Supplementary Information

Structural, Electrochemical and Photophysical Behavior of Ru(II) Complexes with Large Bite Angle Sulfur-Bridged Terpyridyl Ligands

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Ru(II) Complex Synthesis



Scheme S1 Microwave-assisted synthesis of (a) homoleptic complexes $2\mathbf{a}-\mathbf{c}$; and (b) heteroleptic complexes $3\mathbf{a}-\mathbf{c}$.

Structural Characterization

[Ru(TPS)₂][PF₆] (2a)



¹H NMR (400 MHz, CD₃CN) δ 8.02 – 7.93 (m, 6H, H_{9,10}), 7.88 – 7.77 (m, 8H, H_{4,5}), 7.07 (dt, J = 5.9, 1.3 Hz, 4H, H₂), 6.93 (ddd, J = 7.6, 5.9, 1.8 Hz, 4H, H₃). ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 160.1 (C₈), 157.8 (C₆), 157.3 (C₂), 140.1 (C₁₀), 139.8 (C₄), 131.3 (C₉), 128.9 (C₅), 126.8 (C₃). ESI-MS cald. for C₃₀H₂₂N₆F₆PS₄¹⁰²Ru: 840.9473; found 840.9474 [M–PF₆]⁺.

$[Ru(Me-TPS)_2][PF_6]$ (2b)



¹H NMR (400 MHz, CD₃CN) δ 7.95 (d, J = 3.6 Hz, 6H, H_{10,11}), 7.66 (s, 4H, H₅), 6.87 (d, J = 6.1 Hz, 4H, H₂), 6.77 (dd, J = 6.2, 2.0 Hz, 4H, H₃), 2.36 (s, 12H, H₇). ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 160.3 (C₉), 156.9 (C₆), 156.2 (C₂), 152.6 (C₄), 139.8 (C₁₁), 131.1 (C₁₀), 129.0 (C₅), 127.8 (C₃), 20.6 (C₇). ESI-MS cald. for C₃₄H₃₀N₆F₆PS₄¹⁰²Ru: 897.0105; found 897.0100 [M–PF₆]⁺.

$[Ru(CF_3-TPS)_2][PF_6] (2c)$



¹H NMR (600 MHz, CD₃CN) δ 8.16 (dt, J = 2.2, 0.7 Hz, 4H, H₅), 8.07 – 8.04 (m, 6H, H_{10,11}), 7.31 (dt, J = 6.2, 0.7 Hz, 4H, H₂), 7.21 (ddd, J = 6.2, 2.1, 0.7 Hz, 4H, H₃). ¹³C{¹H} NMR (151 MHz, CD₃CN) δ 160.2 (C₆), 158.9 (C₉), 158.8 (C₂), 140.9 (C₁₀), 140.1 (q, J = 36.2 Hz, C₄), 132.3 (C₉), 125.5 (q, J = 4.5 Hz, C₅), 123.0 (q, J = 273.3 Hz, C₇), 122.9 (q, J = 3.0 Hz, C₃). ¹⁹F{¹H} NMR (377 MHz, CD₃CN) δ –65.20 (-CF₃), –72.62 (d, J = 706.4 Hz, PF₆⁻). ESI-MS cald. for C₃₄H₁₈N₆F₁₈PS₄¹⁰²Ru: 1112.8970; found 1112.8972 [M–PF₆]⁺.

$[Ru(tpy)(TPS)][PF_6]$ (3a)



¹H NMR (400 MHz, CD₃CN) δ 8.58 (ddd, J = 5.6, 1.6, 0.7 Hz, 2H, H₁₂), 8.53 (d, J = 8.1 Hz, 2H, H₁₉), 8.41 (ddd, J = 8.1, 1.4, 0.7 Hz, 2H, H₁₅), 8.30 – 8.22 (m, 3H, H_{10,20}), 8.16 (dd, J = 8.5, 6.9 Hz, 1H, H₉), 8.06 (td, J = 7.9, 1.5 Hz, 2H, H₁₄), 7.69 (ddd, J = 7.9, 1.7, 0.7 Hz, 2H, H₅), 7.62 (td, J = 7.7, 1.6 Hz, 2H, H₄), 7.39 (ddd, J = 7.4, 5.6, 1.4 Hz, 2H, H₁₃), 6.88 (ddd, J = 7.5, 6.0, 1.7 Hz, 2H, H₃), 6.73 (ddd, J = 6.0, 1.6, 0.7 Hz, 2H, H₂).¹³C{¹H} NMR (101 MHz, CD₃CN) δ 159.8 (C₁₈), 159.5 (C₁₆), 159.2 (C_{6,8}), 159.1 (C₁₂), 153.6 (C₂), 139.9 (C₁₄), 139.3 (C₄), 137.4 (C₁₀), 131.2 (C_{9,20}), 129.3 (C₅), 127.1 (C₁₃), 126.1 (C₃), 125.7 (C₁₅), 125.7 (C₁₉). ESI-MS cald. for C₃₀H₂₂N₆F₆PS₂¹⁰²Ru: 777.0033; found 777.0037 [M–PF₆]⁺.

