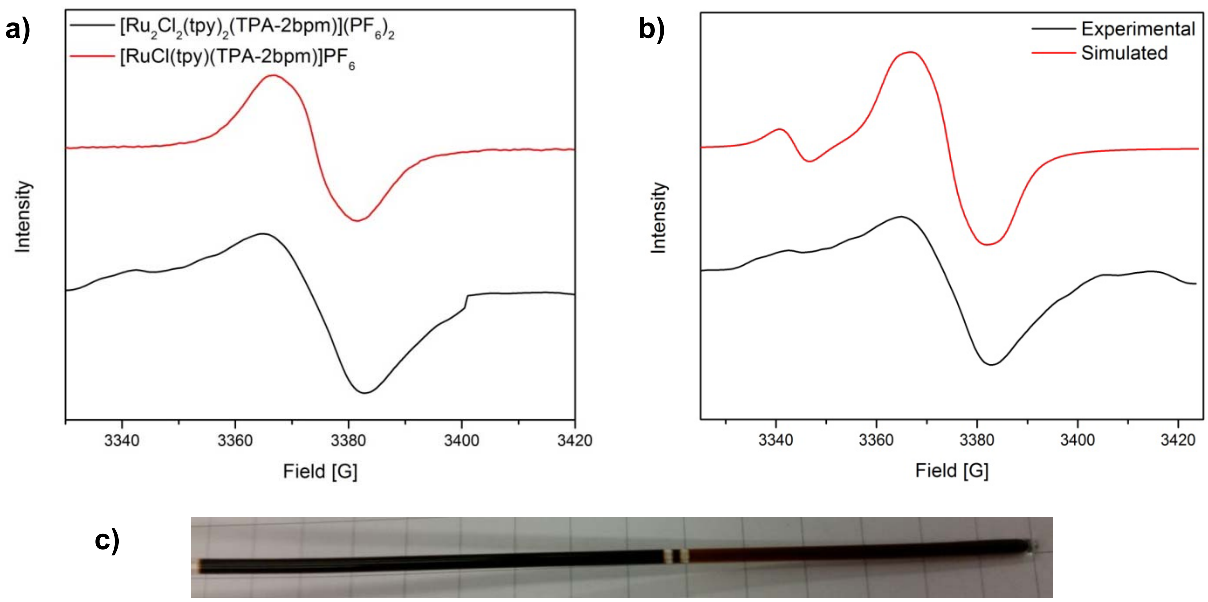


Figure S12. EPR spectroelectrochemistry in $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ electrolyte of a) $[Ru(tpy)Cl(TPA\text{-}2bpm)](PF_6)$ and $[Ru_2(tpy)_2Cl_2(TPA\text{-}2bpm)](PF_6)_2$, b) simulated vs. experimental spectrum of $[Ru_2(tpy)_2Cl_2(TPA\text{-}2bpm)](PF_6)_2$ and c) photo of $[Ru_2(tpy)_2Cl_2(TPA\text{-}2bpm)](PF_6)_2$ during the experiment.

