Experimental details

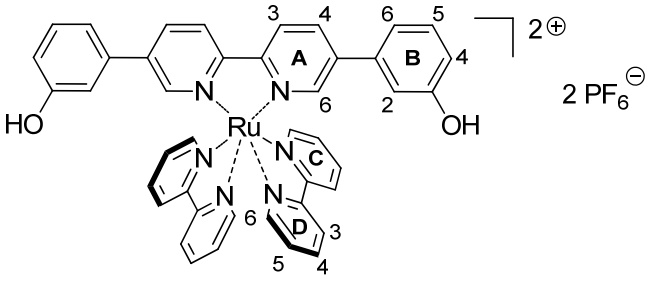
General

^{1}H and ^{13}C NMR spectra were recorded (295 K) on Bruker Avance DRX-500 or DPX-400 MHz spectrometers; chemical shifts relative to residual solvent peaks with TMS $\delta = 0$ ppm for ^{1}H and ^{13}C, and relative to $CF(^{35}Cl)_3$ in $CDCl_3$ for ^{19}F (external reference). NMR spectra were assigned by using distortionless enhancement by polarization transfer (DEPT) and 2D techniques (COSY, NOESY, HMQC and HMBC). Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer (solid samples, Golden Gate diamond attenuated total reflectance accessory). ESI mass spectra were recorded with Finnigan MAT LCQ or Bruker Esquire 3000plus instruments. Electronic absorption and emission spectra were recorded on a Varian Cary 5000 spectrophotometer and a Shimadzu RF-5301 PC spectrofluorometer, respectively. Microwave reactions were carried out in a Biotage Initiator 8 reactor. Solvents were distilled before use, and reactions were carried out under N_2. Electrochemical measurements were performed by using an Eco Chemie Autolab PGSTAT 20 apparatus with a glassy carbon working electrode, platinum mesh for counter electrode, and silver wire as reference electrode. Compounds were dissolved and measured in dry and argon-purged MeCN with 0.1 M $[^{n}Bu_4N][PF_6]$ as supporting electrolyte. The scan rate was 100 mVs^{-1} and ferrocene was added as an internal standard at the end of every experiment.

Compound **1** [E. C. Constable, C. E. Housecroft, B. M. Kariuki and C. B. Smith, *Supramol. Chem.*, 2006, **18**, 305], *cis*-$[Ru(bpy)_2Cl_2]$ [G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947], $[Ru(DMSO)_4Cl_2]$ [I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans*. 1973, 204] were prepared as previously reported. 2,3,4-Tri-O-acetyl-β-D-xylopyranosyl azide was used as received (Alrich).

Compounds:

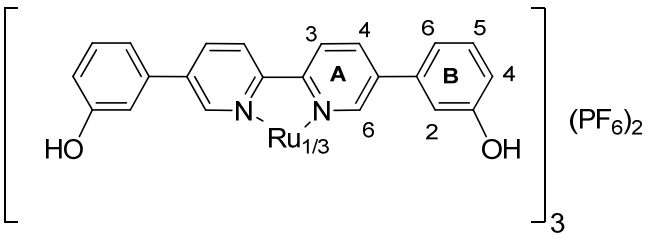
$[Ru(\mathbf{1})(bpy)_2][PF_6]_2$



Ligand **1** (336 mg, 987 μmol) and *cis*-$[Ru(bpy)_2Cl_2]$ (483 mg, 240 μmol) were suspended in EtOH (5 cm^3). The reaction mixture was heated in a microwave reactor for 45 min to 145 °C. An aqueous NH_4PF_6 solution (100 cm^3, 4.00 mmol) was added to the resulting orange solution. An orange precipitate formed which was filtered and washed with water (50 cm^3) and Et_2O (50 cm^3) yielding $[Ru(\mathbf{1})(bpy)_2][PF_6]_2$ (911 mg, 872 μmol, 88%) as an orange

powder. ^{1}H NMR (400 MHz, CD_3CN) δ/ppm = 8.56 (d, J = 8.5 Hz, 2H, H^{A3}), 8.50 (q, J = 7.5 Hz, 4H, H^{C3+D3}), 8.28 (dd, J = 8.5, 2.0 Hz, 2H, H^{A4}), 8.07 (qd, J = 7.9 Hz, 1.4, 4H, H^{C4+D4}), 7.90 – 7.86 (m, 2H, H^{C6}), 7.83 – 7.79 (m, 2H, H^{D6}), 7.77 (d, J = 1.8, 2H, H^{A6}), 7.49 – 7.39 (m, 4H, H^{C5+D5}), 7.28 (s, 2H, OH), 7.25 (t, J = 7.9 Hz, 2H, H^{B5}), 6.94 – 6.85 (m, 4H, H^{B4+B6}), 6.85 – 6.80 (m, 2H, H^{B2}). ^{13}C NMR (101 MHz, CD_3CN) δ/ppm = 158.67, 158.24, 157.97, 156.46, 153.11, 153.01, 149.96, 140.76, 138.91, 138.85, 137.40, 136.77, 131.67, 128.68, 128.64, 125.51, 125.34, 125.30, 119.60, 117.51, 114.83. ESI MS: *m/z* 377.1 $[M\text{-}2PF_6]^{2+}$ (calc. 377.1), 898.7 $[M\text{-}PF_6]^{+}$ (calc. 899.1). IR (solid/ cm^{-1}): $\tilde{\nu}$ 3637m, 2849w, 1626m, 1603m, 1464m, 1447m, 1423m, 1379m, 1242m, 1219m, 816s. Found C 47.53, H 3.25, N 7.61; $C_{42}H_{34}F_{12}N_6O_2P_2Ru \cdot H_2O$ requires C 47.51, H 3.23, N 7.92%.