 $[Ru(tpy)(Me-TPS)][PF_6]$ (3b)



¹H NMR (400 MHz, CD₃CN) δ 8.54 (dd, J = 5.6, 1.5 Hz, 2H, H₁₃), 8.49 (d, J = 8.1 Hz, 2H, H₂₀), 8.37 (d, J = 7.9 Hz, 2H, H₁₆), 8.25 – 8.19 (m, 3H, H_{10,21}), 8.12 (dd, J = 8.6, 6.9 Hz, 1H, H₁₁), 8.02 (td, J = 7.9, 1.5 Hz, 2H, H₁₅), 7.52 (d, J = 2.1 Hz, 2H, H₅), 7.36 (ddd, J = 7.3, 5.7, 1.4 Hz, 2H, H₁₄), 6.69 (dd, J = 6.3, 2.1 Hz, 2H, H₃), 6.51 (d, J = 6.1 Hz, 2H, H₂), 2.19 (s, 6H, H₇). ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 159.8 (C₁₉), 159.5 (C₉), 159.3 (C₁₇), 158.9 (C₁₃), 158.3 (C₆), 152.5 (C₂), 152.2 (C₄), 139.9 (C₁₁), 139.8 (C₁₅), 137.2 (C₁₀), 131.2 (C₂₁), 129.8 (C_{5,14}), 127.1 (C₃), 125.6 (C₁₆), 125.4 (C₂₀), 20.3 (C₇). ESI-MS cald. for C₃₂H₂₆N₆F₆PS₂¹⁰²Ru: 805.0346; found 805.0347 [M–PF₆]⁺.

 $[Ru(tpy)(CF_3-TPS)][PF_6]$ (3c)



¹H NMR (600 MHz, CD₃CN) δ 8.54 – 8.51 (m, 4H, H_{20,13}), 8.41 (ddd, *J* = 8.1, 1.4, 0.7 Hz, 2H, H₁₆), 8.30 – 8.23 (m, 3H, H_{10,21}), 8.18 (dd, *J* = 8.4, 7.1 Hz, 1H, H₁₁), 8.07 (td, *J* = 7.8, 1.5 Hz, 2H, H₁₅), 7.96 (dt, *J* = 2.2, 0.7 Hz, 2H, H₅), 7.42 – 7.36 (m, 2H, H₁₄), 7.09 – 7.03 (m, 2H, H₃), 6.91 (dt, *J* = 6.3, 0.7 Hz, 2H, H₂). ¹³C{¹H} NMR (151 MHz, CD₃CN) δ 161.8 (C₆), 159.5 (C₁₉), 159.4 (C₁₇), 159.3 (C₁₃), 158.4 (C₉), 155.3 (C₂), 140.24 (C₁₅), 140.19 (C₁₁), 139.2 (q, *J* = 35.6 Hz, C₄), 138.2 (C₁₁), 131.6 (C₁₀), 127.2 (C₁₄), 126.0 (C₁₆), 125.7 (C₂₀), 125.0 (q, *J* = 3.7 Hz, C₅), 122.7 (q, *J* = 273.2 Hz, C₇), 121.5 (q, *J* = 3.6 Hz, C₅). ¹⁹F{¹H} NMR (377 MHz, CD₃CN)

δ –65.6 (-CF₃), –72.6 (d, J = 706.4 Hz, PF₆⁻). ESI-MS cald. for C₃₂H₂₀N₆F₁₂PS₂¹⁰²Ru: 912.9780; found 912.9783 [M–PF6]⁺.



Fig. S1 ¹H NMR spectrum of **1,2-bis(4-(trifluoromethyl)pyridin-2-yl)disulfane** in CD₂Cl₂ at 25 °C (400 MHz).



Fig. S2 ¹³C{¹H} NMR spectrum of 1,2-bis(4-(trifluoromethyl)pyridin-2-yl)disulfane in CD_2Cl_2 at 25 °C (400 MHz).



Fig. S4 ¹H NMR spectrum of 1a in CD₂Cl₂ at 25 °C (400 MHz).





Fig. S6 ¹H NMR spectrum of 1b in CD_2Cl_2 at 25 °C (400 MHz).



Fig. S7 ${}^{13}C{}^{1H}$ NMR spectrum of 1b in CD₂Cl₂ at 25 °C (400 MHz).



Fig. S8 ¹H NMR spectrum of 1c in CD_2Cl_2 at 25 °C (400 MHz).



Fig. S10 ${}^{19}F{}^{1}H$ NMR spectrum of 1c in CD₂Cl₂ at 25 °C (377 MHz).



Fig. S12 ${}^{13}C{}^{1}H$ NMR spectrum of 2a in CD₃CN at 25 °C (101 MHz).



Fig. S14 ${}^{13}C{}^{1}H$ NMR spectrum of 2b in CD₃CN at 25 °C (101 MHz).



Fig. S15 ¹H NMR spectrum of 2c in CD₃CN at 25 °C (600 MHz).



Fig. S16 ${}^{13}C{}^{1}H$ NMR spectrum of 2c in CD₃CN at 25 °C (151 MHz).



Fig. S18 ¹H NMR spectrum of 3a in CD₃CN at 25 °C (400 MHz).



Fig. S20 ¹H NMR spectrum of 3b in CD₃CN at 25 °C (400 MHz).



Fig. S22 ¹H NMR spectrum of 3c in CD₃CN at 25 °C (600 MHz).



Fig. S24 ${}^{19}F{}^{1}H$ NMR spectrum of 3c in CD₃CN at 25 °C (377 MHz).

Crystallographic Studies

Table S1 Crystallographic Data for complexes 2a–2c and 3a–3c.