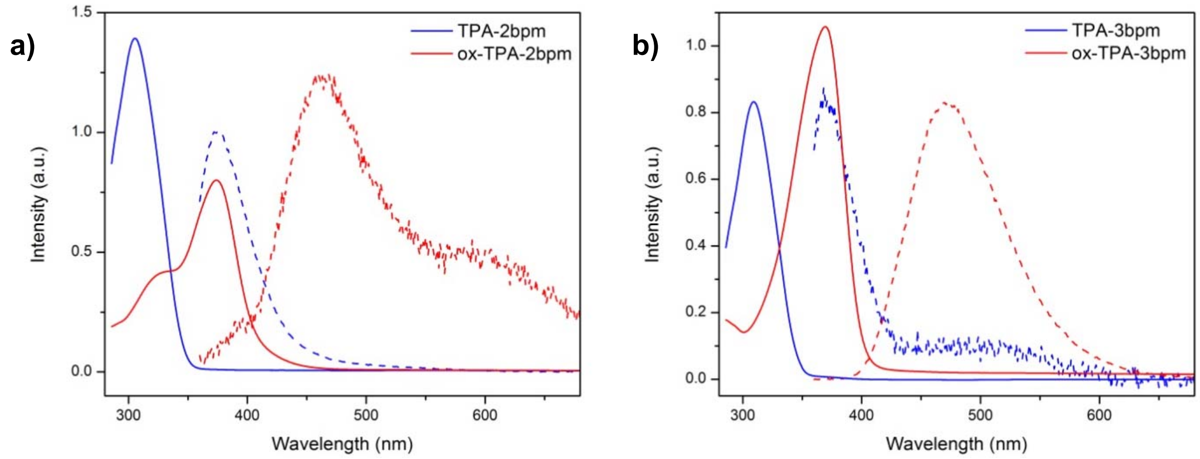


Figure S13. Absorbance and fluorescence spectra of a) **TPA-2bpm, ox-TPA-2bpm** and b) **TPA-3bpm**, **ox-TPA-3bpm** as solutions in acetonitrile.

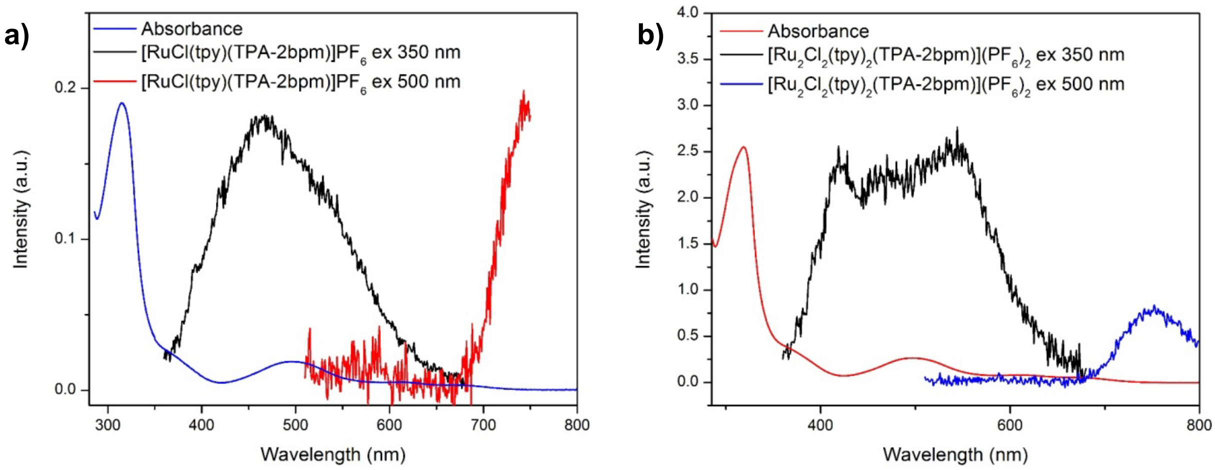


Figure S14. Absorbance and fluorescence spectra of a) $[RuCl(tpy)(TPA\text{-}2bpm)]PF_6$ and b) $[Ru_2Cl_2(tpy)_2(TPA\text{-}2bpm)](PF_6)_2$ upon excitation at 350 (28570 cm^{-1}) and 500 nm (20000 cm^{-1}).