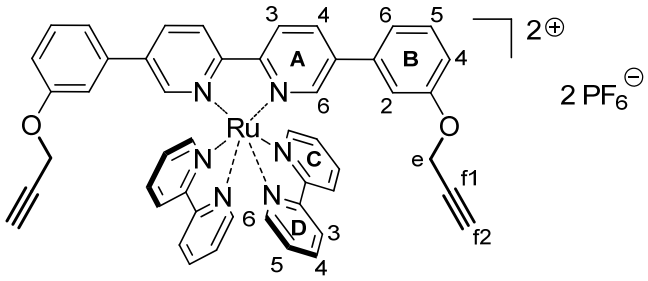
$[Ru(\mathbf{1})_3][PF_6]_2$



Ligand **1** (200 mg, 587 μmol) and $[Ru(DMSO)_4Cl_2]$ (94.8 mg, 196 μmol) were suspended in ethylene glycol (7 cm^3). The reaction mixture was stirred in a microwave reactor for 30 min at 230 °C. The resulting orange solution was added to 100 cm^3 of aqueous NH_4PF_6 (4.00 mmol). An orange precipitate formed which was filtered and washed with water (300 cm^3) and Et_2O (100 cm^3) yielding $[Ru(\mathbf{1})_3][PF_6]_2$ (271 mg, 98%). ^{1}H NMR (400 MHz, CD_3CN) δ/ppm = 8.60 (d, J = 8.5 Hz, 6H, H^{A3}), 8.30 (dd, J = 1.9, 8.5 Hz, 6H H^{A4}), 8.00 (d, J = 1.8 Hz, 6H H^{A6}), 7.23 (t, J = 8.1 Hz, 12H, H^{B5+OH}), 6.93 – 6.83 (m, 18H, $H^{B2+B4+B6}$). ^{19}F NMR (376 MHz, CD_3CN) δ/ppm = –73.98 (d, J = 707 Hz). ^{13}C NMR (101 MHz, CD_3CN) δ/ppm = 158.61, 156.53, 150.90, 140.48, 137.38, 136.81, 131.59, 125.35, 119.67, 117.49, 114.93. ESI MS: *m/z* 561.4 $[M–2PF_6]^{2+}$ (calc. 561.1), 1121.6 $[M–2PF_6–H]^{+}$ (calc. 1121.3) 1267.4 $[M–PF_6]^{+}$ (calc. 1267.2). UV-Vis (MeCN, λ_{max}(nm) [ε/ (cm^{-1} M^{-1})]) = 467.0 [13900], 321.0 [102000]. Emission (MeCN, λ_{max}(nm)) = 625. IR (solid / cm^{-1}) $\tilde{\nu}$ 3522w, 3105w, 1740m, 1599m, 1583m, 1462m, 1448m, 1375m, 1304m, 1204m, 1165m, 997w, 893m, 824s, 779m, 731w,

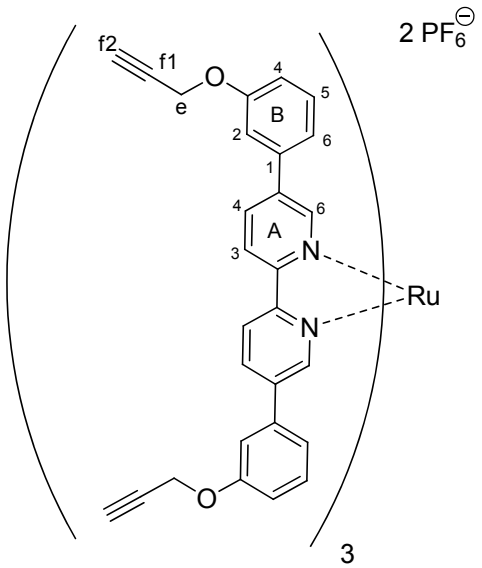
698w. Found C 54.77, H 3.68, N 5.64; $C_{66}H_{48}F_{12}N_6O_6P_2Ru \cdot 2H_2O$ requires C 54.74, H 3.62, N 5.80 %.