Compound	$2\mathbf{a} \cdot [2(\mathbf{C}_2\mathbf{H}_3\mathbf{N})]$	2b	$2c \cdot [1.5(C_3H_6O)]$	$3a \cdot [C_2H_3N]$	$\mathbf{3b} \cdot [2(C_3H_6O)]$	3c
	$\cdot [(C_2H_5)_2O]$			$\cdot [(C_2H_5)_2O]$		
CCDC	1935271	1935272	1935270	1935274	1935273	1935275
number						
Empirical	$[C_{30}H_{22}N_6RuS_4]$	[C ₃₄ H ₃₀ N ₆ Ru	$[C_{34}H_{18}F_{12}N_6Ru$	$[C_{30}H_{22}N_6RuS_2]$	$[C_{32}H_{26}N_6RuS_2]$	$[C_{32}H_{20}F_6N_6]$
formula	$[PF_6]_2 \cdot [2(C_2H_3N)]$	$S_4][PF_6]_2$	$S_4][PF_6]_2$	$[PF_6]_2 \cdot [C_2H_3N]$	$[PF_6]_2 \cdot [2(C_3H_6O)]$	$RuS_2][PF_6]_2$
	$\cdot [(C_2H_5)_2O]$		$\cdot [1.5(C_3H_6O)]$	$\cdot [(C_2H_5)_2O]$		
Formula	1106.95	1041.89	1343.39	1001.62	1065.87	1057.67
weight						
Temperature/	100.15	100.15	100.15	100.15	100.15	100.15
Κ						
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	P2 ₁	P-1	P-1	C2/c
a/Å	11.5073(16)	15.70(4)	11.8439(13)	10.560(9)	10.6394(10)	15.6153(12)
b/Å	13.617(2)	13.41(3)	13.1556(14)	11.093(10)	11.7675(11)	16.4630(13)
c/Å	28.041(4)	22.34(5)	16.6663(18)	17.565(15)	18.0797(16)	13.6597(13)
$\alpha/^{\circ}$	90	90	90	86.58(2)	81.743(4)	90
β/°	93.835(3)	102.04(5)	107.866(3)	73.703(16)	77.414(4)	93.481(3)
γ/°	90	90	90	77.28(3)	85.367(4)	90
Volume/Å ³	4384.0(11)	4601(18)	2471.6(5)	1927(3)	2183.4(4)	3505.1(5)
Ζ	4	4	2	2	2	4
$\rho_{calc}g/cm^3$	1.677	1.504	1.805	1.727	1.621	2.004
µ/mm ⁻¹	0.713	0.672	0.684	0.696	0.622	0.793
F(000)	2223.0	2088.0	1330.0	1003.0	1076.0	2088.0
Crystal	$0.23 \times 0.2 \times 0.15$	0.399 ×	0.302 imes 0.282 imes	0.3 imes 0.09 imes	0.456 imes 0.301 imes	0.3 imes 0.111 imes
size/mm ³		0.201 imes 0.09	0.25	0.05	0.08	0.03
Radiation	MoK α (λ =	MoK α (λ =	MoK α (λ =	MoK α (λ =	MoK α (λ =	MoK α (λ =
	0.71073)	0.71073)	0.71073)	0.71073)	0.71073)	0.71073)
2Θ range for	2.912 to 60.094	3.728 to	3.614 to 49.868	2.416 to 61.232	2.328 to 52.98	3.598 to

data		56.756				56.664
collection/°						
Index ranges	$\begin{array}{l} -16 \leq h \leq 15, -19 \\ \leq k \leq 19, -39 \leq l \leq \\ 39 \end{array}$	$\begin{array}{l} -19 \leq h \leq 20, \\ -17 \leq k \leq 15, \\ -28 \leq l \leq 29 \end{array}$	$\begin{array}{l} -13 \leq h \leq 13, - \\ 15 \leq k \leq 15, -19 \\ \leq l \leq 19 \end{array}$	$\begin{array}{l} -15 \leq h \leq 15, - \\ 15 \leq k \leq 15, -24 \\ \leq l \leq 25 \end{array}$	$\begin{array}{l} \text{-13} \leq h \leq 13, \text{-14} \leq \\ k \leq 14, \text{-20} \leq l \leq 22 \end{array}$	$\begin{array}{l} -20 \leq h \leq 20, \ \text{-} \\ 21 \leq k \leq 21, \ \text{-} \\ 18 \leq l \leq 18 \end{array}$
Reflections collected	56991	44457	31339	40622	33911	27250
Independent reflections	12809 [$R_{int} =$ 0.0598, $R_{sigma} =$ 0.0504]	$11405 [R_{int} = 0.0788, R_{sigma} = 0.0980]$	8399 [R _{int} = 0.0771, R _{sigma} = 0.0916]	11508 [$R_{int} =$ 0.0267, $R_{sigma} =$ 0.0392]	8485 [$R_{int} = 0.0829$, $R_{sigma} = 0.0901$]	$4365 [R_{int} = 0.0611, R_{sigma} = 0.0456]$
Data/restraints /parameters	12809/206/648	11405/0/573	8399/1897/839	11508/47/607	8485/0/574	4365/0/278
Goodness-of- fit on F ²	1.020	0.996	1.079	1.062	1.023	1.049
Final R indexes [I>=2σ (I)]	$R_1 = 0.0352, wR_2$ = 0.0710	$R_1 = 0.0484,$ w $R_2 =$ 0.0918	$R_1 = 0.0734,$ $wR_2 = 0.1811$	$R_1 = 0.0417,$ $wR_2 = 0.0998$	$R_1 = 0.0564, wR_2 = 0.1049$	$R_1 = 0.0370,$ $wR_2 = 0.0778$
Final R indexes [all data]	$R_1 = 0.0545, wR_2$ = 0.0787	$R_1 = 0.0904,$ w $R_2 =$ 0.1029	$R_1 = 0.1004,$ $wR_2 = 0.1953$	$R_1 = 0.0525,$ $wR_2 = 0.1049$	$R_1 = 0.0954, wR_2 = 0.1194$	$R_1 = 0.0592,$ $wR_2 = 0.0870$
Largest diff. peak/hole / e Å ⁻³	0.74/-0.88	1.03/-0.65	2.27/-1.52	1.54/-0.59	1.68/-1.26	0.90/-0.70
Flack parameter			0.50(9)			