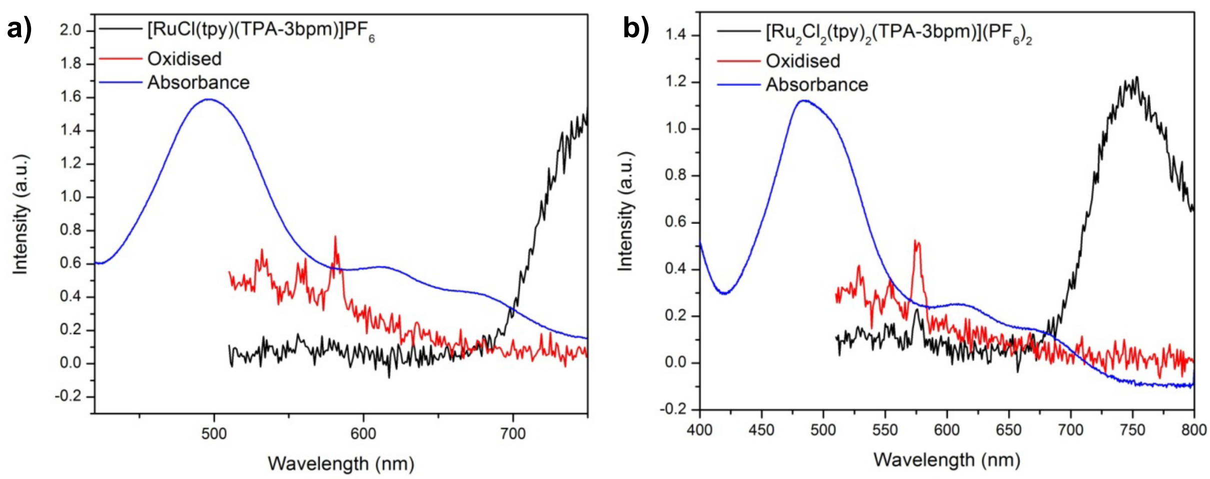


Figure S15. Absorbance and fluorescence spectra of a) $[RuCl(tpy)(TPA\text{-}3bpm)]PF_6$ and b) $[Ru_2Cl_2(tpy)_2(TPA\text{-}3bpm)](PF_6)_2$ and their oxidised species upon excitation at 490 nm (no fluorescence at 320 nm).

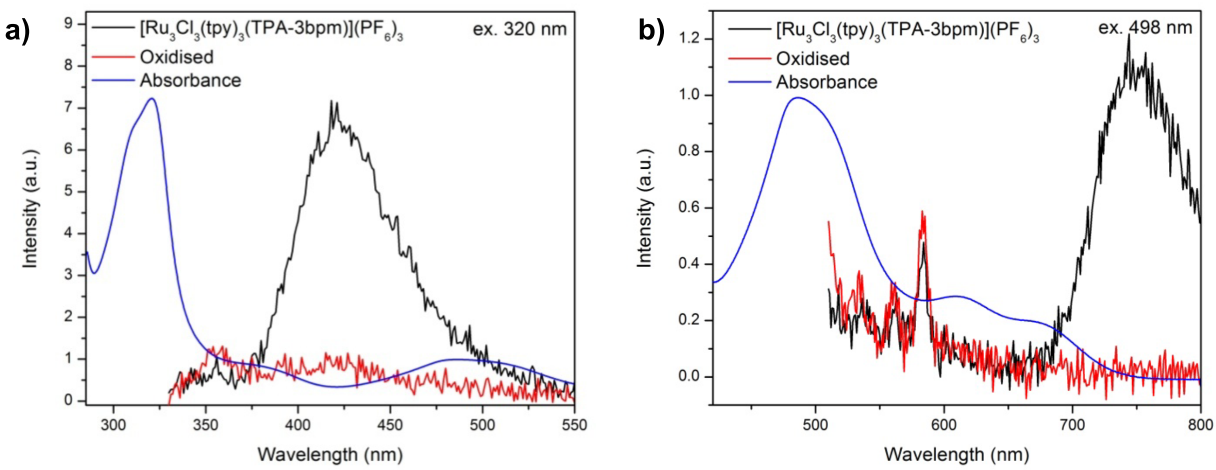


Figure S16. Absorbance and Fluorescence spectra of $[Ru_3Cl_3(tpy)_3(TPA\text{-}3bpm)](PF_6)_3$ upon excitation at 320 nm and 495 nm.

<u>References</u>

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