[Ru(**2**)(bpy)$_2$][PF$_6$]$_2$



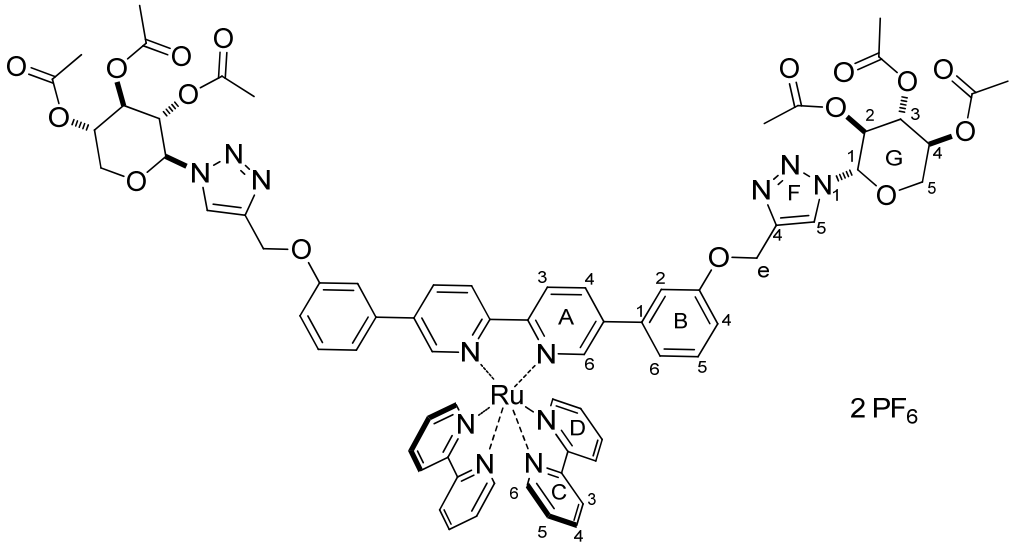
[Ru(**1**)(bpy)$_2$][PF$_6$]$_2$ (581 mg, 556 μmol) and Cs_2CO_3 (725 mg, 2.23 mmol) were dissolved in dry DMF (10 cm^3) and the mixture was stirred at 80°C for 1 h. Propargyl bromide (553 μL, 5.56 mmol, 80% in toluene, stabilized) was added dropwise and the solution was stirred overnight at 80°C. The product was precipitated with aqueous NH_4PF_6 (100 cm^3, 6.00 mmol), collected on a frit and washed with water (10 cm^3) and Et_2O (50 cm^3). Filtration over Al_2O_3 yielded [Ru(**2**)(bpy)$_2$][PF$_6$]$_2$ (554 mg, 494 μmol, 89%) as an orange solid. ^{1}H NMR (400 MHz, CD_3CN) δ/ppm = 8.61 (d, J = 8.5 Hz, 2H, H^{A3}), 8.53 (dd, J = 7.9, 5.2 Hz, 4H, H^{C3+D3}), 8.33 (dd, J = 8.5, 1.9 Hz, 2H, H^{A4}), 8.13 – 8.00 (m, 4H, H^{C4+D4}), 7.91 (d, J = 5.4 Hz, 2H, H^{C6}), 7.83 (m$_c$, 4H, H^{A6+D6}), 7.47 – 7.42 (m, 4H, H^{C5+D5}), 7.38 (t, J = 8.0 Hz, 2H, H^{B5}), 7.10 – 6.98 (m, 6H, H$^{B2+B4+B6}$), 4.79 – 4.68 (m, 4H, H^e), 2.82 (t, J = 2.3 Hz, 2H, H^{f2}). ^{13}C NMR (101 MHz, CD_3CN) δ/ppm = 159.16 (C^{B3}), 158.23, 157.97, 156.62, 153.13, 153.06, 150.03, 140.48, 138.96, 138.89, 137.35, 136.92 (C^{B5}), 131.68, 128.70, 128.68, 125.55, 125.42, 125.34, 121.31, 117.11 (C^e), 114.55 (C^{B2}), 79.48 (C^{f1}), 77.38 (C^{f2}), 56.78 (C^e). ESI MS m/z 975.0 [M-PF$_6$]$^+$ (calc. 975.2), 829.1 [M- 2PF$_6$-H]$^+$ (calc. 829.2). Found C 50.16, H 3.22, N 7.18; $C_{48}H_{36}F_{12}N_6O_2P_2Ru \cdot 1.5H_2O$ requires C 50.27, H 3.43, N 7.33%.