$[Ru(TPS)_2][PF_6]_2 (2a)$	Angle (°)	$[Ru(Me-TPS)_2][PF_6]_2 (\mathbf{2b})$	Angle (°)
N1-Ru1-N2	90.25(7)	N1-Ru1-N2	89.70(11)
N1-Ru1-N3	178.97(7)	N1-Ru1-N3	178.25(10)
N1-Ru1-N4	84.31(6)	N1-Ru1-N4	85.61(17)
N1-Ru1-N5	89.17(6)	N1-Ru1-N5	87.61(11)
N1-Ru1-N6	96.26(7)	N1-Ru1-N6	98.44(16)
N2-Ru1-N3	90.38(7)	N2-Ru1-N3	91.01(11)
N2-Ru1-N4	91.25(6)	N2-Ru1-N4	89.93(14)
N2-Ru1-N5	178.41(6)	N2-Ru1-N5	177.28(10)
N2-Ru1-N6	88.79(6)	N2-Ru1-N6	89.99(15)
N3-Ru1-N4	94.87(6)	N3-Ru1-N4	92.79(16)
N3-Ru1-N5	90.21(6)	N3-Ru1-N5	91.67(11)
N3-Ru1-N6	84.56(6)	N3-Ru1-N6	83.16(16)
N4-Ru1-N5	90.17(7)	N4-Ru1-N5	89.48(15)
N4-Ru1-N6	179.43(6)	N4-Ru1-N6	175.95(10)
N5-Ru1-N6	89.80(6)	N5-Ru1-N6	90.78(15)
$[Ru(CF_3-TPS)_2][PF_6]_2 (2c)$	Angle (°)	$[Ru(tpy)(TPS)][PF_6]_2 (\mathbf{3a})$	Angle (°)
N1-Ru1-N2	89.5(5)	N1-Ru1-N2	91.18(9)
N1-Ru1-N3	179.2(5)	N1-Ru1-N3	178.60(7)
N1-Ru1-N4	84.1(4)	N1-Ru1-N4	92.72(9)
N1-Ru1-N5	89.0(5)	N1-Ru1-N5	88.68(9)
N1-Ru1-N6	93.4(4)	N1-Ru1-N6	86.86(9)
N2-Ru1-N3	90.3(5)	N2-Ru1-N3	90.12(9)
N2-Ru1-N5	178.4(6)	N2-Ru1-N5	178.20(7)
N2-Ru1-N4	89.1(5)	N2-Ru1-N4	102.62(8)
N2-Ru1-N6	90.3(5)	N2-Ru1-N6	98.52(8)
N3-Ru1-N4	96.6(4)	N3-Ru1-N4	86.49(9)
N3-Ru1-N5	91.3(5)	N3-Ru1-N5	90.03(9)
N3-Ru1-N6	85.9(4)	N3-Ru1-N6	93.45(9)
N4-Ru1-N5	90.4(5)	N4-Ru1-N5	79.17(8)
N4-Ru1-N6	177.4(5)	N4-Ru1-N6	158.85(8)
N5-Ru1-N6	90.2(5)	N5-Ru1-N6	79.68(8)
$[Ru(tpy)(Me-TPS)][PF_6]_2 (\mathbf{3b})$	Angle (°)	$[Ru(tpy)(CF_3-TPS)][PF_6]_2 (3c)$	Angle (°)

Table S2 Selected bond angles for complexes 2a-2c and 3a-3c.

N1-Ru1-N2	90.15(13)	N1-Ru1-N2	89.74(7)
N1-Ru1-N3	178.08(14)	N1-Ru1-N2 ¹	89.74(7)
N1-Ru1-N4	86.49(14)	N1-Ru1-N3	100.91(7)
N1-Ru1-N5	89.10(14)	N1-Ru1-N3 ¹	100.91(7)
N1-Ru1-N6	93.86(14)	N1-Ru1-N4	180.0
N2-Ru1-N3	91.60(14)	N2-Ru1-N2 ¹	179.49(13)
N2-Ru1-N4	103.10(14)	N2-Ru1-N3	87.18(9)
N2-Ru1-N5	176.73(16)	N2 ¹ -Ru1-N3	92.92(9)
N2-Ru1-N6	97.50(14)	N2-Ru-N4	90.26(7)
N3-Ru1-N4	92.33(14)	N2 ¹ -Ru1-N4	90.26(7)
N3-Ru1-N5	89.20(14)	N3-Ru1-N3 ¹	158.17(13)
N3-Ru1-N6	86.71(14)	N3-Ru1-N4	79.09(7)
N4-Ru1-N5	80.03(15)	N3 ¹ -Ru1-N4	79.09(7)
N4-Ru1-N6	159.40(13)		
N5-Ru1-N6	79.38(15)		

$[Ru(TPS)_2][PF_6]_2 (\mathbf{2a})$	Length (Å)	$[Ru(Me-TPS)_2][PF_6]_2 (\mathbf{2b})$	Length (Å)
Ru1-N1	2.095(2)	Ru1-N1	2.099(5)
Ru1-N2	2.098(2)	Ru1-N2	2.089(5)
Ru1-N3	2.096(2)	Ru1-N3	2.075(5)
Ru1-N4	2.102(2)	Ru1-N4	2.108(5)
Ru1-N5	2.096(2)	Ru1-N5	2.089(5)
Ru1-N6	2.098(2)	Ru1-N6	2.087(5)
$[Ru(CF_3-TPS)_2][PF_6]_2 (2c)$	Length (Å)	$[Ru(tpy)(TPS)][PF_6]_2 (3a)$	Length (Å)
Ru1-N1	2.128(13)	Ru1-N1	2.117(2)
Ru1-N2	2.113(12)	Ru1-N2	2.124(2)
Ru1-N3	2.083(11)	Ru1-N3	2.110(2)
Ru1-N4	2.079(12)	Ru1-N4	2.089(2)
Ru1-N5	2.099(12)	Ru1-N5	1.958(2)
Ru1-N6	2.109(12)	Ru1-N6	2.086(2)
$[Ru(tpy)(Me-TPS)][PF_6]_2 (\mathbf{3b})$	Length (Å)	$[Ru(tpy)(CF_3-TPS)_2][PF_6]_2 (3c)$	Length (Å)
Ru1-N1	2.117(4)	Ru1-N1	2.143(3)
Ru1-N2	2.127(3)	Ru1-N2	2.112(2)
Ru1-N3	2.111(4)	Ru1-N2 ¹	2.112(2)
Ru1-N4	2.089(4)	Ru1-N3	2.105(2)
Ru1-N5	1.960(4)	Ru1-N3 ¹	2.105(2)
Ru1-N6	2.083(4)	Ru1-N4	1.975(3)
Ru1-N6	2.083(4)	Ru1-N4	1.975(3)

Table S3 Selected bond lengths for complexes 2a-2c and 3a-3c.

CRYSTALLOGRAPHIC DETAILS AND ORTEP DIAGRAMS

[Ru(TPS)₂][PF₆]₂ (2a)

A yellow prism shaped crystal of $[C_{30}H_{22}N_6RuS_4] \cdot [2(C_2H_3N)] \cdot [(C_2H_5)_2O]$ having approximate dimensions of $0.23 \times 0.20 \times 0.15$ mm was mounted on a nylon loop. The data were collected at a temperature of $-183.0 + 0.1^{\circ}C$ to a maximum 2 Θ value of 60.1°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 56991 reflections that were collected, 12809 were unique (Rint = 0.060); equivalent reflections were merged.

The complex crystallized with two molecules of C_2H_3N and a single $C_4H_{10}O$ in the asymmetric unit, whereby the acetonitrile solvent molecules are disordered over four positions. All nonhydrogen atoms were refined anisotropically. A series of SIMU and RIGU commands were used to ensure reasonable geometries and displacement parameters of the solvent atoms. A list of the constraints and restraints used in this refinement can be found within the CIF. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement on F² was based on 56991 reflections and 648 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³



Fig. S25 Asymmetric unit of 2a with thermal ellipsoids drawn are at 50 % probability level.

[Ru(Me-TPS)₂][PF₆]₂ (2b)

A yellow plate shaped crystal of $[C_{34}H_{30}N_6RuS_4][PF_6]_2$, having approximate dimensions of $0.39 \times 0.20 \times 0.090$ mm was mounted on a nylon loop. The data were collected at a temperature of $-183.0 + 0.1^{\circ}C$ to a maximum 2 Θ value of 56.8°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 44457 reflections that were collected, 11405 were unique (Rint = 0.079); equivalent reflections were merged. One of the PF₆ anions are disordered and was modeled in two orientations. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle

of full-matrix least-squares refinement on F² was based on 44457 reflections and 573 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³





[Ru(CF₃-TPS)₂][PF₆]₂ (2c)

A yellow plate shaped crystal of $[C_{34}H_{18}F_{12}N_6RuS_4][PF_6]_2 \cdot [1.5(C_3H_6O)]$, having approximate dimensions of $0.250 \times 0.282 \times 0.302$ mm was mounted on a nylon loop. The data were collected at a temperature of $-183.0 + 0.1^{\circ}C$ to a maximum 2 Θ value of 49.9°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures.

Of the 31339 reflections that were collected, 8399 were unique (Rint = 0.077); equivalent reflections were merged. Both PF_6 anions are disordered and was modeled in two orientations respectively. A series of SIMU, RIGU, SADI and EADP commands were used to ensure

reasonable geometries and displacement parameters of the atoms in the asymmetric unit. Due to the nature of the chiral space group a twin law and BASF command was applied to the refinement. A list of the constraints and restraints used in this refinement can be found within the CIF. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement on F² was based on 31339 reflections and 839 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³



Fig. S27 Asymmetric unit of 2c with thermal ellipsoids drawn are at 50 % probability level.[Ru(tpy)(TPS)][PF₆]₂ (3a)

A red needle shaped crystal of $[C_{30}H_{22}N_6RuS_2][PF_6]_2 \cdot [C_2H_3N] \cdot [C_4H_{10}O]$, having approximate dimensions of $0.30 \times 0.090 \times 0.05$ mm was mounted on a nylon loop. The data were collected at a temperature of $-183.0 + 0.1^{\circ}C$ to a maximum 2 Θ value of 61.2° . Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 40622

reflections that were collected, 11508 were unique (Rint = 0.027); equivalent reflections were merged. One of the PF₆ anions are disordered and was modeled in two orientations. The complex crystallized with solvent molecules C_2H_3N and C_2H_6O in the asymmetric unit, whereby the acetonitrile molecule is disordered over two positions. A series of SIMU and EADP commands were used to ensure reasonable geometries and displacement parameters of the solvent and counter-anion atoms. A list of the constraints and restraints used in this refinement can be found within the CIF. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix leastsquares refinement on F^2 was based on 40622 reflections and 607 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³



Fig. S28 Asymmetric unit of 3a with thermal ellipsoids drawn are at 50 % probability level.