[Ru(**2**)$_3$][PF$_6$]$_2$



$[Ru(\mathbf{1})_3][PF_6]_2$ (202 mg, 143 μmol) and Cs_2CO_3 (932 mg, 2.83 mmol) were dissolved in dry DMF (10 cm^3) and the mixture was stirred at 80°C for 1 h. Propargyl bromide (427 μL, 4.29 mmol, 80% in toluene, stabilized) was added dropwise and the solution was stirred for 1 d at 80°C. Further propargyl bromide (427 μL, 4.29 mmol, 80% in toluene, stabilized) was added and the reaction mixture was stirred again for 1 d at 80°C. The product was precipitated with aqueous NH_4PF_6 (100 cm^3, 4.00 mmol), collected on a frit and washed with water (10 cm^3) and Et_2O (50 cm^3). Filtration over Al_2O_3 yielded $[Ru(\mathbf{2})_3][PF_6]_2$ (99.5 mg, 60.7 μmol, 42%) as an orange solid. ^{1}H NMR (500 MHz, CD_3CN) δ/ppm = 8.66 (d, J = 8.6 Hz, 6H, H^{A3}), 8.38 (dd, J = 8.5, 1.9 Hz, 6H, H^{A4}), 8.08 (d, J = 1.7 Hz, 6H, H^{A6}), 7.38 (t, J = 8.3 Hz, 6H, H^{B5}), 7.11 (d, J = 7.9 Hz, 6H, H^{B6}), 7.06 – 7.01 (m, 12H, H^{B2+B4}), 4.75 – 4.63 (m, 12H, H^{e}), 2.77 (t, J = 2.3 Hz, 6H, H^{f1}). ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 159.10 (C^{B3}), 156.65 (C^{A2}), 151.02 (C^{A6}), 140.13 (C^{A5}), 137.23 (C^{A4}), 136.98 (C^{B1}), 131.68 (C^{B5}), 125.53 (C^{A3}), 121.35 (C^{B6}), 117.04 (C^{B4}), 114.57 (C^{B2}), 79.42 (C^{f1}), 77.33 (C^{f2}), 56.71 (C^{e}). ESI MS m/z 1494.4 $[M\text{-}PF_6]^+$ (calc. 1495.3), 674.9 $[M\text{-}2PF_6]^{2+}$ (calc. 675.6). IR (solid / cm^{-1}): $\tilde{\nu}$ 3278m, 2940w, 1585m, 1464m, 1295w, 1196m, 1019m, 1009m, 834m, 824m, 819s, 805m, 766w, 719m, 690w, 676w, 630m, 623m, 616w. Found C 60.24, H 3.90, N 5.07; $C_{48}H_{60}F_{12}N_6O_6P_2Ru{\cdot}2H_2O$ requires C 60.18, H 3.85, N 5.01%.

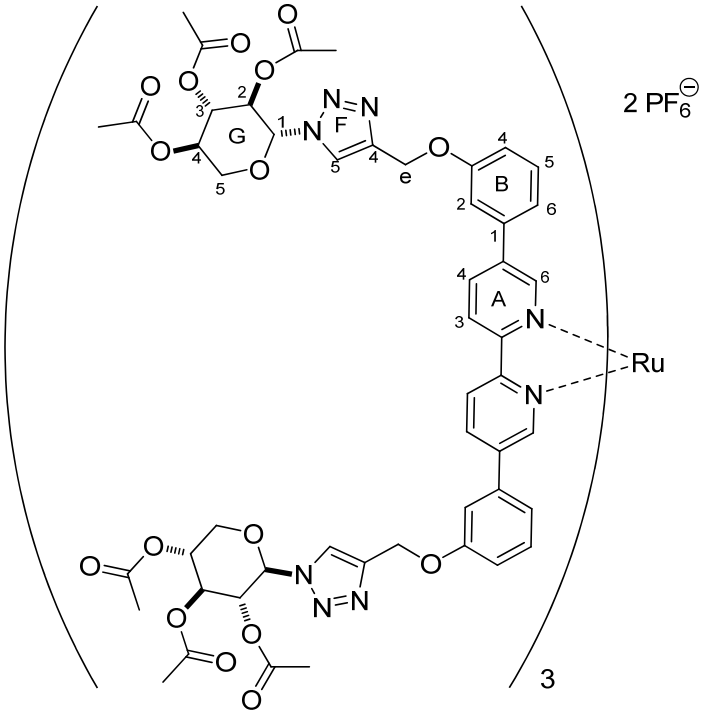
$[Ru(\mathbf{4})(bpy)_2][PF_6]_2$



$[Ru(\mathbf{2})(bpy)_2][PF_6]_2$ (217 mg, 194 μmol), 2,3,4-tri-O-acetyl-β-D-xylopyranosyl azide (118.3 mg, 393 μmol), $CuSO_4{\cdot}5H_2O$ (4.8 mg, 19.4 μmol) and ascorbic acid (6.8 mg, 38.6 μmol) were stirred in DMF (5 cm^3) at room temperature under N_2 for 3 days. The crude product, obtained after removal of the solvent, was filtered over Al_2O_3 yielding a mixture of the two diastereoisomers of $[Ru(\mathbf{4})(bpy)_2][PF_6]_2$ (311 mg, 180 μmol, 93%) as an orange solid. ^{1}H NMR (500 MHz, CD_3CN) δ/ppm = 8.58 (d, J = 8.5 Hz, 2H, H^{A3}), 8.55 – 8.47 (m, 4H, H^{C3+D3}), 8.36 – 8.27 (m, 2H, H^{A4}), 8.11 – 8.01 (m, 6H, $H^{C4+D4+F5}$), 7.89 (d, J = 5.5 Hz, 2H, H^{C6}), 7.81 (m_c, 4H, H^{D6+A6}), 7.45 – 7.40 (m, 4H, H^{C5+D5}), 7.36 (t, J = 8.1 Hz, 2H, H^{B5}), 7.06 (d, J = 8.2 Hz, 2H, H^{B6}), 7.06 – 7.01 (m, 4H, H^{B2+B4}), 5.93 (d, J = 9.1 Hz, 2H, H^{G1}), 5.56 (t, J = 9.4 Hz, 2H, H^{G2}), 5.46 (t, J = 9.6 Hz, 2H, H^{G3}), 5.21 – 5.10 (m, 6H, H^{e+G4}), 4.20 (dd, J =