[Ru(tpy)(Me-TPS)][PF₆]₂ (3b)

A red plate shaped crystal of $[C_{32}H_{26}N_6RuS_2][PF_6]_2 \cdot [2(C_3H_6O)]$, having approximate dimensions of $0.46 \times 0.30 \times 0.080$ mm was mounted on a nylon loop. The data were collected at a temperature of $-183.0 + 0.1^{\circ}C$ to a maximum 2 Θ value of 53.0°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 33911 reflections that were collected, 8485 were unique (Rint = 0.08); equivalent reflections were merged. The complex crystallized with two molecules of C₃H₆O in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions.

The final cycle of full-matrix least-squares refinement on F^2 was based on 33911 reflections and 574 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³



Fig. S29 Asymmetric unit of 3b with thermal ellipsoids drawn are at 50 % probability level.

$[Ru(tpy)(CF_3-TPS)][PF_6]_2 (3c)$

A red plate shaped crystal of $[C_{32}H_{20}N_6RuS_2]$ [PF₆]₂, having approximate dimensions of 0.30 × 0.11 × 0.030 mm was mounted on a nylon loop. The data were collected at a temperature of - 183.0 + 0.1°C to a maximum 2 Θ value of 56.7°.

Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 27250 reflections that were collected, 4365 were unique (Rint = 0.06); equivalent reflections were merged. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement on F² was based on 27250 reflections and 278 variable parameters and converged. All refinements were performed using the ShelXL¹ via the OLEX2² interface. ORTEP diagrams were generated using PLATON.³



Fig. S30 Asymmetric unit of 3c with thermal ellipsoids drawn are at 50 % probability level.

Octahedricity

The *O*-value (octahedricity-value) measures the mean absolute deviation of the set of N-Ru-N angles from their ideal octahedral values (Equation S1). This equation enables determining how much a complex deviate from ideal octahedral geometry (where an octahedricity value = 0 represents an ideal octahedral geometry).^{4,5}

$$0 = \sqrt{\frac{1}{15} \sum_{i=1}^{15} (i - \theta)^2}_{\hat{\theta}}$$

(Equation S1)

 $\hat{\partial}_i = 180$ for *trans* N-Ru-N angles and 90 for *cis* N-Ru-N angles $\theta =$ experimental N-Ru-N angles determined from structural data



[Ru(dgpy)₂]³⁺

Pal, A.K.; Zaccheroni, N.; Campagnac, S.; Hanan, G.S. *Chem. Commun.*, 2014, **50**, 6846–6849



[Ru(pbpy)₂]²⁺

Wolpher, H.; Johansson, O.; Abrahamsson, M.; Kritikos, M.; Sun, L.; Åkermark, B. *Inorg. Chem. Commun.*, 2004, **7**, 337–340



[Ru(ddpd)(EtOOC-tpy)]²⁺

Breivogel, A.; Meister, M.; Förster, C.; Laquai, F.; Heinze, K. *Chem. Eur. J.*, 2013, **19**, 13745–13760



$[Ru(L_{ket})_2]^{2+}$

Schramm, F.; Meded, V.; Fliegl, H.; Fink, K.; Fuhr, O.; Qu, Z.; Klopper, W.; Finn, S.; Keyes, T. E.; Ruben M. *Inorg. Chem.*, 2009, **48**, 5677–5684



[Ru(Ph-tpy)(dgpy)]²⁺

Pal, A.K.; Zaccheroni, N.; Campagnac, S.; Hanan, G.S. *Chem. Commun.*, 2014, **50**, 6846–6849



[Ru(ttpy)(bpe)]²⁺

Abrahamsson, M.; Wolpher, H.; Johansson, O.; Larsson, J.; Kritikos, M.; Eriksson, L.; Norrby, P-O.; Bergquist, J.; Sun, L.; Åkermark, B.; Hammarström, L. Inorg. Chem., 2005, **44**, 3215–3225

Chart S1 Chemical structures of literature Ru(II) complexes used for crystallographic comparisons: $[Ru(dgpy)_2]^{3+;6}$ $[Ru(L_{ket})_2]^{2+;7}$ $[Ru(pbpy)_2]^{2+;8}$ $[Ru(Ph-tpy)(dgpy)]^{2+;6}$ $[Ru(ddpd)(EtOOC-tpy)]^{2+;9}$ $[Ru(ttpy)(bpe)]^{2+.10}$

Electrochemical Studies

	Oxidation			1	st Reduction	
	ipa [µA]	ipc [µA]	Ratio (ipa/ipc)	ipc [µA]	ipa [µA]	Ratio (ipc/ipa)
2b	15	12.5	1.2	_	_	-
2b	17.5	12.9	1.35	_	_	-
2c	15.8	5.83	2.7	_	_	-
3 a	20	10	2	13.8	8.8	1.6
3b	13.3	8.3	1.6	11	9	1.2
3 c	11.7	15	1.1	_	_	-

Table S4. Peak current ratios for quasi-reversible redox events for complexes 2a–c and 3a–c.



Fig. S31 Cyclic voltammograms of homoleptic species 2a in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



Fig. S32 Cyclic voltammograms of homoleptic species **2b** in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



Fig. S33 Cyclic voltammograms of homoleptic species 2c in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



Fig. S34 Cyclic voltammograms of homoleptic species 3a in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



(a)

(b)

Fig. S35 Cyclic voltammograms of homoleptic species **3b** in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



Fig. S36 Cyclic voltammograms of homoleptic species **3c** in dry, N₂-sparged MeCN. (a) Forward and (b) reverse sweeps shown. Sweep rates of 100 mVs⁻¹. Potentials were recorded vs. ferrocene as an added internal standard.



Scheme S2 Proposed scheme illustrating the redox behavior of the Ru(II) species.

(b) 2.0x10⁶ (a) _{6x10⁵} 2a 3a 77 K 77 K 100 K 100 K 150 K 150 K 5x10⁵ 200 K 200 K 1.5x10⁶ 250 K 300 K 250 K 300 K 4x10⁵ 3x10⁵ Counts 1.0x10⁶ 2x10⁵ 5.0×10^{5} 1x10⁵ 0 0.0 700 700 600 650 750 600 650 750 550 800 800 Wavelength (nm) Wavelength (nm) (c) (d) 7x10⁵ 5x10⁵ 77 K 100 K 77 K 100 K 3b 2b 6x10⁵ 150 K 150 K 4x10⁵ 200 K 200 K 250 K 250 K 5x10⁵ 300 K 300 K st 3x10⁵ O 2x10⁵ \$4x10⁵ 3x10⁵ 2x10⁵ 1x10⁵ 1x10⁵ 0 0 550 600 650 700 750 800 600 650 700 750 800 Wavelength (nm) Wavelength (nm) (f) 1.4x10⁶ (e) 5x10⁴ 77 K 3c 77 K 2c 300 K 100 K 1.2x10⁶ 150 K 4x10⁴ 200 K 250 K 1.0x10⁶ 300 K 3x10⁴ st ^{3x104} 2x10⁴ stuno 0 6.0x10⁵ $4.0x10^{5}$ 1x10⁴ 2.0x10⁵ 0 0.0

Fig. S37 Variable temperature (77–300 K) photoluminescence studies of homoleptic (**2a–c**) and heteroleptic (**3a–c**) Ru(II) complexes. Samples drop-cast as neat thin films from acetone on to quartz substrates. $\lambda_{ex} = 450$ nm.

550

600

650

700

Wavelength (nm)

750

800

Photoluminescence Studies

550

600

650 700

Wavelength (nm)

750

800

Computational Calculations



Fig. S38 Overlay of experimental and absorption spectra of homoleptic complexes (a) **2a**; (b) **2b**; and (c) **2c** in MeCN with their predicted transitions and oscillator strength, as calculated by TD-DFT.



Fig. S39 Overlay of experimental and absorption spectra of heteroleptic complexes (a) **3a**; (b) **3b**; and (c) **3c** in MeCN with their predicted transitions and oscillator strength, as calculated by TD-DFT.

[Ru(TPS) ₂][PF ₆] ₂ (2a)						
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment		
3.1637	391.90	0.0002				
3.2082	386.46	0.0407	H -> L 94.3%	MLCT		
3.2173	385.37	0.0001				
3.2856	377.36	0.0010				
3.2940	376.39	0.0007				
3.3442	370.74	0.0000				
3.3982	364.85	0.0008				
3.4292	361.55	0.0000				
3.5294	351.29	0.0218	H-2 -> L+1 92.5%	MLCT		
3.5525	349.01	0.0092	H -> L+2 92.0%	MLCT		
3.5948	344.90	0.0000				
3.6163	342.85	0.0211				
3.6343	341.15	0.0000				
3.6349	341.09	0.0057				
3.6352	341.07	0.0020				
3.6579	338.95	0.0263				
3.6934	335.69	0.0139				
3.7154	333.70	0.0297				
3.7646	329.34	0.0051				
3.7714	328.75	0.0000				

Table S5. Selected TD-DFT transitions for **2a** in the ground-state.

[Ru(Me-TPS) ₂][PF ₆] ₂ (2b)						
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment		
3.147	393.98	0.0458	H -> L 95.7%	MLCT		
3.1576	392.65	0.0002				
3.1906	388.59	0.0004				
3.2144	385.71	0.0002				
3.2692	379.25	0.0005				
3.2827	377.69	0.0000				
3.2989	375.83	0.0006				
3.3786	366.97	0.0000				
3.4617	358.16	0.0242	H-2 -> L+1 94.8%	MLCT		
3.58	346.32	0.0000				
3.5892	345.44	0.0114	H -> L+3 91.9%	MLCT		
3.6392	340.69	0.0000				
3.6425	340.38	0.0105				
3.65	339.68	0.0227				
3.6585	338.89	0.0115				
3.6791	337.00	0.0140				
3.69	336.00	0.0164				
3.7227	333.05	0.0366				
3.8033	325.99	0.0039				
3.8076	325.62	0.0033				

Table S6. Selected TD-DFT transitions for **2b** in the ground-state.

$[Ru(CF_3-TPS)_2][PF_6]_2 (2c)$						
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment		
3.1457	394.14	0.0019				
3.2121	385.99	0.0000				
3.2617	380.12	0.0043	H -> L 93.4%	MLCT		
3.3133	374.20	0.0003				
3.3174	373.74	0.0000				
3.3348	371.79	0.0190	H -> L+2 91.8 %	MLCT		
3.4275	361.73	0.0002				
3.4276	361.72	0.0269	H-1 -> L 93.4%	MLCT		
3.4412	360.29	0.0388				
3.448	359.58	0.0000				
3.4821	356.06	0.0637				
3.4954	354.71	0.0000				
3.5259	351.64	0.0000				
3.5321	351.02	0.0003				
3.5446	349.78	0.0168				
3.5622	348.06	0.0063				
3.581	346.23	0.0496				
3.6029	344.12	0.0183				
3.6231	342.20	0.0000				
3.6839	336.56	0.0283				

Table S7. Selected TD-DFT transitions for **2c** in the ground-state.