11.6, 5.6 Hz, 2H, H^{G5eq}), 3.72 (t, J = 11.1 Hz, 2H, H^{G5ax}), 2.02 (s, 6H, $H^{G4\text{-}Me}$), 2.00 (s, 6H, $H^{G3\text{-}Me}$), 1.76 (s, 3H, $H^{G2\text{-}Me}$), 1.73 (s, 3H, $H^{G2\text{-}Me'}$). ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 170.99 ($C^{G4,\ C=O}$), 170.94 ($C^{G3,\ C=O}$), 169.99 ($C^{G2,\ C=O}$), 159.89 (C^{B3}), 159.87 ($C^{B3'}$), 158.26 (C^{C2}), 157.98 (C^{D2}), 156.58 (C^{A2}), 153.12 ($C^{C6/D6}$), 153.10 ($C^{C6/D6}$), 150.04 (C^{A6}), 150.01 ($C^{A6'}$), 144.88 (C^{F4}), 140.52 (C^{A5}), 138.93 ($C^{C4/D4}$), 138.88 ($C^{C4/D4}$), 137.29 (C^{B1}), 137.25 ($C^{B1'}$), 136.79 (C^{A4}), 131.72 (C^{B5}), 128.70 ($C^{C5/D5}$), 128.67 ($C^{C5/D5}$), 128.66 ($C^{C5'/D5'}$), 125.63 ($C^{C3/D3}$), 125.59 ($C^{C3/D3}$), 125.43 (C^{A3}), 125.38 ($C^{A3'}$), 124.03 (C^{F5}), 123.98 ($C^{F5'}$), 120.96 (C^{B6}), 117.47 (C^{B4}), 117.37 ($C^{B4'}$), 114.35 (C^{B2}), 114.26 ($C^{B2'}$), 86.79 (C^{G1}), 86.77 ($C^{G1'}$), 72.91 (C^{G3}), 71.32 (C^{G2}), 71.31 ($C^{G2'}$), 69.24 (C^{G4}), 66.06 (C^{G5}), 62.49 (C^{e}), 20.98 ($C^{G3\text{-}Me+G4\text{-}Me}$), 20.51 ($C^{G2\text{-}Me}$), 20.49 ($C^{G2\text{-}Me'}$). ESI MS m/z 1576.6 $[M\text{-}PF_6]^+$ (calc. 1577.3), 715.9 $[M\text{-}2PF_6]^{2+}$ (calc. 716.2). IR (solid / cm^{-1}): $\tilde{\nu}$ 3072w, 2943w, 1733s, 1601w, 1589w, 1464m, 1367m, 1209m, 1094m, 1036m, 827s, 763w. UV-Vis (MeCN, λ_{max} (nm), [ε/ (cm^{-1} M^{-1})]) 455 [14500], 320 [54 500], 288 [88300]. Emission (MeCN, λ_{max}(nm), λ_{exc} = 455 nm) 640. Found C 47.48, H 3.85, N 9.51; $C_{70}H_{66}F_{12}N_{12}O_{16}P_2Ru{\cdot}2.5H_2O$ requires C 47.57, H 4.05, N 9.51 %.

$[Ru(\mathbf{4})_3][PF_6]_2$

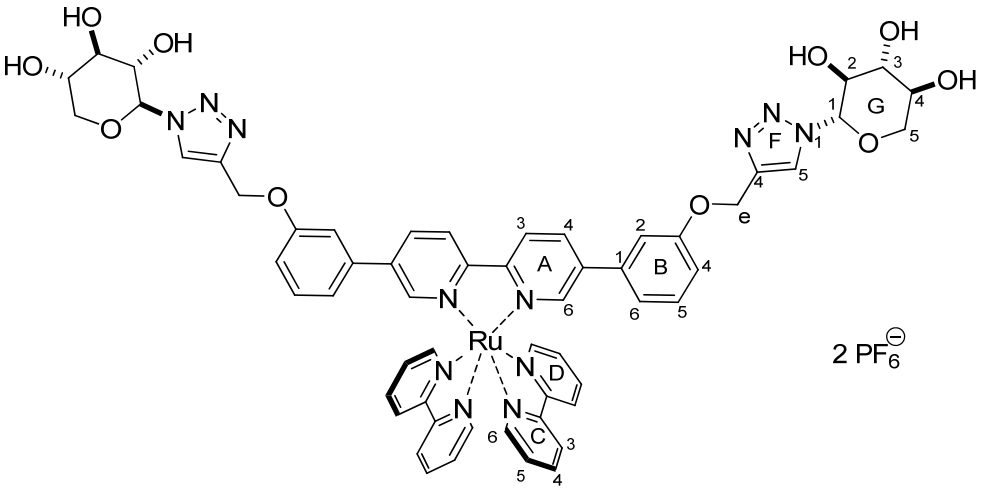


$[Ru(\mathbf{2})_3][PF_6]_2$ (75.6 mg, 46.6 μmol), 2,3,4-tri-O-acetyl-β-D-xylopyranosyl azide (112.4 mg, 373 μmol), $CuSO_4{\cdot}5H_2O$ (2.3 mg, 9.32 μmol) and ascorbic acid (3.3 mg, 18.6 μmol) in DMF (5 cm^3) were stirred at room temperature under an atmosphere of nitrogen for 3 days. The crude product, obtained after removal of the solvent, was taken in CH_2Cl_2 (50 cm^3) and extracted with water (150 cm^3). The organic solution was then reduced to 5 cm^3 and addition of 60 cm^3 of ether yielded a precipitate which was collected on a frit and washed with water (15 cm^3) and ether (20 cm^3). A mixture of the two diastereoisomers of $[Ru(\mathbf{4})_3][PF_6]_2$ (150 mg, 43.6 μmol, 93 %) was obtained as an orange solid. ^{1}H NMR (500 MHz, CD_3CN) δ/ppm =

8.63 (m_c, 6H, $H^{A3+A3'}$), 8.35 (d, J = 8.2 Hz, 6H H^{A4}), 8.09 (s, 6H, H^{A6}), 8.03 (s, 6H, H^{F5}), 7.28 (m_c, 6H, H^{B5}), 7.09 – 7.01 (m, 12H, H^{B2+B6}), 6.99 (d, J = 8.3 Hz, 6H, H^{B4}), 5.97 – 5.85 (m, 6H, H^{G1}), 5.55 (t, J = 9.3 Hz, 6H, H^{G2}), 5.50 – 5.42 (m, 6H, H^{G3}), 5.22 – 5.11 (m, 6H, H^{G4}), 5.02 (m_c, 12H, H^{e}), 4.19 (dd, J = 11.2, 5.1 Hz, 6H, H^{G5eq}), 3.71 (t, J = 11.0 Hz, 6H, H^{G5ax}), 2.02 (s, 18H, $H^{G4\text{-}Me}$), 1.98 (s, 18H, $H^{G3\text{-}Me}$), 1.74 (s, 9H, $H^{G2\text{-}Me}$), 1.72 (s, 9H, $H^{G2\text{-}Me'}$). ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 170.97 ($C^{G3/G4,\ C=O}$), 170.92 ($C^{G3/G4,\ C=O}$), 170.00 ($C^{G2,\ C=O}$), 169.97 ($C^{G2',\ C=O}$), 159.77 (C^{B3}), 159.75 ($C^{B3'}$), 156.63 (C^{A2}), 150.97 (C^{A6}), 144.73 (C^{F4}), 144.72 ($C^{F4'}$), 140.12 (C^{A5}), 137.11 (C^{B1}), 137.06 ($C^{B1'}$), 136.75 (C^{A4}), 136.70 ($C^{A4'}$), 131.65 (C^{B5}), 125.76 (C^{A3}), 125.64 ($C^{A3'}$), 124.05 (C^{F3}), 124.00 ($C^{F3'}$), 121.01 (C^{B6}), 120.96 ($C^{B6'}$), 117.48 (C^{B4}), 114.03 (C^{B2}), 113.97 ($C^{B2'}$), 86.75 (C^{G1}), 72.90 (C^{G3}), 71.30 (C^{G2}), 69.22 (C^{G4}), 66.04 (C^{G5}), 62.33 (C^{e}), 20.99 ($C^{G3/G4\text{-}Me}$), 20.97 ($C^{G3/G4\text{-}Me}$), 20.53 ($C^{G2\text{-}Me}$), 20.51 ($C^{G2\text{-}Me'}$).

ESI MS m/z 1578.1 $[M\text{-}2PF_6]^{2+}$ (calc. 1578.5). IR (solid / cm^{-}): $\tilde{\nu}$ 2949w, 1734s, 1585w, 1464m, 1367m, 1303w, 1205s, 1083m, 1034m, 834s, 828s. UV-Vis (MeCN, λ_{max} (nm), [ε/ (cm^{-1} M^{-1})]) 472 [12750], 322 [119100]. Emission (MeCN, λ_{max}(nm), λ_{exc} = 472 nm) 638. Found C 50.91, H 4.45, N 9.37; $C_{150}H_{150}F_{12}N_{24}O_{48}P_2Ru{\cdot}5H_2O$ requires C 50.92, H 4.56, N 9.50%.