[Ru(tpy)(TPS)][PF ₆] ₂ (3a)							
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment			
2.6192	473.37	0.0112	H-1 -> L 97.6%	MLCT			
2.648	468.22	0.0037	H-2 -> L 69.4% H -> L 28.8%	MLCT/LLCT			
2.8241	439.02	0.0293	H-2 -> L 26.8% H -> L 58.4%	MLCT/LLCT			
2.9934	414.19	0.0229	H -> L+1 91.9%	MLCT/LLCT			
3.0854	401.84	0.0087	H-2 -> L+1 92.0%	MLCT			
3.0947	400.63	0.0619					
3.1503	393.56	0.0001					
3.3478	370.35	0.0003					
3.3636	368.61	0.0016					
3.3923	365.49	0.0051					
3.4376	360.67	0.0005					
3.4564	358.71	0.0229					
3.5313	351.10	0.0167					
3.5686	347.43	0.0176					
3.5868	345.67	0.0005					
3.6065	343.78	0.0191					
3.6415	340.48	0.0041					
3.6456	340.09	0.0358					
3.7452	331.05	0.0309					
3.8287	323.83	0.0014					

Table S8. Selected TD-DFT transitions for **3a** in the ground-state.

[Ru(tpy)(Me-TPS)][PF ₆] ₂ (3b)							
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment			
2.5766	481.19	0.0117	H-1 -> L 97.7%	MLCT			
2.6257	472.19	0.0037	H-2 -> L 72.0% H -> L 26.2%	MLCT/LLCT			
2.7922	444.04	0.0264	H-2 -> L 24.1% H -> L 59.0%	MLCT/LLCT			
2.9622	418.55	0.0251	H -> L+1 93.2%	MLCT/LLCT			
3.0539	405.99	0.0623	H-1 -> L+1 82.0%	MLCT			
3.0561	405.69	0.0072					
3.1499	393.61	0.0004					
3.3118	374.37	0.0002					
3.3445	370.71	0.0007					
3.3999	364.67	0.0038					
3.4484	359.54	0.0003					
3.4546	358.90	0.0296					
3.5207	352.16	0.0152					
3.6392	340.69	0.0237					
3.6571	339.02	0.0001					
3.6656	338.24	0.0274					
3.7061	334.54	0.0336					
3.7223	333.08	0.0109					
3.7688	328.98	0.0158					
3.8151	324.98	0.0039					

Table S9. Selected TD-DFT transitions for **3b** in the ground-state.

[Ru(tpy)(CF ₃ -TPS)][PF ₆] ₂ (3c)								
<i>E</i> [eV]	<i>E</i> [nm]	f	Contribution	Assignment				
2.7114	457.27	0.0104	H-1 -> L 96.4%	MLCT				
2.7134	456.93	0.0047	H-2 -> L 58.8% H -> L 38.7%	MLCT/LLCT				
2.893	428.57	0.0339	H-2 -> L 36.9% H -> L 53.0%	MLCT/LLCT				
3.0705	403.79	0.0182	H -> L+1 91.1%	MLCT/LLCT				
3.1475	393.91	0.0225	H-1 -> L+1 47.5%, H-1 -> L+10 30.7%	MLCT/LLCT				
3.1685	391.30	0.0165						
3.1689	391.25	0.0098						
3.2113	386.09	0.0121						
3.2271	384.20	0.0044						
3.2484	381.68	0.0723						
3.2899	376.86	0.0005						
3.3187	373.59	0.0272						
3.3592	369.09	0.0105						
3.4043	364.20	0.0042						
3.4266	361.83	0.0003						
3.4796	356.32	0.0082						
3.5095	353.28	0.0207						
3.5999	344.41	0.0320						
3.6739	337.47	0.0398						
3.829	323.80	0.0059						

 Table S10. Selected TD-DFT transitions for 3c in the ground-state.





HOMO-1: -6.49 eV

HOMO: -6.37 eV



LUMO: –2.37 eV

LUMO+1: –2.21 eV

Fig. S40 Frontier orbital plots of **2a** illustrating the HOMO–1, HOMO, LUMO and LUMO+1 distributions.



Fig. S41 Frontier orbital plots of **2b** illustrating the HOMO–1, HOMO, LUMO and LUMO+1 distributions.



Fig. S42 Frontier orbital plots of **2c** illustrating the HOMO–1, HOMO, LUMO and LUMO+1 distributions.

3a: [Ru(tpy)(TPS)][PF₆]₂



LUMO: -2.80 eVLUMO+1: -2.57 eVFig. S43 Frontier orbital plots of 3a illustrating the HOMO-1, HOMO, LUMO and LUMO+1distributions.



Fig. S44 Frontier orbital plots of **3b** illustrating the HOMO–1, HOMO, LUMO and LUMO+1 distributions.



Fig. S45 Frontier orbital plots of **3c** illustrating the HOMO–1, HOMO, LUMO and LUMO+1 distributions.

Complex	Ru	Tpy Ligand	Assignment
2a	1.89 e–	_	MC
2b	1.86 e–	_	MC
2c	1.88 e–	_	MC
3 a	1 e–	1 e–	MLCT
3 b	1 e–	1 e–	MLCT
3c	1.80 e–	_	MC

 Table S11. Spin densities for the six Ru(II) species 2a-c and 3a-c.





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