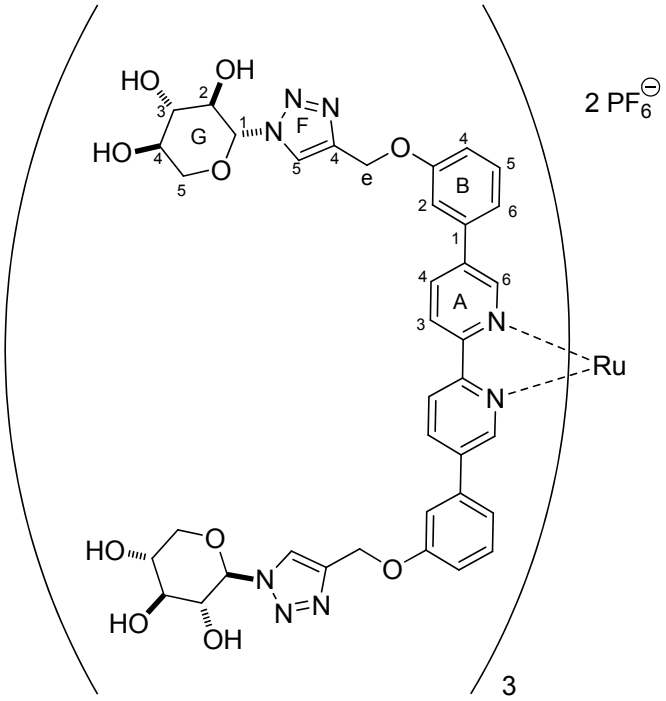
[Ru(**5**)(bpy)$_2$][PF$_6$]$_2$



[Ru(**4**)(bpy)$_2$][PF$_6$]$_2$ (111 mg, 64.4 μmol) and sodium methoxide (3.5 mg, 64.4 μmol) were dissolved in dry MeOH (20 cm^3) and the mixture was stirred for 2 h at 50°C. The solvent was reduced to 5 cm^3 and aqueous NH_4PF_6 (50 cm^3, 4.00 mmol) was added. The precipitate was collected on a frit and washed with water (10 cm^3) and Et_2O (20 cm^3) yielding compound [Ru(**5**)(bpy)$_2$][PF$_6$]$_2$ (73.7 mg, 50.1 μmol, 78%) as an orange solid. ^{1}H NMR (500 MHz, CD_3CN) δ/ppm = 8.58 (d, J = 8.6 Hz, 2H, H^{A3}), 8.56 – 8.48 (m, 4H, H^{C3+D3}), 8.32 (dd, J = 8.5, 1.7 Hz, 2H, H^{A4}), 8.10 – 8.02 (m, 6H, $H^{C4+D4+F5}$), 7.89 (d, J = 5.5 Hz, 2H, H^{C6}), 7.83 – 7.80 (m, 4H, H^{A6+D6}), 7.46 – 7.40 (m, 4H, H^{C5+D5}), 7.37 (t, J = 7.9 Hz, 2H, H^{B5}), 7.11 – 7.07 (m, 4H, H^{B2+B6}), 7.03 (d, J = 7.8 Hz, 2H, H^{B4}), 5.51 (d, J = 9.2 Hz, 2H, H^{G1}), 5.22 – 5.10 (m,

4H, H^{e}), 3.97 (dd, J = 11.3, 5.4 Hz, 2H, H^{G5eq}), 3.89 (t, J = 8.8 Hz, 2H, H^{G2}), 3.79 (s, 2H, $H^{G3\text{-}OH}$), 3.71 (s, 2H, $H^{G2\text{-}OH}$), 3.69 – 3.59 (m, 2H, H^{G4}), 3.55 – 3.39 (m, 6H, $H^{G3,\ G5ax,\ G4\text{-}OH}$). ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 160.00 (C^{B3}), 158.24 ($C^{C2/D2}$), 157.96 ($C^{C2/D2}$), 156.57 (C^{A2}), 153.11 ($C^{C6/D6}$), 153.08 ($C^{C6/D6}$), 150.03 (C^{A6}), 144.55 (C^{F4}), 140.53 (C^{A5}), 138.91 ($C^{C4/D4}$), 138.86 ($C^{C4/D4}$), 137.31 (C^{B1}), 136.81 (C^{A4}), 131.71 (C^{B5}), 128.69 ($C^{C5/D5}$), 128.65 ($C^{C5/D5}$), 125.59 (C^{C3+D3}), 125.37 (C^{A3}), 124.20 (C^{F5}), 120.92 (C^{B6}), 117.33 (C^{B4}), 114.31 (C^{B2}), 89.34 (C^{G1}), 78.25 (C^{G3}), 73.38 (C^{G2}), 70.29 (C^{G4}), 69.39 (C^{G5}), 62.56 (C^{e}). ^{19}F NMR (376 MHz, CD_3CN) δ/ppm –72.14 (d, J = 707 Hz). UV-Vis (MeCN, λ_{max} (nm), [ε/ (cm^{-1} M^{-1})]) 455 [19900], 319 [58900]. Emission (MeCN, λ_{max}(nm), λ_{exc} = 455 nm) 640. MS (ESI) m/z 589.9 $[M–2PF_6]^{2+}$ (calc. 590.2), 1324.5 $[M–PF_6]^{+}$ (calc. 1325.2). IR (solid / cm^{-1}): $\tilde{\nu}$ 3328m br, 2931w, 1601w, 1585w, 1464m, 1445m, 1297m, 1202m, 1041m, 1007m, 825s, 810s, 762m, 729w. Found C 45.20, H 4.06, N 10.73; $C_{58}H_{54}F_{12}N_{12}O_{10}P_2Ru{\cdot}4H_2O$ requires C 45.17, H 4.05, N 10.90 %.

$[Ru(\mathbf{5})_3][PF_6]_2$



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Complex $[Ru(\mathbf{4})_3][PF_6]_2$ (67.3 mg, 19.5 μmol) and sodium methoxide (1.1 mg, 19.5 μmol) were dissolved in dry MeOH (20 cm^3) and heated to reflux for 3 h. The solvent was reduced to 5 cm^3 and aqueous NH_4PF_6 (50 cm^3, 1.00 mmol) was added. The precipitate was collected on a frit and washed with water (10 cm^3) and Et_2O (20 cm^3) yielding compound $[Ru(\mathbf{5})_3][PF_6]_2$ (26.8 mg, 9.94 μmol, 51%). ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm = 8.94 (m_c, 6H, H^{A3}), 8.51 (d, J = 7.8 Hz, 6H, H^{A4}), 8.39 (s, 6H, H^{F5}), 8.17 (s, 6H, H^{A6}), 7.32 (t, J = 7.9 Hz, 6H, H^{B5}), 7.19 (s, 6H, H^{B2}), 7.11 – 7.05 (m, 12H, H^{B4+B6}), 5.51 (d, J = 9.1 Hz, 6H, H^{G1}), 5.44 (s, 6H, $H^{G2\text{-}OH}$), 5.37 (s, 6H, $H^{G3\text{-}OH}$), 5.21 (s, 6H, $H^{G4\text{-}OH}$), 5.08 (s, 12H, H^{e}), 3.83 (dd, J = 11.0, 5.0 Hz, 6H, H^{G5eq}), 3.78 (s, 6H, H^{G2}), 3.52 – 3.43 (m, 6H, H^{G4}), 3.42 – 3.30 (m, 12H, H^{G3+G5}). ^{19}F NMR (376 MHz, DMSO) δ/ppm = –69.81 (d, J = 711 Hz). ^{13}C NMR (101

MHz, DMSO-d_6) δ/ppm 158.58 (C^{B3}), 155.33 (C^{A2}), 149.80 (C^{A6}), 142.23 (C^{F4}), 137.71 (C^{A5}), 135.76 (C^{B1}), 135.23 (C^{A4}), 130.51 (C^{B5}), 124.41 (C^{A3}), 123.86 (C^{F5}), 119.47 (C^{B6}), 116.02 (C^{B4}), 112.99 (C^{B2}), 88.10 (C^{G1}), 77.06 (C^{G3}), 71.97 (C^{G2}), 69.12 (C^{G4}), 68.36 (C^{G5}), 61.01 (C^{e}). UV-Vis (MeCN, λ_{max} (nm), [ε/ (cm^{-1} M^{-1})]) 476 [10100], 314 [198000]. Emission (MeCN, λ_{max}(nm), λ_{exc} 470 nm) 636. ESI MS *m/z* 1200.3 $[M\text{-}2PF_6]^{2+}$ (calc. 1200.4). IR (solid / cm^{-1}): $\tilde{\nu}$ 3335m_{broad}, 2923w, 2901w, 2853m, 1582m, 1464s, 1444w, 1368w, 1363w, 1298m, 1242m, 1205m, 1199m, 1095m, 1061m, 1043m, 1035m, 1008m, 984m, 899w, 834s, 826s, 780m, 773w. Found C 48.53, H 4.87, N 12.07; $C_{114}H_{114}F_{12}N_{24}O_{30}P_2Ru\cdot 7H_2O$ requires C 48.60, H 4.58, N 11.93%.

Table S1 Redox potentials measured for complexes in argon-purged solutions of acetonitrile except where otherwise noted. $E_{1/2}$ values are given for reversible processes from the cyclovotammetry and are peak potentials for irreversible processes from square wave.

	Potential [V] versus Fc/Fc^+	
	Oxidation	**Reduction**
$[Ru(bpy)_3][PF_6]_2$	0.890	–1.73, –1.93, –2.17
$[Ru(\mathbf{2})(bpy)_2][PF_6]_2$	0.900	–1.60, –1.88, –2.12, –2.42
$[Ru(\mathbf{4})(bpy)_2][PF_6]_2$	0.908	–1.61, –1.89, –2.12, –2.41
$[Ru(\mathbf{4})_3][PF_6]_2$	0.973[b]	–1.95[a], –2.18[a]
$[Ru(\mathbf{5})(bpy)_2][PF_6]_2$	0.91	–1.60[a], –1.87[a], –2.13[a]
$[Ru(\mathbf{5})_3][PF_6]_2$ [b]	0.909	–1.65[a]

[a] Irreversible process, peak potential from square wave. [b] Measured in MeCN and DMSO (7 : 1 by vol.).